

# Characterisation of co-mixed HIP wasteforms for Magnox sludge and clinoptilolite wastes

S A Walling<sup>1</sup>, L J Gardner<sup>1</sup> and N C Hyatt<sup>1\*</sup>

<sup>1</sup>Department of Materials Science & Engineering, The University of Sheffield, Mappin Street, Sheffield, S1 3JD.

\*n.c.hyatt@sheffield.ac.uk

**Abstract.** Co-mixed simulant wasteforms consisting of calcined Magnox sludge simulant and clinoptilolite, with additions of a glass forming frit and CeO<sub>2</sub> or U<sub>3</sub>O<sub>8</sub> were processed using Hot Isostatic Pressing (HIP). This enabled the production of high waste loaded materials, with the successful incorporation of both simulant and active material. These formed heterogeneous glass-ceramic products, with decomposition of raw materials and some vitreous phase formation. The aqueous durability of these materials was assessed over a 28-day period using a modified PCT test, and favourably compared to the durability of an international glass. Overall this verifies the potential for HIP technology to be used in wasteform production, with potential large reductions in waste volume, especially if co-mixed wastes are considered.

## 1. Introduction

The safe conditioning and disposal of nuclear wastes within durable materials is of paramount importance to safeguard current and future generations. Past and present nuclear power generation within the UK has resulted in a legacy of different waste streams, many with unique or challenging chemistries and physical characteristics. Two of the waste streams of interest within the EC THERAMIN project (Thermal Treatment for Radioactive Waste Minimization and Hazard Reduction) are Magnox sludge and spent clinoptilolite (an ion-exchange material). The former of these is a magnesium rich sludge, predominantly resulting from the corrosion of Magnox fuel cladding within various ponds and silos across the Sellafield site. This is predominantly Mg(OH)<sub>2</sub>, with quantities of corroded uranium [1-2]. The clinoptilolite is a naturally occurring heulandite aluminosilicate zeolite used to selectively remove Cs and Sr from waste waters at the SIXEP plant prior to discharge [3-4]. Both of these waste streams are of interest for thermal treatment for different reasons. Magnox sludge is a high volume material, however de-watering of sludge and further calcination would result in a much lower volume of waste if a suitable thermal treatment could be applied. Clinoptilolite on the other hand is chemically very suitable to use as a starting point for glass formation, being rich in Si and Al, in addition to Na, Ca and K. This opens up the potential for co-processed wastes, with a lower amount of glass-forming additives required during thermal treatment, and consequential higher waste loading.

The objective of this work was to assess the suitability of co-processed Magnox sludge simulant and clinoptilolite, using Hot Isostatic Pressing (HIP) technology. This is a batch process within sealed steel canisters, which are subjected to both heat and pressure to form consolidated waste packages. This in-canister thermal treatment greatly limits the loss of volatile species during processing, while able to produce a glass, glass-ceramic or fully ceramic material. Here we have produced both an inactive (using CeO<sub>2</sub>) and an active (using U<sub>3</sub>O<sub>8</sub>) HIP wasteform, both of which have been characterised and subject to



aqueous dissolution to determine their durability and therefore, the suitability of managing co-mixed wastes by HIPing.

## 2. Materials and methods

Two small HIP canisters were prepared, each containing ~50g material (Table 1). These were to simulate co-mixed wastes, with a calcined Magnox sludge simulant (CMgS – a corroded magnesium simulant prepared by NNL), clinoptilolite (Clino), and a glass frit (MW ½ Li glass, a simple sodium lithium borosilicate glass used as the base constituent for UK HLW vitrification) which was added to assist glass formation within the wasteform. To one of these, CeO<sub>2</sub> was added as a uranium surrogate, to the other U<sub>3</sub>O<sub>8</sub> was added on an equimolar basis. The CMgS was calcined at 950 °C for 3 hours to remove water (and will result in conversion of Mg(OH)<sub>2</sub> to MgO), substantially reducing the volume in the process. Both samples achieved a waste loading of ~90%, based on dry materials. Clinoptilolite was similarly treated to remove any excess water (also likely to induce amorphisation). The MW ½ Li glass is supplied as a broken frit with the composition (wt. %) SiO<sub>2</sub> 63.4%, B<sub>2</sub>O<sub>3</sub> 22.5%, Na<sub>2</sub>O 11.4%, Li<sub>2</sub>O 2.7%.

**Table 1.** Composition of radioactive HIP wasteforms

| Can No.                             | CMgS (g) | MW ½ Li (g) | Clino (g) | CeO <sub>2</sub> (g) | U <sub>3</sub> O <sub>8</sub> (g) | Waste loading (wt. %)* |
|-------------------------------------|----------|-------------|-----------|----------------------|-----------------------------------|------------------------|
| HIP – CeO <sub>2</sub>              | 16.57    | 5.03        | 28.12     | 0.30                 | -                                 | 89.94                  |
| HIP – U <sub>3</sub> O <sub>8</sub> | 16.51    | 5.02        | 28.01     | -                    | 0.48                              | 90.84                  |

\*where waste loading refers to CMgS, clinoptilolite and CeO<sub>2</sub>/U<sub>3</sub>O<sub>8</sub> content

To reduce any further pre-processing, the materials were loosely mixed together, and no milling or size reduction was undertaken. This will likely result in a heterogeneous material, however additional processing of real wastes would increase complexity and produce secondary effluents, which then require disposal. For each canister, the dry precursors were batched, and packed into a HIP canister (15 cm<sup>3</sup> volume, 304 stainless steel) using a hydraulic press to enhance packing density (loosely packed material may result in severe can deformation (i.e. uncontrolled final shape) during the HIP process due to material consolidation). The lid was welded, can placed under vacuum while heated to 600 °C to remove any remaining water, then the evacuation tube was crimped and welded to fully seal the canister.

Both canisters were processed using an American Isostatic Press AIP-630H using an Active Furnace Isolation Chamber (AFIC) to ensure safe containment of radioactive material under any mis-operation conditions. HIP canisters were heated to 1250 °C over 260 minutes, then held at temperature for 120 minutes, before cooling to room temperature at 10 °C min<sup>-1</sup>. Varying ramp rates and several hold points on the ramp up were programmed to control canister deformation, overall averaging ~4.7 °C min<sup>-1</sup>. Pressure was increased (using argon) commensurate with temperature, with maximum pressure held during the dwell at maximum temperature. The CeO<sub>2</sub> can was held at an average of 87 MPa, with the U<sub>3</sub>O<sub>8</sub> can held at an average of 70 MPa. Both these were lower than the target pressure due to a small leak in the compressor and a vent valve, but this is unlikely to affect the final phase assemblage,

Post HIP processing the samples were sectioned with a diamond wafering blade using a Buehler Isomet 1000 precision saw, half the can was mounted into resin, then ground and polished to a 1 µm finish for scanning electron microscopy / energy-dispersive X-ray spectroscopy (SEM/EDX), with the other half crushed for X-ray diffraction (XRD) analysis. Powder X-ray diffraction patterns were collected between 5° < 2θ < 70° using a Bruker D2 Phaser diffractometer with a Lynxeye detector and a Ni filtered Cu K<sub>α</sub> 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.

Samples were subjected to short aqueous durability testing using a modified product consistency test (PCT) leaching methodology based on ASTM C1285 (but using a larger particle size). This utilised 10

mL of Type 1 (deionized) water in PFA pots, with sample material crushed and sieved to between 125-250  $\mu\text{m}$ . A surface area / volume of  $10 \text{ m}^{-1}$  was used, based on geometric surface area, with static leaching at 90 °C and sampling at regular intervals up to 28 days. Aliquots of leachant were taken and filtered using 0.2  $\mu\text{m}$  cellulose acetate filters, pH measured, then acidified using ultrapure  $\text{HNO}_3$  and analysed by inductively couple plasma optical emission spectrometry (ICP-OES, Thermo Fisher 6000 iCAP Duo). Normalised mass loss for elements was calculated using data obtained via X-ray fluorescence (XRF) analysis (Table 2), and compared against a well-known international simple glass (ISG)

**Table 2.** XRF composition of HIP –  $\text{CeO}_2$  and HIP –  $\text{U}_3\text{O}_8$  post processing and, ISG (wt. %)

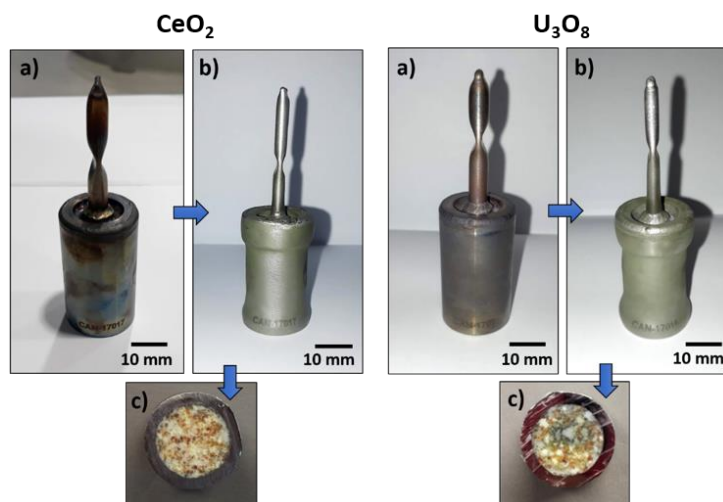
|                         | HIP – $\text{CeO}_2$ | HIP – $\text{U}_3\text{O}_8$ | ISG [5] |
|-------------------------|----------------------|------------------------------|---------|
| $\text{Al}_2\text{O}_3$ | 7.52                 | 7.96                         | 5.9     |
| $\text{B}_2\text{O}_3$  | 2.23                 | 2.11                         | 17.7    |
| $\text{CaO}$            | 1.06                 | 1.04                         | 4.6     |
| $\text{CeO}$            | 0.44                 | -                            | -       |
| $\text{Fe}_2\text{O}_3$ | 0.76                 | 1.02                         | -       |
| $\text{K}_2\text{O}$    | 2.88                 | 3.10                         | -       |
| $\text{Li}_2\text{O}$   | 0.28                 | 0.30                         | -       |
| $\text{MgO}$            | 25.64                | 23.30                        | -       |
| $\text{Na}_2\text{O}$   | 1.98                 | 2.16                         | 12.4    |
| $\text{SiO}_2$          | 55.68                | 56.30                        | 56.3    |
| $\text{TiO}_2$          | <0.10                | 0.16                         | -       |
| $\text{U}_3\text{O}_8$  | -                    | 1.12                         | -       |
| $\text{ZrO}_2$          | <0.10                | 0.10                         | 3.2     |

### 3. Results and discussion

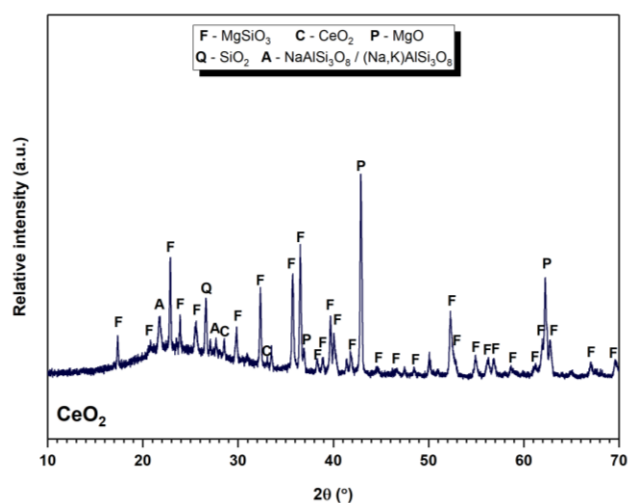
#### 3.1. Wasteform characterisation

Both HIP canisters were successfully processed, with material consolidation and corresponding slight reduction in volume. Photographs of both canisters are shown in Figure 1, both before and after HIP processing. The processed material is quite heterogeneous, but have both formed solidified products with little deleterious interaction with the HIP canister.

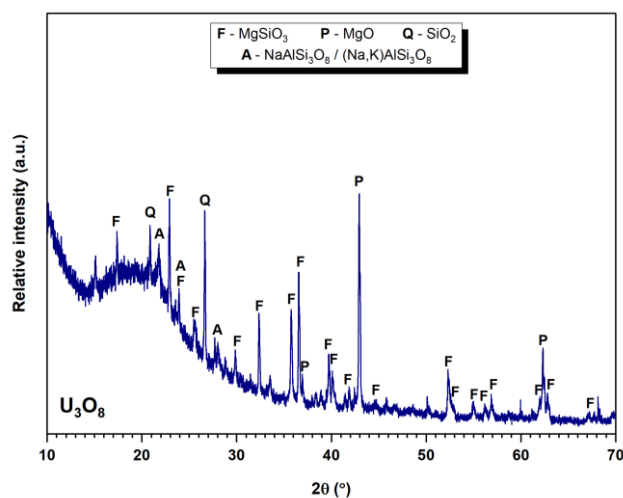
X-ray diffraction analysis of the crushed materials reveals various crystalline phases. For the  $\text{CeO}_2$  sample in Figure 2, forsterite ( $\text{MgSiO}_3$ ), ceria ( $\text{CeO}_2$ ), periclase ( $\text{MgO}$ ) and quartz ( $\text{SiO}_2$ ) were readily identifiable, additionally a feldspar mineral was tentatively assigned, potentially albite ( $\text{NaAlSi}_3\text{O}_8$ ) or anorthoclase ( $(\text{Na,K})\text{AlSi}_3\text{O}_8$ ). Several reflections remain un-assigned, though some of these do correspond to kotoite ( $\text{Mg}_3(\text{BO}_3)_2$ ), this could not be assigned in Figure 2 with confidence without further evidence. The diffraction pattern for the  $\text{U}_3\text{O}_8$  sample (Figure 3) was very similar, identifying the same crystalline phases (except, obviously no  $\text{CeO}_2$ ). This sample exhibited a high background signal (especially the diffuse scattering region between  $\sim 15\text{-}25^\circ 2\theta$ ) from Kapton tape, which was required to minimise loose active powders. Again several reflections remain unassigned, with kotoite ( $\text{Mg}_3(\text{BO}_3)_2$ ) a possible fit for several of the reflections but without further evidence we are unable to commit to this assignment. An additional reflection was evident at  $15^\circ 2\theta$ , which could not be assigned. This might fit anhydrous sodium diuranate ( $\text{Na}_2\text{U}_2\text{O}_7$ ), though little evidence was found for this in further analysis (SEM/dissolution).



**Figure 1.** Photographs of HIP canisters a) after packing and welding, b) post-HIP, c) sectioned canister cross-section.



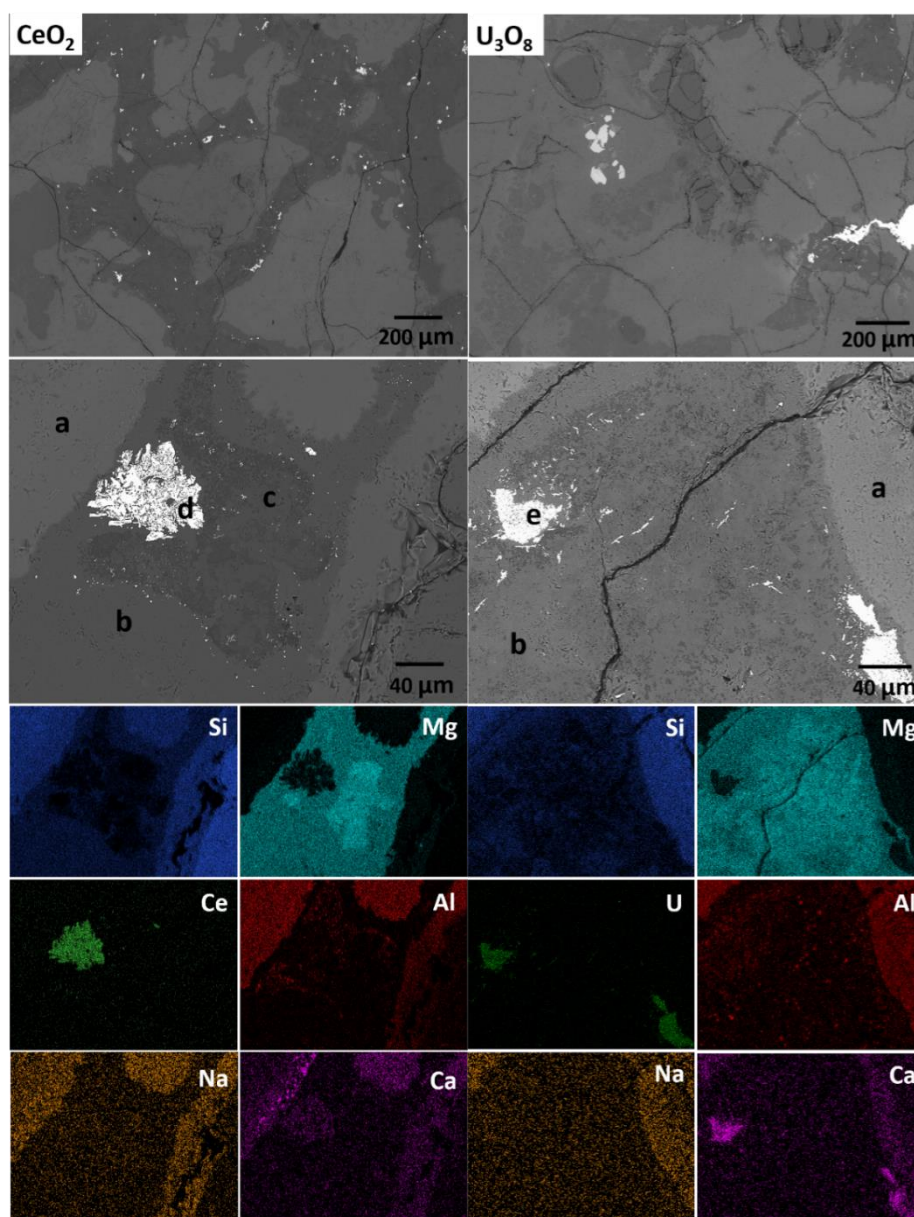
**Figure 2.** X-ray diffraction pattern of HIP – CeO<sub>2</sub>.



**Figure 3.** X-ray diffraction pattern of HIP – U<sub>3</sub>O<sub>8</sub>.

Scanning electron microscopy of the product wasteforms reaffirmed the heterogeneous nature of these materials (Figure 4). Two levels of magnification are presented, alongside elemental mapping to aid phase identification. Both samples were broadly similar in microstructure, with the difference in cracking likely due to damage obtained while cutting the HIP canister or grinding/polishing.

In HIP – CeO<sub>2</sub>, region ‘a’ is likely a partially vitrified clinoptilolite grain (given no clinoptilolite was identified via XRD, it has likely decomposed). This was evidenced by the presence of Ca, Al, Si and Na together (clinoptilolite is nominally (Na<sub>0.5</sub>K<sub>2.5</sub>)(Ca<sub>1.0</sub>Mg<sub>0.5</sub>)(Al<sub>6</sub>Si<sub>30</sub>)O<sub>72</sub>·24H<sub>2</sub>O)). Region ‘b’ is likely an Mg-Na-Si based glass, inside which unreacted MgO particles were visible, labelled as region ‘c’. Presence of Na and Ca within the MgO is likely due to background signal. The bright white region ‘d’ corresponds to unreacted CeO<sub>2</sub>.

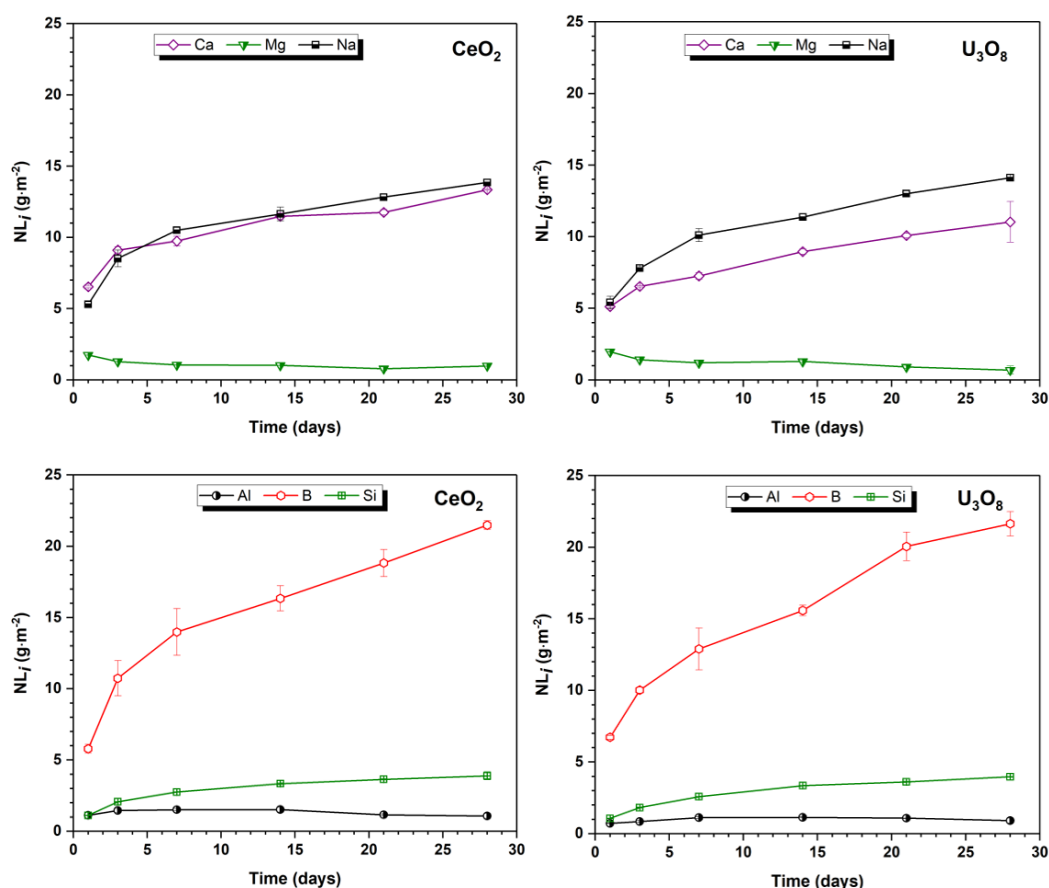


**Figure 4.** SEM/EDX of HIP – CeO<sub>2</sub> (left) and HIP – U<sub>3</sub>O<sub>8</sub> (right).

For HIP –  $\text{U}_3\text{O}_8$ , the sample exhibited much the same microstructure as the  $\text{CeO}_2$  sample with Ca, Al, Si and Na rich region ‘a’, and a Mg-Na-Si glassy phase in region ‘b’. Unreacted MgO is likely present in the centre of the micrograph, evidenced by the more intense Mg EDX signal, however the boundary between this and the Mg-Na-Si glass is not distinct. Region ‘e’ is of interest, as this initially appeared to be unreacted  $\text{U}_3\text{O}_8$ , however upon further analysis, there was also a strong signal from Ca within this region. This could be the presence of a calcium uranate phase, potentially also accounting for one or more of the unassigned XRD reflections (Figure 3).

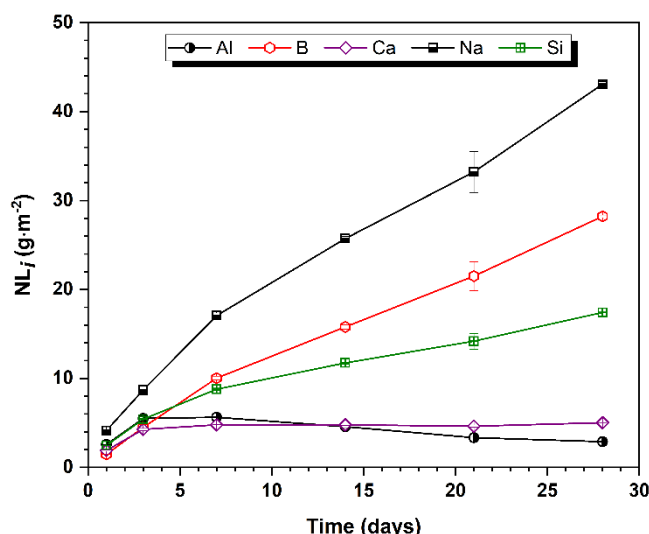
### 3.2. Chemical durability assessment

Although these materials are heterogeneous, it is the overall bulk dissolution of these materials against which we benchmark their durability. The results of the 28-day static dissolution tests are shown in Figure 5 with the normalised mass losses for respective elements from the two wasteforms. These have been compared against the International Simple Glass (ISG), which was tested under the same experiment conditions as an in-house benchmark of durability. Although it should be noted that ISG is a simulant high-level waste glass, not an intermediate- or low-level glass, and as such the required characteristics are different for simulant wasteforms than the wasteforms produced in this study.



**Figure 5.** Normalised elemental mass loss ( $\text{NL}_i$ ) for HIP –  $\text{CeO}_2$  and HIP –  $\text{U}_3\text{O}_8$  up to day 28.





**Figure 6.** Normalised elemental mass loss for ISG, up to day 28.

During dissolution the recorded pH values for the two samples followed the same trend. For HIP – CeO<sub>2</sub> the pH at 1 day was 9.8, decreasing to 9.2 after 28 days. For HIP – U<sub>3</sub>O<sub>8</sub> the pH at day 1 was 9.8, decreasing to 8.9 after 28 days. Alongside this, there is immediate elemental release within the first day for all elements except Ce. Initially Mg and Si were the highest concentration (in mg/L, however the composition is >80 wt.% MgO + SiO<sub>2</sub>), normalising to elemental fraction B, Na and Ca were the highest released elements at 5–7 g·m<sup>-2</sup> for both CeO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> HIP samples. For the CeO<sub>2</sub> sample; B, Na and Ca continued to be released up to 28 days leaching with final release rates of  $21.5 \pm 0.3$  g·m<sup>-2</sup> for B, and  $13.9 \pm 0.2$  g·m<sup>-2</sup> for Na at 28 days. Both Al and Si release were slow, with Al slowly decreasing after the first few days, and Si only slowly increasing. The final Si normalised mass loss ( $3.9 \pm 0.3$  g·m<sup>-2</sup> compared to  $17.0 \pm 0.1$  g·m<sup>-2</sup> in ISG), might indicate comparable higher durability, along with a slightly reduced B normalised mass loss ( $21.5 \pm 0.3$  g·m<sup>-2</sup> compared to  $28.2 \pm 0.1$  g·m<sup>-2</sup> in ISG).

The U<sub>3</sub>O<sub>8</sub> sample follows a very similar trend, with only minor deviations (notably, a lower Ca release rate). The final release rates for B and Na are  $21.6 \pm 0.9$  g·m<sup>-2</sup> and  $14.1 \pm 0.1$  g·m<sup>-2</sup> respectively, with final Si normalised mass loss of  $4.0 \pm 0.1$  g·m<sup>-2</sup>. These are all very close to the release rates determined for the CeO<sub>2</sub> sample, as expected given the close batch composition and phase assemblages. Though we have compared these samples here to the ISG a benchmark, it should be noted that ISG is not in itself a proposed wasteform, instead representing a simplified six-oxide simulant HLW glass for assessing dissolution mechanisms. Their structures are very different, as are their chemistries, however ISG does represent a vitrified product within the envelope of actual vitrified HLW. A well-recognised glass was required for comparison to determine whether, using this leaching methodology, these wasteforms perform adequately.

The relatively similar leaching characteristics of the U<sub>3</sub>O<sub>8</sub> sample compared to the CeO<sub>2</sub> sample corroborate the XRD and SEM analysis that the bulk phase assemblage and microstructure of these materials were similar, and also that no readily soluble Ce or U bearing phases were formed (Ce release was below the ICP-OES limits of detection, while the U normalised mass loss was  $1.2 \pm 0.2$  g·m<sup>-2</sup> at 28 days).

#### 4. Conclusions

Two co-mixed waste simulants containing calcined Magnox sludge simulant and clinoptilolite have been successfully processed using HIP technology, both with CeO<sub>2</sub> as a uranium surrogate, and using U<sub>3</sub>O<sub>8</sub>. Similar phase assemblages and dissolution characteristics were reported for both wasteforms, though with differences in the final Ce/U assemblages. The clinoptilolite crystal structure was destroyed, forming vitreous phases in-between a Mg-Na-Si glassy matrix containing the CeO<sub>2</sub> / calcium-uranium

phases. The chemical durability of these materials was favourable over a 28-day period, though with varying elemental release rates given the heterogeneous nature of the materials produced. Ultimately a high waste loading has been achieved with these materials, demonstrating the possibility of co-mixed wastes, and was able to successfully incorporate uranium – though this process does require the pre-calcination of waste streams to ensure suitability for the HIP process. More widely, the results presented here demonstrate the potential efficacy of hot isostatic pressing for the co-treatment of sludge and spent inorganic ion exchange materials present on the Fukushima Dai-ichi and other legacy decommissioning sites.

## 5. References

- [1] Nuclear Decommissioning Authority 2019 *Waste Stream 2D95.1: Magnox Fuel Storage Pond Sludge* (Moor Row, Cumbria: NDA).
- [2] Gregson C R, Goddard D T, Sarsfield M J and Taylor R J 2011 *J. Nucl. Mater.* **412** 145.
- [3] Nuclear Decommissioning Authority 2019 *Waste Stream 2D26: Ion Exchange Material (Clinoptilolite) and Sand* (Moor Row, Cumbria: NDA).
- [4] Howden M 1987 *Proc. Inst. Mech. Eng., Part A* **201** 1-15.
- [5] Kaspar T C, Ryan J V, Pantano C G, Rice J, Trivelpiece C, Hyatt N C, Corkhill C L, Mann C, Hand R J, Kirkham M A, Crawford C L, Jantzen C M, Du J, Lu X, Harrison M T, Cushman C, Linford M R and Smith N J, 2019 *npj Mater. Degrad.* **3** 15.

## Acknowledgement

The research leading to these results has received funding from the European Union's Horizon 2020 Euratom research and innovation programme under Grant Agreement No 755480 – Theramin and UKRI / EPSRC under grant reference EP/N017617/1. The HIP active upgrade was funded in-part by EPSRC under grant EP/L014041/1 Decommissioning, immobilisation and storage solutions for nuclear waste inventories (DISTINCTIVE). This research utilised the HADES / MIDAS facility at The University of Sheffield established with financial support from EPSRC and BEIS, under grant EP/T011424/1. The authors would like to acknowledge the National Nuclear Laboratory for supply of inactive precursor materials and for continued collaboration.