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Intermediate report on densification
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Abstract

This report summarises a selection of the current work undertaken by each partner within WP 6.5 'Densification', which has seen significant progress. It is the method of verification for MS42 / M6.5, demonstrating that all partners have made progress towards the desired aims and objectives of WP 6.5.

1 Milestone Description

Milestone # 43 / 6.5, associated with Work package 6 'Innovations in solid organic waste treatment and conditioning', Task 5 'Densification' has been completed on 11.08.2022.

The justification for the readiness is described below and complies with the Grant Agreement Description of Action noting verification by delivery of this report.

The readiness of the milestone was reviewed and agreed upon by Thierry Mennecart (SCK CEN) as WP6 leader.

2   Summary

This Intermediate Report on Densification draws together a selection of the current body of work undertaken by each partner towards their respective tasks within WP 6.5. This report does not aim to fully encompass the entirety of the works undertaken, but rather to summarise the experiments undertaken, and key outcomes which together demonstrate substantive progress towards task goals.

All partners have made significant progress towards their respective tasks within WP 6.5, and have fully engaged with the sound management of this subtask. Each partner has a separate section within this report, which will form the basis of the final subtask deliverable.

USFD have made considerable progress towards all task goals. The principal focus has been Hot Isostatic Pressing (HIP) of IRIS ashes from CEA (Incineration Research Installation for Solid waste), and the subsequent characterisation of these wasteforms. Progress has also been made towards HIP of polymeric material, and HIP of wet oxidation sludge simulants.

CEA have undertaken physical and chemical characterisation of IRIS ashes, which have been shared with other partners for further processing / densification. They have made progress with densification of these ashes *via* both palletisation and granulation, with further microstructural analysis of these forthcoming.

NNL have been liaising with USFD regarding the scale-up of the application of HIPing of wet oxidation simulant. Samples are yet to be made while the results of small-scale trials at USFD are pending, but progress is being made towards aligning precursor and pre-processing of materials to ensure continuity between USFD and NNL samples.

KIPT made good progress towards densification of wood ashes under their task goals, however this has been curtailed due to the ongoing war in Ukraine. We do not anticipate further progress at the current time, but have summarised information provided by KIPT during presentations at PREDIS meetings.

Overall, WP 6.5 is making good progress, and has fed into other work packages (e.g. WP 6.6. dissolution studies) where required with both samples and information. There does not appear to be any impediment towards delivering a final densification report that enhances our scientific understanding of wasteform densification *via* a range of suitable densification techniques.

3 The University of Sheffield (USFD)

3.1 Scope of tasks

The University of Sheffield has been tasked, within WP 6.5, with utilising and optimising Hot Isostatic Pressing (HIP) for the thermal treatment of a variety of simulant waste materials. These wastes include:

- IRIS ashes

- Wet oxidation sludge (or simulants)

- Polymeric material (organic ion exchange resins)

Both the IRIS ashes and the wet oxidation sludges are generated by a separate thermal treatment process (WP 6.3), with the volume reduced residues (ashes or sludges) being suitable for consolidation *via* HIP processing. Densification of polymeric material (organic ion exchange resins) is a direct thermal treatment process, with no other pre-treatment process envisaged (other than some simple drying).

All of these materials have been, or are due to be, processed using the HIP at USFD, with post-HIP characterisation undertaken on the resulting products. Some of these materials (particularly the IRIS ashes) have already been transferred to WP 6.6 for dissolution testing. Larger scale trials of HIP processing of wet oxidation sludge simulants are due to be undertaken by NNL, once small-scale trials at USFD have narrowed the formulation envelope.

3.2 HIP processing

The nuclear research HIP (AIP6-30H) at the University of Sheffield was commissioned in 2011 with maximum operating temperatures of 1350 °C (molybdenum furnace) and 2100 °C (graphite furnace) with a maximum pressure of 200 MPa (30,000 psi). HIP samples are often prepared using straight-walled stainless steel (304) HIP canisters, though other engineered canisters which collapse in a pre-determined fashion are also utilised.

Wasteform production using a HIP typically involves the conversion of a powdered or granular material into a solid block. This is achieved by packing the loose material into a steel canister, which is sealed and then transferred to the HIP pressure vessel where both heat and pressure are applied. This results in a solid product fully encased within the steel container.

At Sheffield, material (ash, sludge, resin) is packed into the canister by filling partway with material, then pressing this into the canister with a short metal plunger (slightly smaller than the internal canister diameter) and applying 2 tons of pressure from a hydraulic press. This process is repeated until the canister is ~4/5 full. The lid is then screwed on, being careful to avoid any powder ingress into the threads (to ensure a clean welding process).

The canister lid is then welded into position prior to the bakeout process, where a vacuum is applied to the evacuation tube (atop the canister lid) inside a furnace at a specified temperature. This drives off any residual water and ensures that a vacuum is kept. After a set period (e.g. 12 hours), the evacuation tube is crimped off and welded shut, resulting in a hermetically sealed canister.

Once the canister is prepared, it is placed within a secondary container (e.g. steel crucible) and loaded into the Hot Isostatic Press pressure vessel, which is then closed and prepared for operation.

The HIP process itself involves the application of both heat (applied *via* a furnace within the HIP) and pressure (applied isostatically *via* argon gas). Typically, both temperature and pressure are both increased concurrently until the desired temperature and pressure are achieved. The canisters are held at these conditions for a given period of time (typically 2-4 hours), before both temperature and pressure are lowered in a controlled manner.

This results in uniform application of pressure across the canister while at temperature, with sample densification, and a reduction in the HIP canister volume (Figure 3.1).

Figure 3.1. HIP canister with evacuation tub attached, before (left) and after (right) HIP processing.

Following HIPing, the canisters are sectioned and opened using a Buehler IsoMet 1000 Precision Cutter equipped with a cubic boron nitride wafering blade. Both the top and bottom sections of the are canisters removed, followed by the two opposing sides (Figure 3.2). This allows the manual removal of the remaining two canister sides (when the wasteform does not bind to the steel), resulting in a solid monolith and several offcuts for further analysis.

Solid off-cut pieces removed from the canisters are utilised for XRD analysis. The bottom of the canister is used for SEM analysis (allowing analysis of both bulk, and wasteform-canister interface), embedding the entire bottom piece within cold setting epoxy resin, then sequentially grinding and polishing to a 1 μm finish. The resulting SEM stub is depicted in Figure 3.3.
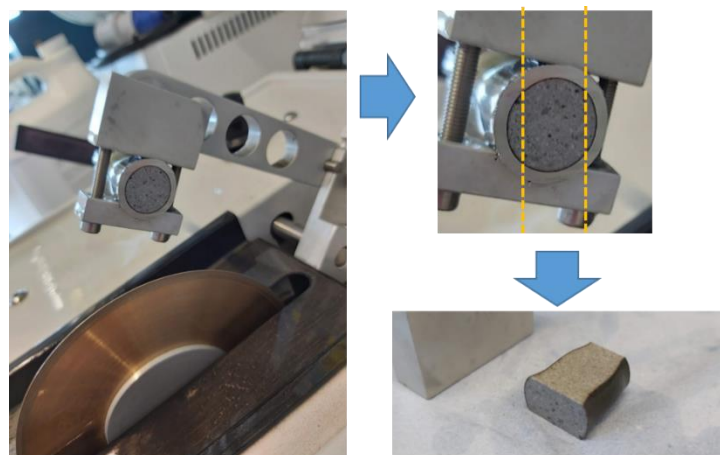

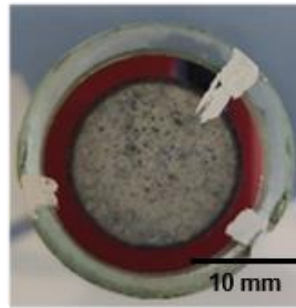**Figure 3.2.** Sectioning of canister post-HIP.

Figure 3.3. Sample prepared for SEM analysis, after embedding in resin, grinding/polishing, then carbon coating and applying conductive silver dag.

3.3 Progress to date

Progress has been made on all HIPing all the materials required under WP 6.5. Processing, characterising, and analysing the IRIS ashes has taken precedence due to the requirement to produce material for dissolution testing in WP 6.6, and for delivery of HIPed material to SCK-CEN. Initial scoping trials (using cold press and sintered pellets) have been undertaken for wet oxidation sludge simulants. Furthermore, a trial to HIP polymeric material (ion exchange resin) was undertaken, though was unable to progress to HIPing.

3.3.1 IRIS ash HIP

3.3.1.1 IRIS ash characterisation & processing conditions

Simulant IRIS ash was supplied to USFD by CEA. The material has a loose, light grey appearance, with significant particle heterogeneity (photograph in Figure 3.4). The ash weighed 305 g, and occupied a cylindrical space approximately 9 cm high by 12.5 cm wide (1104 cm^3), resulting in a bulk density of 0.28 g/cm^3.


Figure 3.4. Photograph of as-received simulant IRIS ash.

CEA supplied the ash chemical composition, as detailed in Table 3.1. ~75 wt. % of the material consists of SiO_2 + Al_2O_3 + CaO, with further contributions from P_2O_5, K_2O, ZnO, MgO. A number of minor components also exist.

Table 3.1 IRIS ash chemical composition.

Component	Weight %
SiO_2	29.35
Al_2O_3	28.46
CaO	13.55
ZnO	7.17
MgO	4.53
K_2O	3.60
P_2O_5	3.24
Cl	1.74
SO_3	1.41
Na_2O	0.95
TiO_2	0.69
Fe_2O_3	0.63
NiO	0.61
Bi_2O_3	0.24
BaO	0.15
Cr_2O_3	0.08

Powder X-ray diffraction (XRD) analysis of the received ash is shown in Figure 3.5. This reveals a complex, diffraction pattern with both crystalline and poorly-crystalline components identified. Phase matching determined the presence of crystalline anorthite ($CaAl_2Si_2O_8$), diopside ($MgCaSi_2O_6$), chlorapatite ($Ca_5(PO_4)_3Cl$), and anhydrite ($CaSO_4$), in addition to a minor contribution from gypsum ($CaSO_4 \cdot 2H_2O$), and an unidentified poorly crystalline material at ~35 - 38° 2θ.
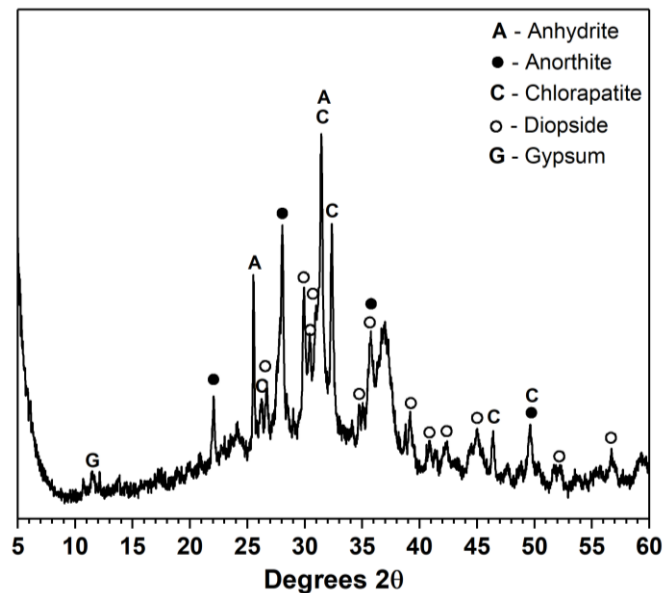
Figure 3.5. XRD pattern of as-received ash.

To process this material *via* HIP, it was decided to trial direct HIP of the as-received material. In parallel, several trials used varying additive materials. Though these ashes contain a significant proportion of glass forming elements, their partially crystalline nature and relatively low SiO_2 content (29 wt. %), high Al_2O_3 content

(28 wt.%) and only moderate alkali content (NaO + K_2O = 4.6 wt. %) is likely to require a high processing temperature, or the addition of a chemical flux to reduce the melting point, to form a glassy or vitrified product. The processing conditions for these ashes are limited to a certain extent by the HIP equipment and materials. The HIP at USFD is limited to a continuous maximum temperature of 1320-1350 °C due to melting point of the stainless steel canisters and operation limit of the furnace.

A further potential variable is the particle size of the ash material. A smaller particle size may increase reactivity and produce a denser product, however this increases the processing required. To determine the effect of both this, and the addition of fluxes, the following HIP trials were undertaken:

- HIP of as-received ash (no grinding, or additives)
- HIP of ground ash
- HIP of ground ash with 5 wt.% addition of sodium tetraborate
- HIP of ground ash with 5 wt.% addition of sodium aluminate

The processing conditions for all IRIS ash HIP canisters were: 1250 °C maximum temperature, 100 MPa pressure, 2-hour dwell at maximum temperature, 10 °C/min ramp up. Each canister was baked out at 300 °C for at least 12 hours to remove any residual water from the material before sealing the canister.

3.3.1.2   As-received ash (HIP)

Direct HIP conditioning of the as-received ash was performed. 15.89 g of the as-received ash was packed into the canister. The canister was successfully welded, baked out and vacuum achieved (e.g. hermetically sealed). HIPing was successful, with a photograph of the final product (after sectioning off the bottom) shown in Figure 3.6. A solid product was formed, appearing to be heterogeneous in nature, based on different shades of grey detectable by eye traversing the sample diameter.
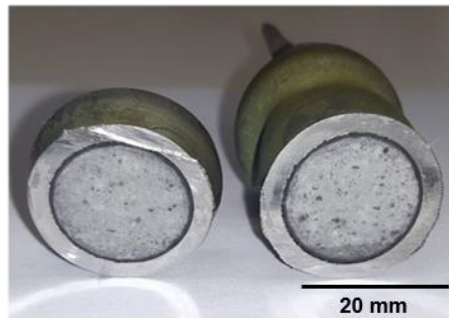

Figure 3.6. Photograph of sectioned canister after HIPing as-received ash.

XRD of the bulk material (Figure 3.7) revealed a highly crystalline product, with retention of many of the minerals present in the ash before HIPing, alongside the formation of some new mineral phases. Phase matching identified anorthite ($CaAl_2Si_2O_8$), diopside ($MgCaSi_2O_6$), chlorapatite ($Ca_5(PO_4)_3Cl$), leucite ($KAlSi_2O_6$), and spinel ('$MgAl_2O_4$', but likely with Zn, Fe and Cr substitutions). Anhydrite and gypsum have disappeared, whilst leucite and spinel have been formed. Some change in the crystalline assemblages may have occurred during the bake-out temperature, however typically (without sintering aids or milling) spinel and leucite tend to form in higher temperature environments >800-1000 °C [1-3].
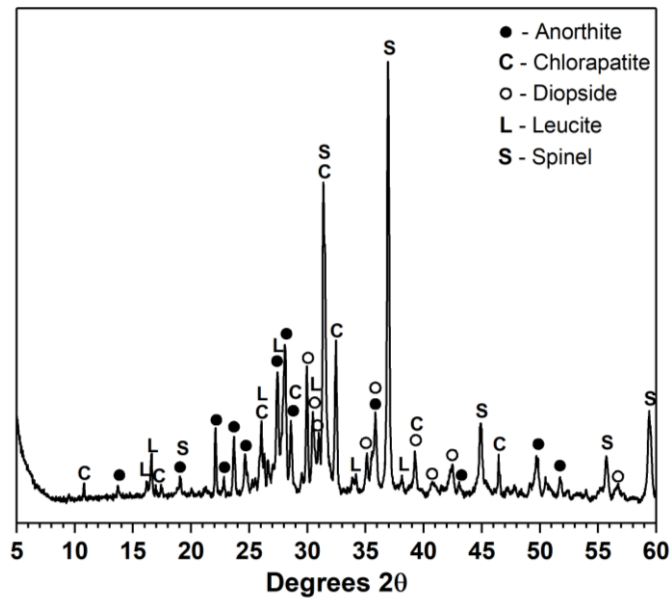
Figure 3.7. XRD pattern of HIPed as-received ash.

Scanning Electron Microscopy (SEM) analysis of the bulk material (Figure 3.8) revealed a heterogeneous product, which was partially vitrified. There is clear phase separation (evident more clearly by the elemental maps, e.g. Al, Si and Ca) and noticeable porosity. There appear to be several Zn-S hotspots, along regions rich in Ca-P-Cl regions, which were assigned to chlorapatite, as identified *via* XRD.

The interface between the bulk solidified ash and the canister wall (Figure 3.8) shows clear migration of Cr from the stainless steel canister into the bulk wasteform, with S migration into the steel. During processing, the ash appears to have formed a slightly aggressive melt (or partial melt), demonstrated by erosion of the internal canister wall (highlighted with arrows in Figure 3.9). The bulk material appears to have shrunk during cooling, resulting in a gap between the canister and the bulk material. Significant interaction with the canister wall is undesirable as this may damage the canister integrity (in a very aggressive melt held at high temperatures for longer during processing), and can result in an inhomogeneous wasteform due to introduction of steel elements (particularly Fe, Cr, Ni) which may form unexpected crystalline phases.
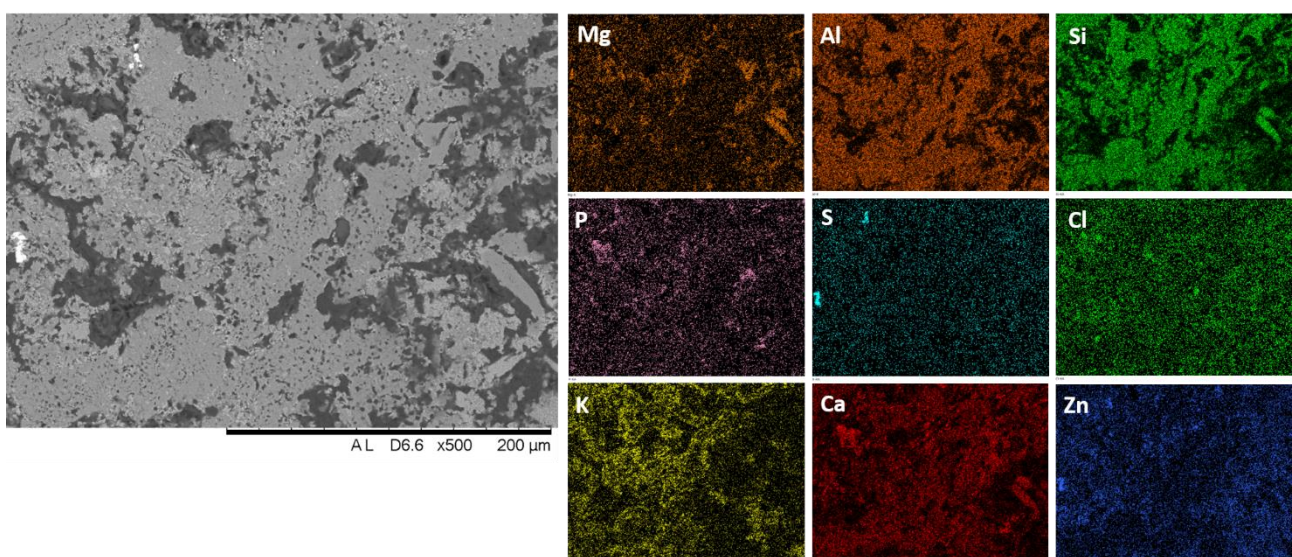

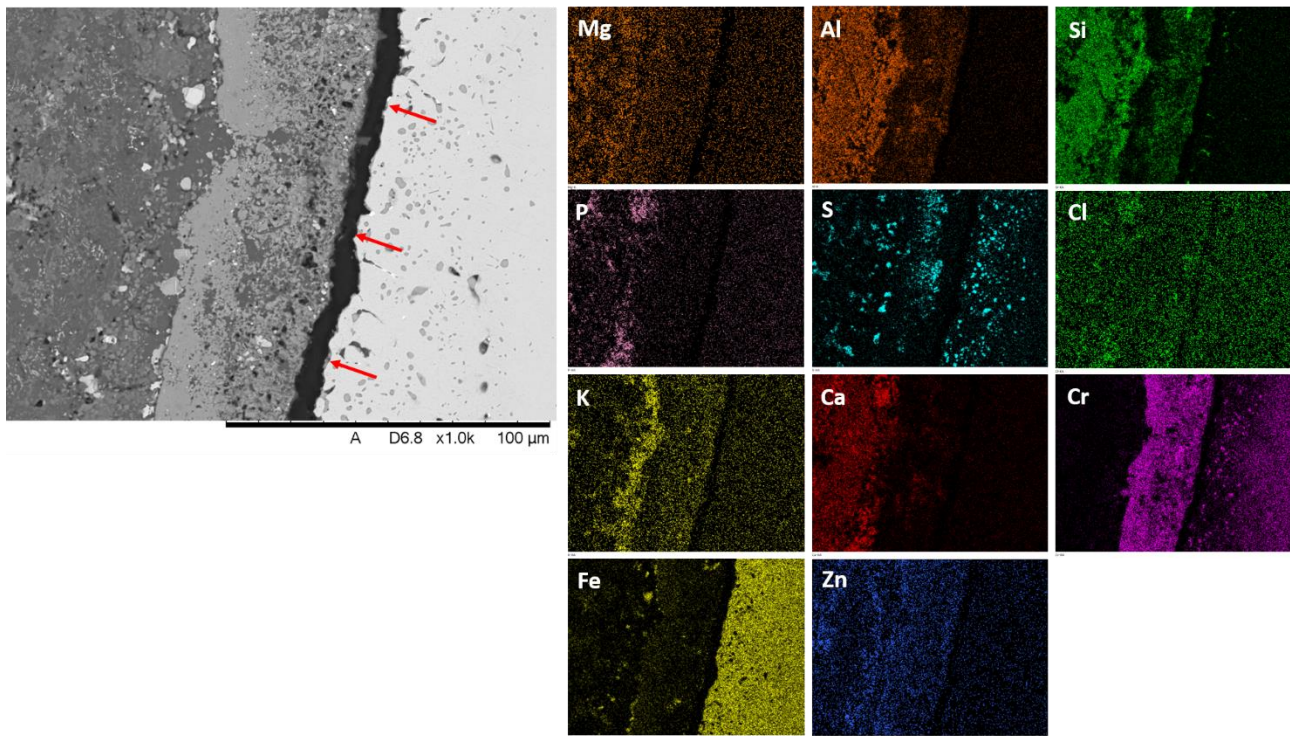**Figure 3.8.** SEM micrograph and EDX maps of HIPed as-received ash.

Figure 3.9. SEM micrograph and EDX maps of HIPed as-received ash / canister interface.

In summary, direct HIPing of the as-received ashes formed a solidified product which, at least partially, melted to form a crystalline multi-phase wasteform. Significant porosity was observed, giving rise to a lower density product overall. Such porosity may influence the aqueous durability of the wasteform through introduction of high surface area. The as-received ash deleteriously interacted with the internal stainless steel canister wall, although not enough to risk the structural integrity of the canister.

Further optimisation of this wasteform was undertaken *via* size reduction of the ash, with a view to enhancing the solid-state reaction and minimising porosity, and also through addition of chemical fluxes to lower the melting point.

3.3.1.3   Size reduced ash (ground, no additives)

This HIP trial tested the effect of size reduction *via* grinding on the final wasteform properties. The IRIS ash is extremely friable; therefore, manual hand grinding (using a pestle and mortar) was utilised rather than ball milling.

To prepare the canister, 20 g of as-received ash was hand ground for 5 minutes in a porcelain pestle and mortar. 19.35 g of powdered material was packed into the canister (using the aforementioned method), which was then processed as per the standard for these IRIS ashes: HIP canister bake-out and evacuation and subsequent HIPing (1250 °C, 100 MPa for 2 hours).

The HIP processing was successful. After removal of the canister top, bottom, and side walls, a monolith was obtained, photographed in Figure 3.10. This was a solid product, with clear discoloration where the wasteform was touching the internal canister walls.
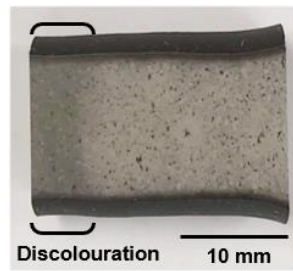
Figure 3.10. Photograph of HIPed ground ash, after removal from canister.

XRD analysis of the bulk material (Figure 3.11) exhibited the same crystalline assemblage as the HIPed as-received (unground) ash sample, with anorthite ($CaAl_2Si_2O_8$), diopside ($MgCaSi_2O_6$), chlorapatite ($Ca_5(PO_4)_3Cl$), leucite ($KAlSi_2O_6$), and spinel ('$MgAl_2O_4$', but likely with Zn, Fe and Cr substitutions). This wasteform was extremely crystalline, with many overlapping reflections. In comparison with the as-received HIPed sample (Figure 3.7), the intensity of the XRD reflections was increased, suggesting that the size reduction process resulted in increased crystallinity upon HIP processing.
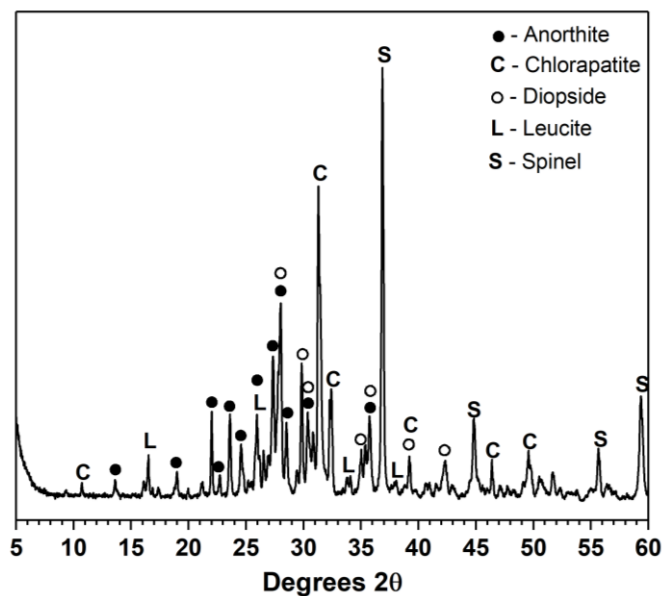

Figure 3.11. XRD pattern of HIPed ground ash.

SEM of the bulk material (Figure 3.12) revealed a heterogeneous material, with a much reduced porosity compared to the HIPed unground ash. There is a clear phase separation, with Mg and Zn anti-correlated with Si. This suggests that Zn may be incorporated within the Mg/Zn-bearing spinel phase identified by XRD. The wasteform-canister interface (Figure 3.13) has been eroded by the ash during processing, with pieces of steel embedded within the wasteform up to 100 µm away from the canister wall (spots a & b in Figure 3.13). As for the unground HIP sample, there was a clear alteration region at the canister-sample interface.
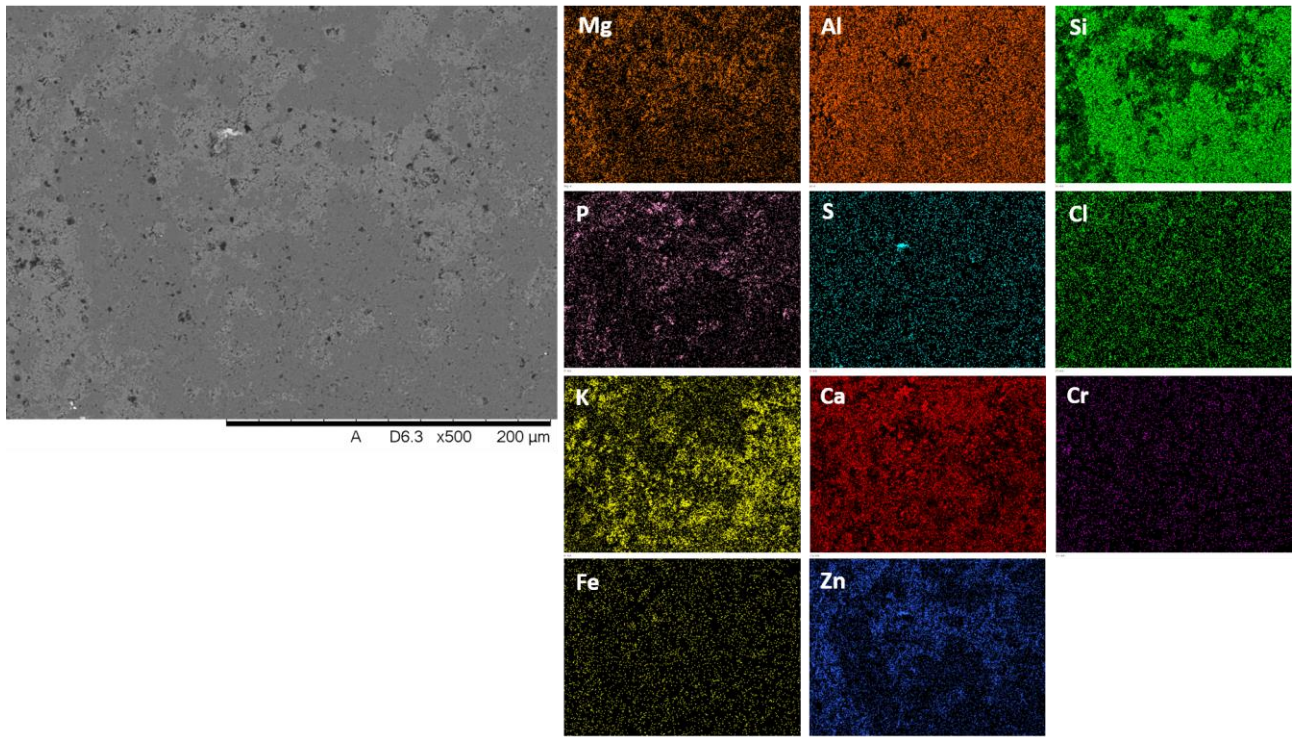
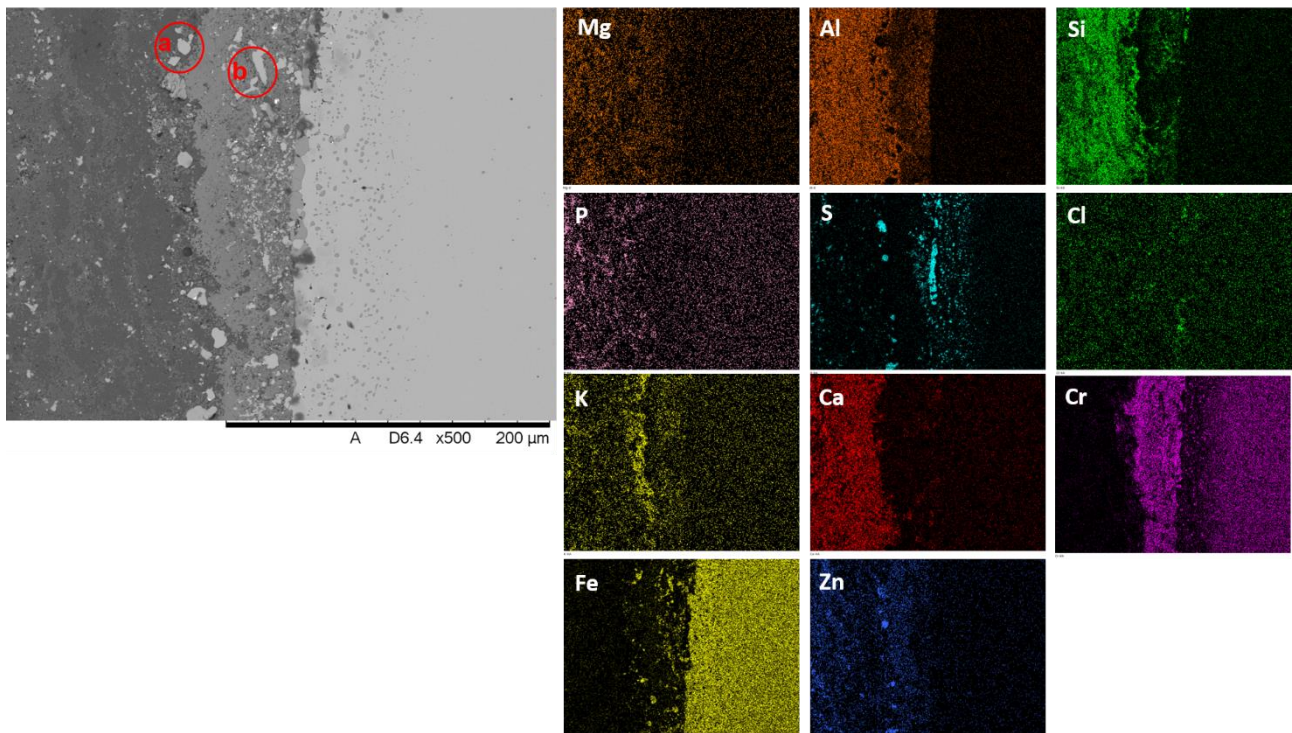**Figure 3.12.** SEM micrograph and EDX maps of HIPed ground ash.

Figure 3.13. SEM micrograph of HIPed ground ash / canister interface.

In summary, gentle dry grinding of the IRIS ash produced a solidified and dense wasteform. There was a clear phase separation in the final product, however with extensive high temperature solid-state reactions (potentially due to the increased surface area from grinding). The sample was easily removed from the HIP canister without any cracking of the solid monolith. As such, this formulation appeared to be more successful

than the unground HIP trial (primarily due to greater reaction and less obvious widespread porosity) and was taken forward for dissolution testing under WP 6.6.

3.3.1.4   Size reduced ash with sodium aluminate (ground, 5 wt% NaAlO₂)

In an attempt to lower the temperature of reaction, and to promote glass formation, an alkali additive was included in the formulation. Sodium aluminate ($NaAlO_2$) powder, often utilised in glass-forming applications, was mixed with the as-received ash, as follows: 19 g of as-received ash was mixed with 1 g of sodium aluminate (technical grade, Fisher Scientific) to create the 5 wt. % addition of $NaAlO_2$. The combined powder was hand ground for 5 minutes in a porcelain pestle and mortar to homogenise (in accordance with the previous trial). 19.18 g of the combined, ground material was used to pack the HIP canister using the standard method discussed previously.

HIP processing (1250 °C and 100 MPa for 2 hours) was successful, leading to the formation of a dense solidified monolith. A photograph of the resulting product after canister removal is shown in Figure 3.14.
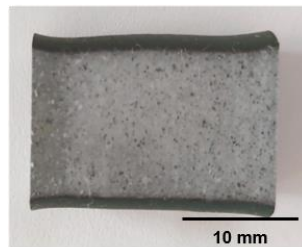

Figure 3.14. Photograph of HIPed ground ash with sodium aluminate, after removal from canister.

XRD analysis of the bulk material again revealed similar crystalline phases, with anorthite ($CaAl_2Si_2O_8$), diopside ($MgCaSi_2O_6$), chlorapatite ($Ca_5(PO_4)_3Cl$), leucite ($KAlSi_2O_6$), and spinel ('$MgAl_2O_4$', but likely with Zn, Fe and Cr substitutions). The material is very crystalline, with particularly intense reflections for spinel and chlorapatite when compared to the previous trials.
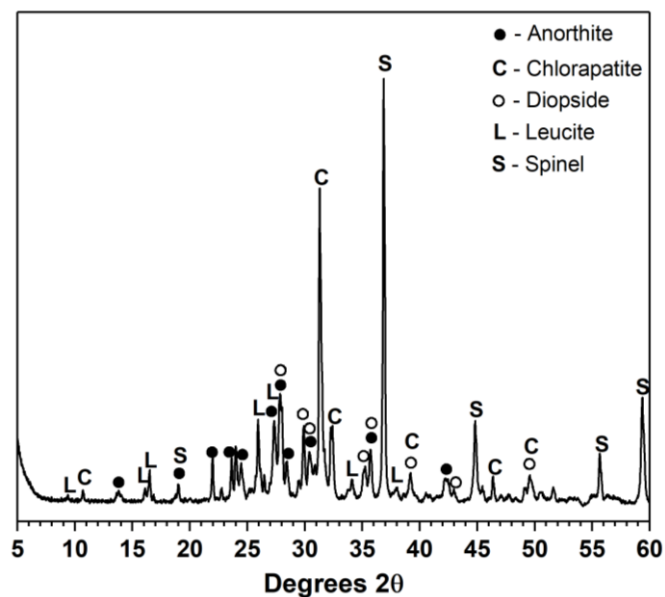

Figure 3.15. XRD pattern of HIPed ground ash with sodium aluminate.

SEM of the bulk material (Figure 3.16) revealed a much more homogeneous product than for samples without additives. There remains some porosity, although this was spherical in nature indicating that it formed within a melt. There was evidence of some phase separation, especially evidenced by the K EDX map (Figure 3.16-K). Very small crystallites <5 μm were present throughout the sample, with larger clusters clearly enriched in P (likely chlorapatite based on XRD analysis). The canister wall (Figure 3.17) appears to have been corroded, with some Cr diffusing from the steel, forming a particularly strong band enriched in Cr. There was migration of S (from the IRIS ash) into the steel canister, and a formation of Zn-S enriched particles near the canister wall (compared to no visible hotspots in the bulk material in Figure 3.16). These are likely zinc sulphide, formed under the reducing conditions imposed by the stainless steel canister. Although erosion of the canister wall occurred, it appeared to be less aggressive than for the as-received ash (both packed unground, and the ground sample).
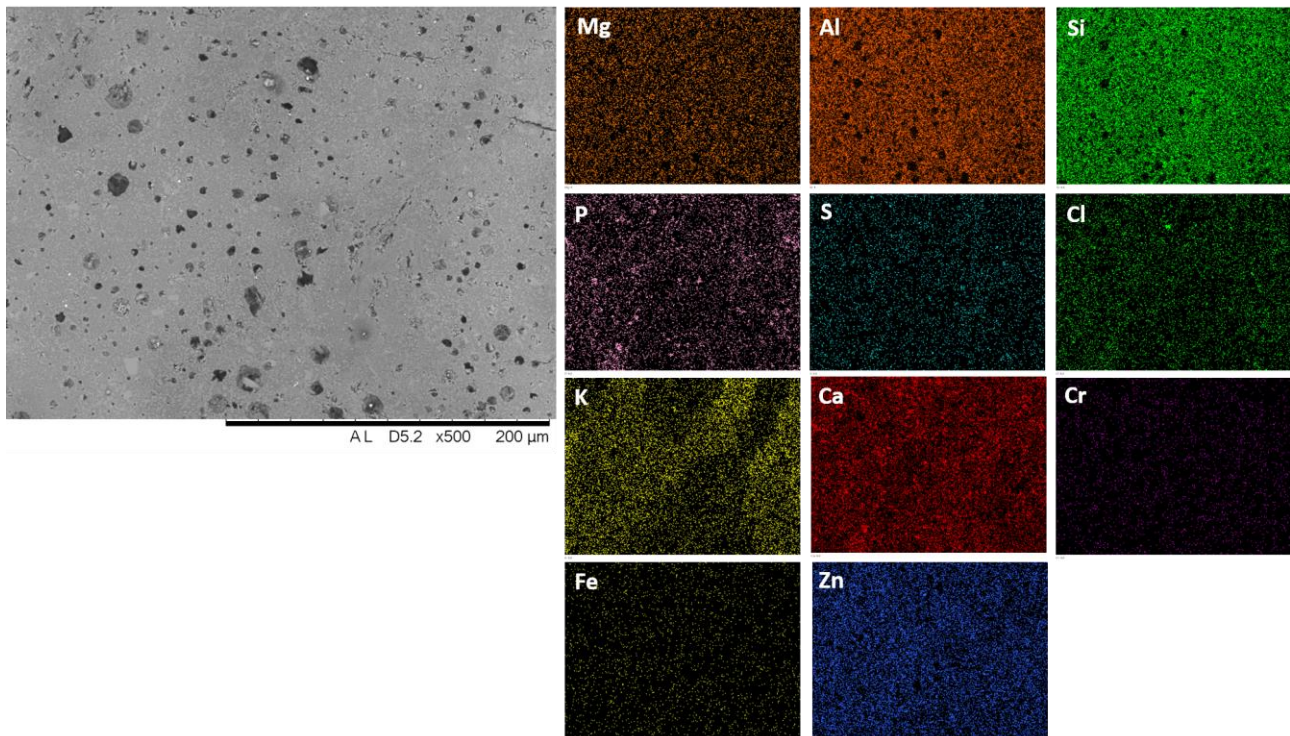

Figure 3.16. SEM micrograph and EDX maps of HIPed ground ash + sodium aluminate.
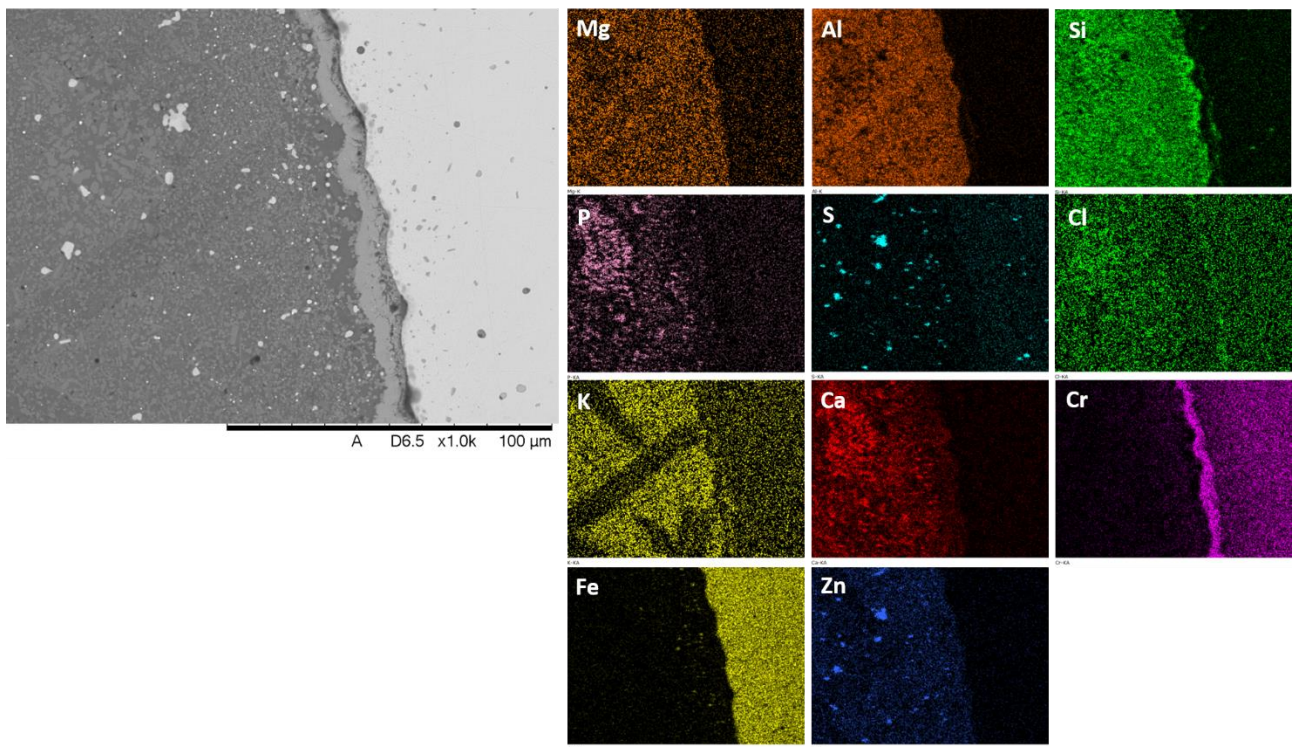
Figure 3.17. SEM micrograph of HIPed ground ash + sodium aluminate / canister interface.

In summary, the addition of 5 wt. % sodium aluminate into the IRIS ashes appears to have successfully formed a solidified wasteform. The final product was a dense material, which did not break or shatter on removal from the HIP canister. Although still a largely crystalline material, the presence of spherical pores indicated that some ash melting and consolidation occurred. Due to the success of this formulation, this wasteform was taken forward for dissolution testing under WP 6.6.

3.3.1.5   Size reduced ash with sodium tetraborate (ground, 5 wt.% $Na_2B_4O_7$)

In a further attempt to form a more homogeneous product, the addition of sodium tetraborate ($Na_2B_4O_7$) was trialled. This is a more traditional flux in glass making, and acts effectively to reduce the melt temperature. The material was processed in the same way as for the previous addition. 19 g of as-received ash was mixed with 1 g anhydrous sodium tetraborate (99%, Sigma-Aldrich). The combined material was hand ground for 5 minutes in a porcelain pestle and mortar to homogenise the batch. The blended, ground material was packed into the HIP canister to a total of 19.26 g.

The HIP process (1250 °C and 100 MPa for 2 hours) was successful, with a photograph in Figure 3.18 depicting the solid monolith following canister removal, with the IRIS ash densified into a solid product.
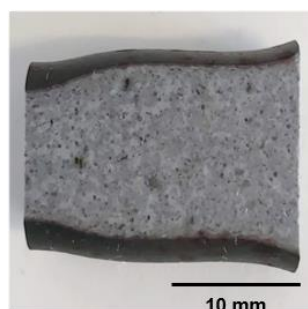
Figure 3.18. Photograph of HIPed ground ash + sodium tetraborate, after removal from canister.

XRD analysis was undertaken on monoliths (from cutting the material out of the canister) both the bulk material, and on the interfacial zone (the black section at the top and bottom of Figure 3.18). The interfacial region (Figure 3.19, defined here as the 'outside face' of the HIPed ground ash with sodium tetraborate) revealed a poorly crystalline diffuse reflection characteristic of the formation of a glassy material (i.e. with no long-range order). Also observed were diffraction peaks indexed as zincochromite ($ZnCr_2O_4$) / magnetite (Fe_3O_4), haematite (Fe_2O_3), which are challenging to distinguish since they occupy the same crystal structure.

XRD analysis of the bulk material (Figure 3.20) revealed a very different phase assemblage when compared with the other HIPed wasteforms investigated in this study. Only spinel ($ZnAl_2O_4$ / $MgAl_2O_4$ likely) and chlorapatite ($Ca_5(PO_4)_3Cl$) reflections were visible, in addition to a region of diffuse scattering, indicating the formation of a glassy phase. There were no reflections for any crystalline silicates remaining from the original ash (e.g. anorthite, diopside, etc.), indicating that the extent of wasteform decomposition was the greatest of all the formulations trialled.
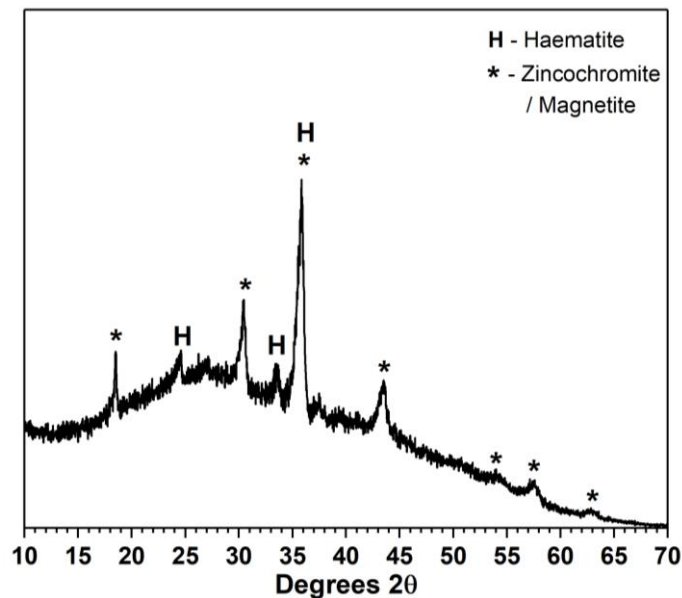

Figure 3.19. XRD pattern of the outside face of HIPed ground ash with sodium tetraborate (after canister removal).
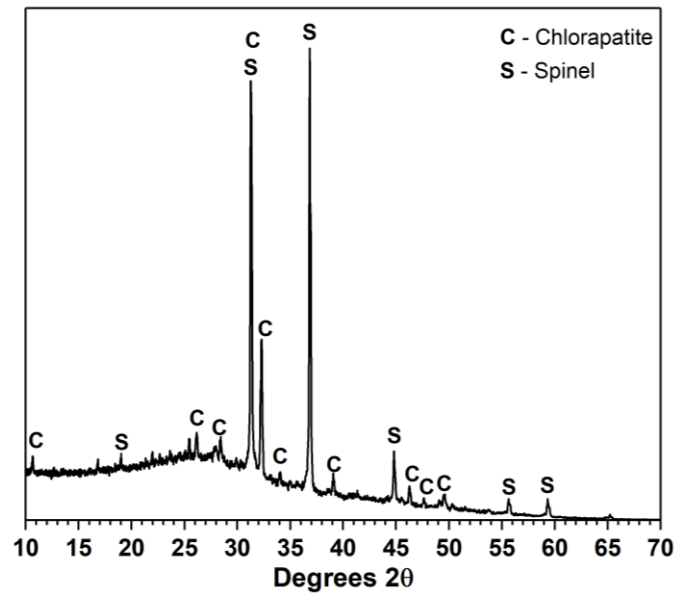
Figure 3.20. XRD pattern of the bulk material of HIPed ground ash with sodium tetraborate.

SEM analysis of the bulk material (Figure 3.21) shows a morphology indicative of crystalline materials incorporated within a glassy matrix. Larger crystallites from ~10-50 µm (including some elongated crystallites) were assigned as chlorapatite (elemental maps: Cl, Al, Si) and the much smaller crystallites as spinel. The canister-ash interface (Figure 3.22) shows Cr migration into the melt (in agreement with previous samples); however, this reaction appeared to be less corrosive than previous formulations (as received, ground, and with sodium aluminate), as evidenced by the retention of the largely linear canister edge. The Cr migration resulted in the formation of zincochromite in a narrow band near the canister wall (spot a, Figure 3.22). As per previous samples, S hotspots are observed in the canister (highlighted in spot b, Figure 3.22).
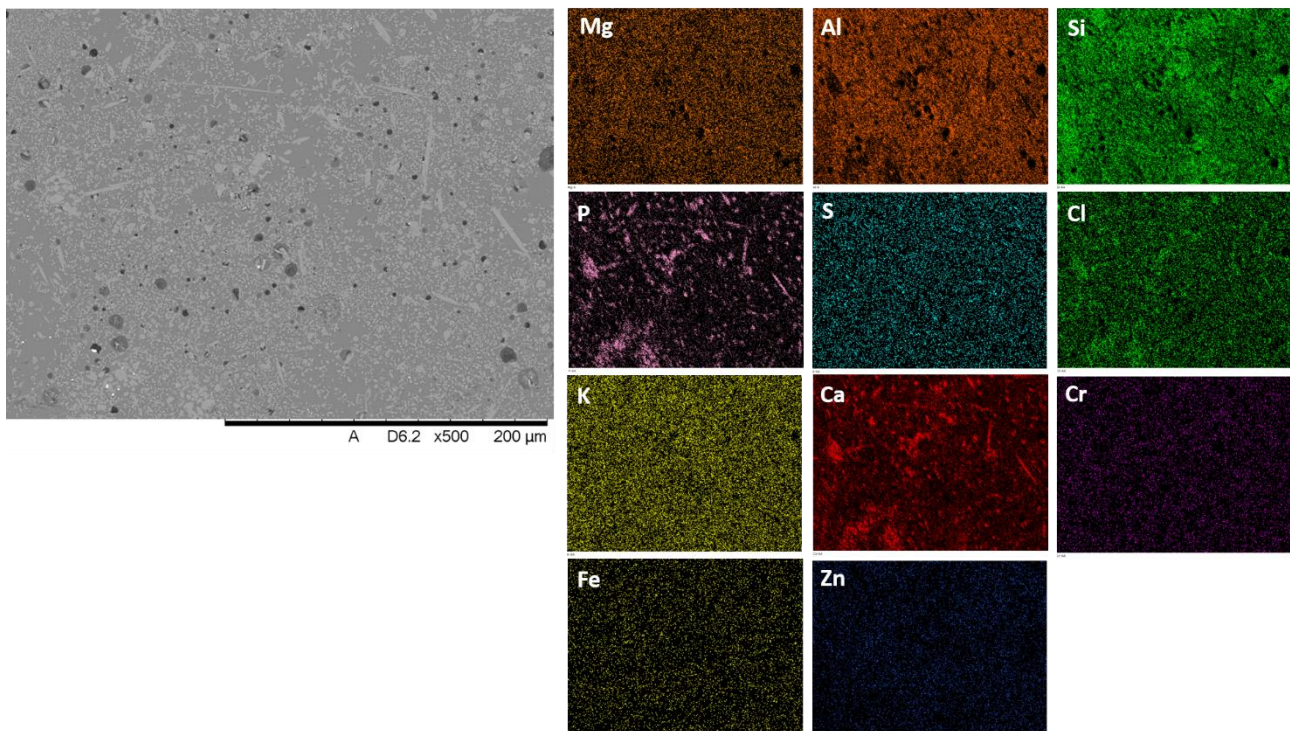

Figure 3.21. SEM micrograph and EDX maps of HIPed ground ash with sodium tetraborate.
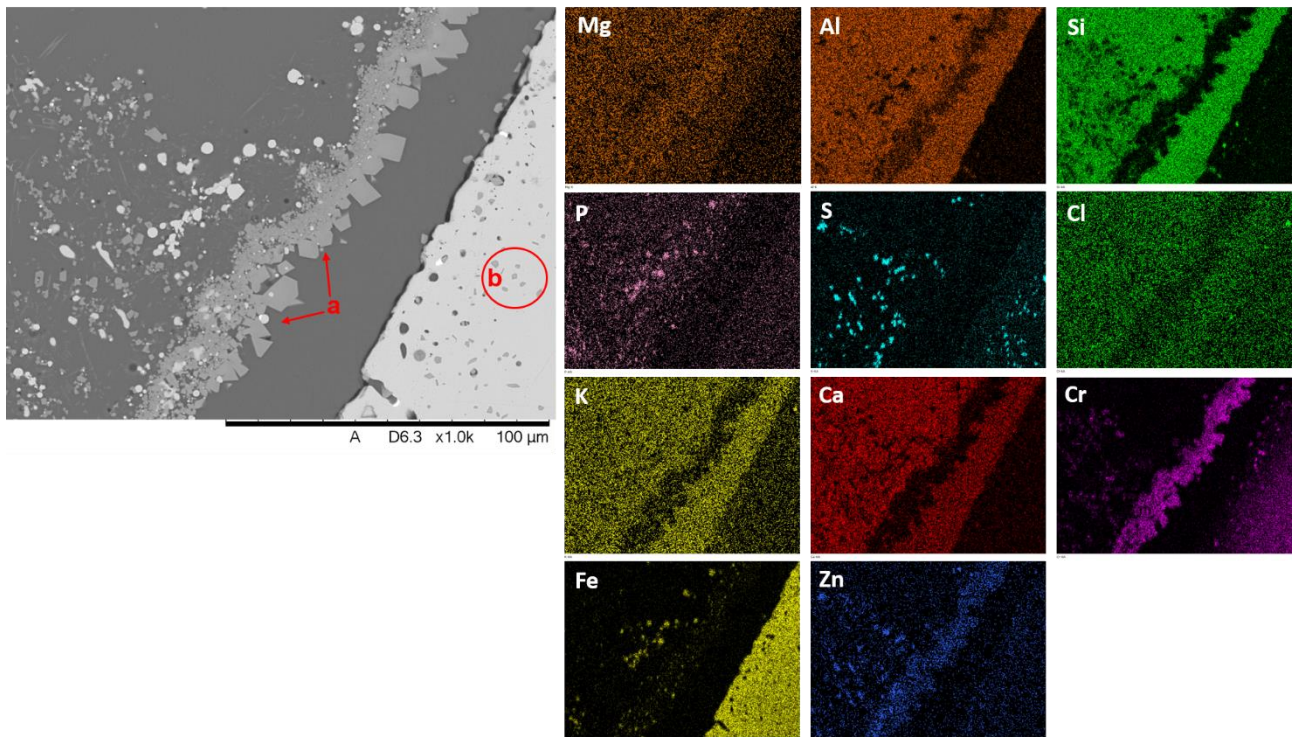
Figure 3.22. SEM micrograph and EDX maps of HIPed ground ash with sodium tetraborate / canister interface.

Sodium tetraborate was the most successful additive, resulting in a glass-ceramic material in which the ash was almost completely melted. Although some canister-wasteform interaction occurred, it appeared to be less aggressive towards the canister than other formulations. Due to these positive outcomes, this formulation will also be taken forward for dissolution trials in WP 6.6.

3.3.1.6   Canisters prepared for SCK CEN

For WP 6.6, USFD were required to provide HIP samples to SCK CEN for long-term dissolution trials. These HIP samples were fabricated using the most promising formulation determined here in WP 6.5.

Two HIP canisters were prepared using a ground blend of 95 wt. % IRIS ash and 5 wt. % $Na_2B_4O_7$. Canisters were successfully packed, HIPed, and sectioned (Figure 3.23). The resulting monolith was sent to SCK CEN for further preparation and size reduction for their dissolution testing.
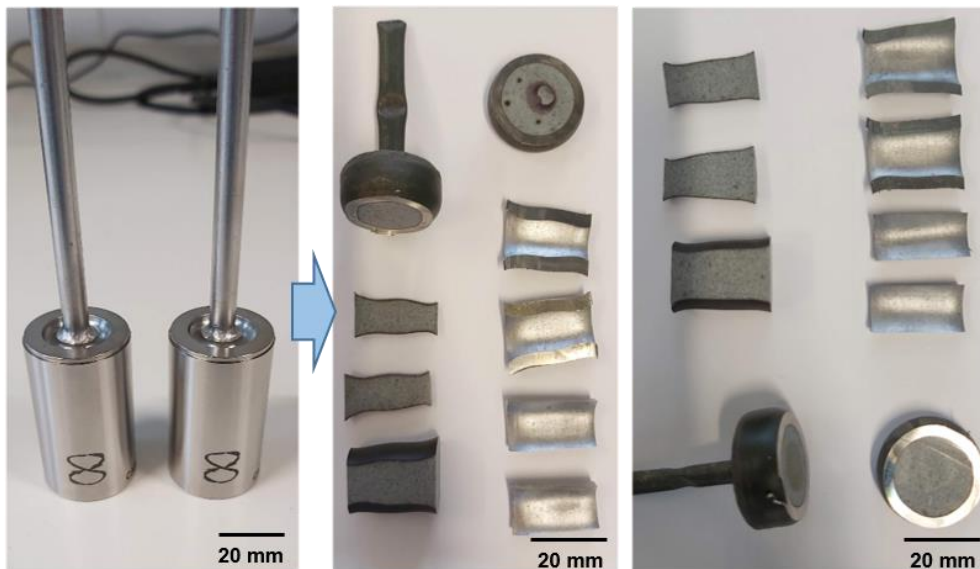
Figure 3.23. Photograph of samples prepared for SCK CEN, samples sent highlighted in yellow after sectioning and removal from the canister.

3.3.1.7   Preparation of samples for dissolution tests

To allow for long-term dissolution trials under WP 6.6, the HIPed samples produced in WP 6.5 were further size reduced. A total of 3 formulations were chosen for dissolution: (1) ground ash, (2) ground ash with 5 wt. % $NaAlO_2$, (3) ground ash with 5 wt. % $Na_2B_4O_7$.

HIPed samples were sectioned to remove all faces in contact with the canister to ensure only the bulk sample was utilised (and not the canister-wasteform interaction zone), as demonstrated in Figure 3.24. The resulting cuboid was then cut in such a way as to produce a series of small cuboids for dissolution testing. Due to the small size of the HIP canisters, and the densification during HIP processing, very small cubes were required to maximise the number of samples that could be prepared from each canister. Between 9-12 cuboids were prepared from each canister, with sides an average 4-5 mm length, and an average resulting surface area of 1.26 cm^2. Surfaces were not ground or polished further, and therefore retained the finish provided by the CBN blade.
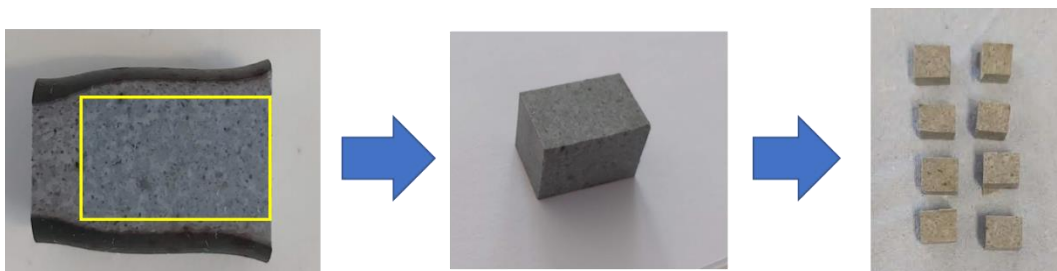
Figure 3.24. Photograph of HIPed ash size reduction (N.B. for this sample the cubes were further trimmed to ensure flat faces, and two further cubes were recovered from an off-cut piece).

3.3.2   Wet oxidation residue HIP

This section of the work package (WP 6.5) relates to Hot Isostatic Pressing (HIP) of simulant residues arising from Fenton wet oxidation of organic ion exchange resins, performed within the scope of WP 6.3. The Fenton process utilised involves the addition of hydrogen peroxide and a mixed iron/copper sulfate catalyst, combined

with heat (<100 °C) and agitation to degrade the organic material. This results in a sodium sulfate rich liquid waste, with an iron and copper rich sludge. Processing of nuclear ion exchange resins (e.g. from primary circuit decontamination) through this process will result in the partitioning of many radionuclides into the iron and copper-rich sludge. It is proposed that the HIP process may be applied to filtered and dried sludge.

WP 6.3 specifically treated a mixed bed nuclear grade cation:anion exchange resin (IRN-150). Characterisation of the resulting sludge revealed a poorly crystalline copper and iron rich material (roughly equimolar Fe:Cu), which upon heating to 600 °C (HIP canister bakeout temperature) produced a mixture of Fe_2O_3 and CuO. This mixture was used as a simulant material (required due to the high volume reduction achieved during the wet oxidation process), which would allow aligning between USFD and NNL scaled up HIP canisters. The wet oxidation rig at USFD produces very minor quantities of sludge per run, making this unfeasible to produce enough material for a full HIP campaign.

Preliminary investigations into the potential for HIP processing of this material has begun. This has initially focussed on cold pressing and sintering pellets of varying compositions, to determine their stability at varying temperatures and the resulting phase assemblage. These results will be utilised to formulate compositions taken forward for small-scale HIP trials.

3.3.2.1   Preliminary CuO–Fe$_2$O$_3$ scoping trials

This preliminary trial investigated three different formulations along the CuO-Fe_2O_3 binary phase diagram, starting from the $CuO/(CuO+Fe_2O_3)$ value determined from the real wet oxidation sludge (0.67 – an equimolar Cu:Fe composition). Literature [4] infers that this composition should result in the formation of delafossite ($CuFeO_2$), which was targeted in the first formulation. The addition of extra Fe_2O_3 pushes the system towards the formation of spinel ($CuFe_2O_4$): the second formulation. The formation of a spinel phase (formulation number three) would be beneficial for retention of certain radionuclides (e.g. activation products) likely to be within real wet oxidation sludge, such as Ni, Co and Mn. These could potentially form $NiFe_2O_4$, $CoFe_2O_4$, and $MnFe_2O_4$, respectively, with an excess of Fe_2O_3. Literature also suggests the maximum processing temperature would be ~1080 °C before melting occurs for much of the CuO-Fe_2O_3 phase diagram (Figure 3.25).
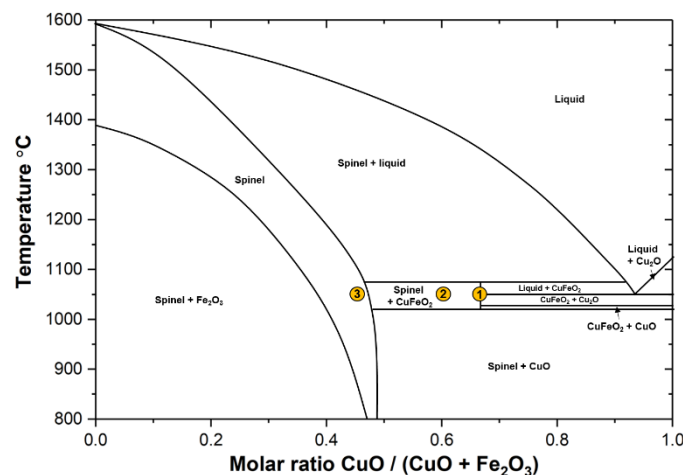

Figure 3.25. CuO-Fe_2O_3 phase diagram with target formulations labelled, adapted from Shishin, et al. [4].

On this basis, three formulations were part of the preliminary trial, starting from the wet oxidation sludge composition, then working towards the Fe_2O_3 end of the phase diagram, with the aim to forming spinel in the third composition (all as molar formulations), as follows:

- **(1)** 1 CuO : 0.5 Fe_2O_3 ($CuO/(CuO+Fe_2O_3)$ = 0.67) to target delafossite ($CuFeO_2$)
- **(2)** 1 CuO : 0.67 Fe_2O_3 ($CuO/(CuO+Fe_2O_3)$ = 0.60) to target delafossite + spinel (e.g. $CuFe_2O_4$)
- **(3)** 1 CuO : 1.22 Fe_2O_3 ($CuO/CuO+Fe_2O_3$ = 0.45) to target spinel

For each formulation, the required quantities of Fe_2O_3 (98%, Alfa Aesar) and CuO (99%, Alfa Aesar) were weighed out, then intimately mixed by ball milling in isopropanol for 10 minutes (at 500 rpm using ZrO_2 mill pot and 3 mm milling media). The resulting slurry was recovered from the milling media, then dried in an oven at 90 °C. Two pellets were pressed for each formulation, using 0.5 g of material per 10 mm diameter pellet. All pellets were placed on a zirconia boat (Figure 3.26), and heated up to 1050 °C in a muffle furnace (10 °C/min ramp rate, standard atmospheric conditions) and held at temperature for 4 hours.
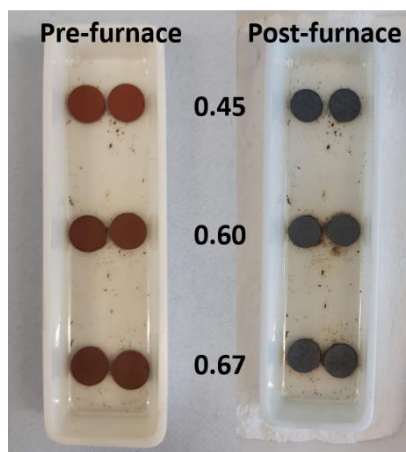

Figure 3.26. Pellets pre- and post-furnace, arranged by $CuO/(CuO+Fe_2O_3)$ ratios.

All formulations appeared to sinter well with no noticeable melting, although both the 0.60 and 0.67 formulations very slightly stuck to the crucible. This may indicate the requirement to slightly reduce the processing temperature in the future. Samples are due to be analysed *via* XRD and SEM to determine the phase assemblage and whether suitable sintering has occurred.

Determining the final assemblage of these pellets is necessary to constrain the milling parameters and chemical precursors prior to developing a HIPed wasteform at a small scale. Successful HIP at this scale will enable larger scale trials at NNL, with information already being shared to arrive at a joint formulation / processing method. It is likely that trials at USFD will then move towards incorporation of simulated decontamination resin radionuclides *via* the addition of nickel, cobalt, and cerium oxides to determine the extent, and nature, of their incorporation within the candidate formulations.

3.3.3   Polymer HIP

The potential for treatment of polymeric material via HIP was investigated. The polymeric material chosen was a mixed bed cation-anion nuclear grade exchange resin (Amberlite IRN-150, Figure 3.27). This is the same resin that was treated *via* Fenton wet oxidation within WP 6.3.

The treatment of polymeric material *via* HIP presents challenges due to mismatch between the high temperatures preferred for wasteform consolidation (especially within steel canisters, which typically begin to soften at temperatures of >500 °C), and the low temperatures required to avoid thermal degradation of the polymeric material. The minimum temperature for a HIP run is likely to be ~100-130 °C based on the temperature rise caused by compression of argon into the HIP pressure vessel.

Figure 3.27. Photograph of IRN-150 resin.

It was decided to undertake two trials to investigate the feasibility of HIP to immobilise ion exchange resin. The first focused on direct immobilisation (i.e., no additive), while the second explored the potential for embedding the resin within a separate polymer matrix of LDPE (Thermo Scientific, powder, low density, 500 µm). As the aim is not to decompose the material, rather to consolidate or potentially melt the resin, the maximum processing temperature was key. Literature suggested the resin undergoes decomposition from ~300 °C onwards, whilst LDPE decomposition is higher, at ~390 °C (though melting before this temperature) [5-7].

The resin was prepared by drying overnight in an oven at 90 °C to remove as much water as possible. Two trials were planned:

1) Dried IRN-150
2) Dried IRN-150 + LDPE

HIP qualification / bakeout was scheduled to be performed at room temperature under vacuum, then intended to be HIPed at 200 °C under 100 MPa pressure. It was unknown whether the HIP canister would deform well at this temperature. Typically using HIPing, the combination of temperature (enough to begin softening the steel, >500 °C) and pressure allows the canisters to be compressed down and around the waste whilst protecting / minimising stress on the welds. Using such low temperatures, with small canisters that have relatively thick steel walls, may not produce ideal deformation. Despite this, the constraint on the upper temperature was the polymer degradation temperature.

3.3.3.1   Dried IRN-150 direct HIP

Dried IRN-150 resin was packed directly into a stainless steel HIP canister using a uniaxial press and metal plunger (as per the IRIS ash sample packing). The resin flowed into the canister smoothly, though did not pack densely even with the application of 2 tons of pressure (some resin beads were heard to audibly crack). A total of 2.85 g of dried resin was packed into the canister, as demonstrated in Figure 3.28, which shows the canister before the lid was screwed on.

Figure 3.28. Trial 1 after packing (before addition of lid).

During the welding of the canister, which is a high temperature process, a dark brown pungent liquid oozed out of an as-yet unwelded section of the canister lid; this gap in the weld is shown in Figure 3.29. The technician attempted to clean the top of the canister with a wire brush, and resume welding; however, the liquid began oozing out again preventing completion of the weld. This liquid was likely to be melted resin that formed during the high temperature welding process. Due to the potential degradation of the resin within the, and inability to seal the HIP canister, this sample was not taken forward for HIP treatment.
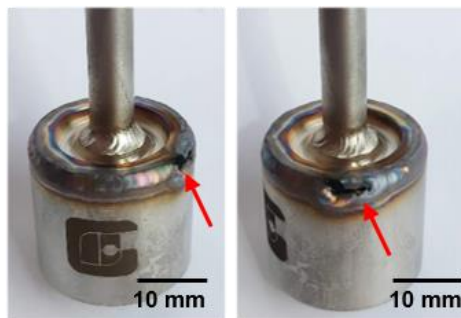

Figure 3.29. Trial 1 after welding, showing incomplete weld.

3.3.3.2 Dried IRN–150 + LDPE

A canister was packed using dried IRN-150 and LDPE powder. 10 g of dried IRN-150 was mixed with 10 g LDPE and mixed together manually for 5 minutes (resulting in a 50% dried resin loading). A total of 3.6 g of this combined material was packed into a HIP canister using a uniaxial press and metal rod. This canister packed very well, with notable compaction due to the fine LDPE powder that helped to keep the resin in place during packing. Figure 3.30 shows a photograph of the packed resin / LDPE batch in the canister prior to screwing on the lid.
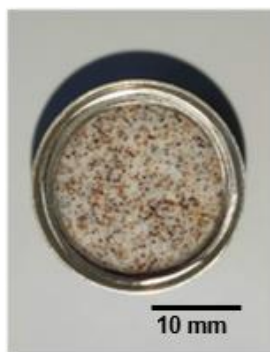
Figure 3.30. Trial 2 after packing (before addition of lid).

Although this canister packed well, a similar melting event occurred during the attempt to weld the lid. Although the technician attempted to complete the weld quickly (and at a lower power setting than the previous failed attempt), liquid material escaped from the canister during welding, leaving an unwelded section (photographed after cooling in Figure 3.31).
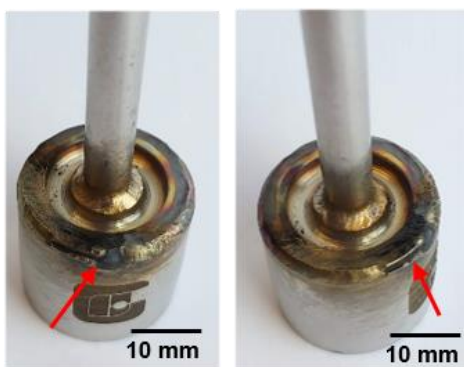

Figure 3.31. Trial 2 after welding, showing incomplete weld.

Given that the material inside the canister was degraded by the welding heat, and since the HIP canister could not be sealed, this sample was unable to be HIPed. A potential solution could be to use larger, taller canisters, with 50% packing, where the top of the canister could be filled with steel spacers to mitigate the degradation of the polymer. However, there would still be a high risk that the polymer within the canister had been exposed to excess temperature, resulting in polymer melting or thermal degradation.

Using the equipment and canisters available at USFD, it was deemed that HIP of polymeric material is not achievable; however, this may be revisited in the future if a suitable way forward is found, while minimising the potential risk, e.g. due to expulsion of liquid material, to the Sheffield HIP equipment.

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4 French Alternative Energies and Atomic Energy Commission (CEA)

4.1 IRIS process

4.1.1 Description of the IRIS process

The ashes considered in these studies come from the IRIS incineration pilot process (Installation for Research on Incineration of Solids) developed at CEA Marcoule for R&D support and devoted to the treatment of the organic waste contaminated by α-emitting actinides from glove boxes in the nuclear industry. This pilot is working exclusively under inactive environment, and the ashes produced come from the incineration of a mix of different organic solids and IER resins (Figure 4.1). This leads to achieve a volume reduction of the waste to about a 30 factor. IRIS is a three-step process implemented in rotating kilns. The first step consists in oxidative pyrolysis at 550 °C, producing pitch that is then processed in a calcining step at 900 °C in oxygen-enriched atmosphere. The off-gases arising from the thermal treatments include a volatile hydrocarbon fraction that is oxidized at 1100 °C in an afterburner. This multistep process has two advantages. The elimination of chlorine at low temperature in the pyrolyzer limits corrosion problems and allows operation with low gas flow, which also limits particle entrainment. Adding oxygen during the pyrolysis step oxidizes the heavy hydrocarbons that produce tars capable of forming deposits in the ducts. Forming during the pyrolysis step, the pitch drops into the calciner being a rotary kiln heated at 900 °C. The pitch remains around 2 hours in this furnace and is transformed into ashes having a very low carbon content (< 1%). Before discharge to atmosphere, the gas stream is submitted to caustic scrubbing to eliminate the volatile acids. The material balance in the process is about as follow: a feeding rate of 4 kg/h produces around 1550 g/h of pitch, 111 g/h of ashes and 47 g/h of dust.
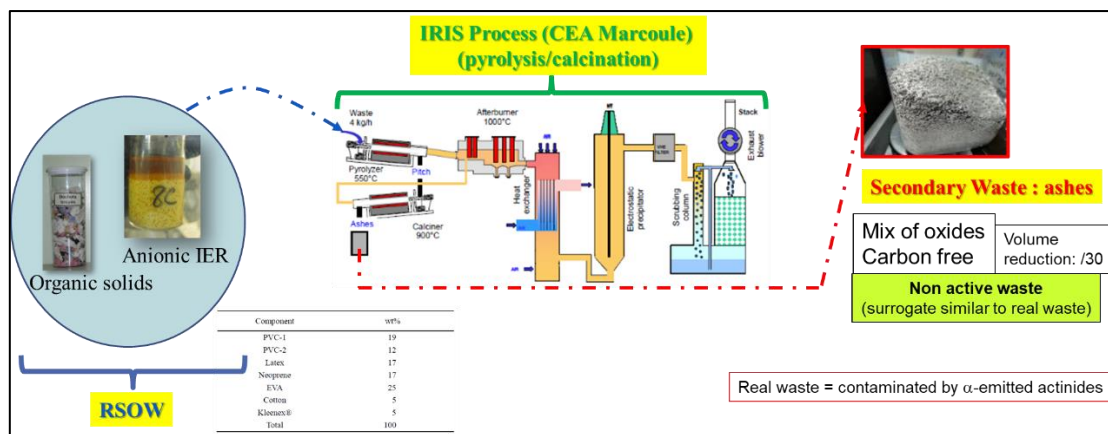

Figure 4.1. Description of the IRIS process

4.1.2 Chemical and structural characterizations of the ashes

The ashes produced have a high flying behaviour with a density of 0.2 g.cm^{-3} and their particle size is mainly centered between 0.1 to 1 mm (Figure 4.2).
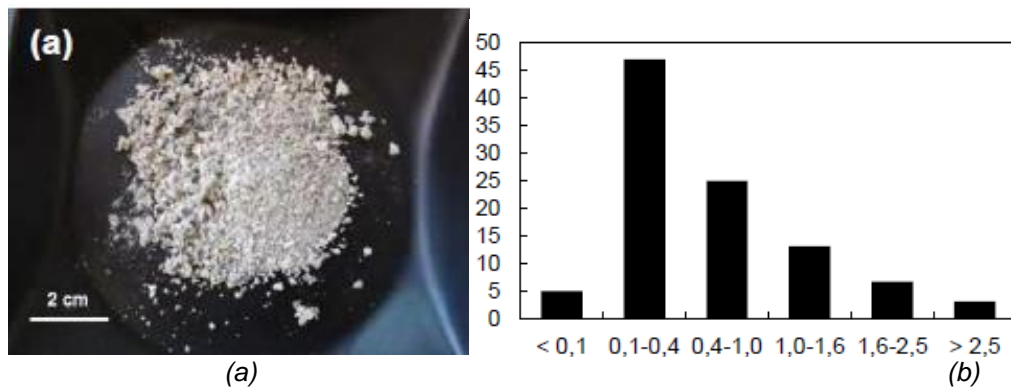
(a)   *(b)*

Figure 4.2. (a) IRIS ashes general morphology, (b) IRIS ashes granulometric class

Elementary chemical characterisations have been done. The ashes are mainly composed of aluminium, silicon, calcium and zinc (Table 4.1).

Table 4.1. Chemical analysis of the IRIS ashes

Component	%weight		Component	%w
C	0,200		Cl	1,74
F	0,005		SO3	1,41
Cl	1,744		BaO	0,15
S	0,566		Cr2O3	0,08
Ba	0,131		Al2O3	28,46
Cr	0,057		Fe2O3	0,63
Co	0,001		MgO	4,53
Cu	0,002		K2O	3,60
Sn	0,001		TiO2	0,69
Li	0,001		P2O5	3,24
Al	15,061		Na2O	0,95
Fe	0,441		CaO	13,55
Mg	2,732		SiO2	29,35
K	2,997		NiO	0,61
Ti	0,414		ZnO	7,17
P	1,830		Bi2O3	0,12
Na	0,705			
Ca	9,684			
Si	13,720			
Ni	0,481			
Pb	0,000			
Zn	5,763			
Bi	0,109			
Σ	56,644			
O (difference)	43,356			

SEM and structural characterizations have been done. The micro particles have a very porous aspect and are partially amorphous. The crystallized phase are composed of ringwoodite and anorthite.
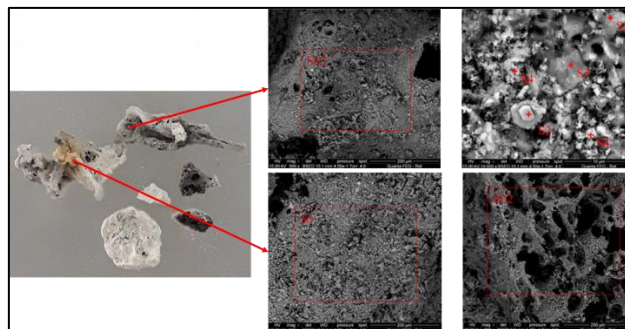

Figure 4.3. SEM analysis of the IRIS ashes

4.1.3 Densification

The immobilization of the ashes waste is studied according to different routes, with the objective to get a densified monolith.

The first route is compaction. Ashes are shaped to get pellets obtained either starting from the raw ashes, either from a mix of ashes and glass as vitrification agent. The pellets are then heat-treated to get a densified and sintered monolith. The interest of an adjuvant made of sodium silicate has been evaluated.

Pellets of ten millimeters in diameter and weighing zero point five grams have been shaped, using a uniaxial press. Various pressure strength from sixty four to two hundred megapascal have been tested. The best mechanical performances have been achieved with the two hundred pressed pellets (Figure 4.4).

Granulates have been shaped using a granulator mixer and many parameters as operating speed, granulation times and water addition have been evaluated. The best parameters have been defined to get quite homogeneous sizes of granulates but their mechanical strength are weak, making them very difficult to handle, and their mechanical performance are difficult to assess.
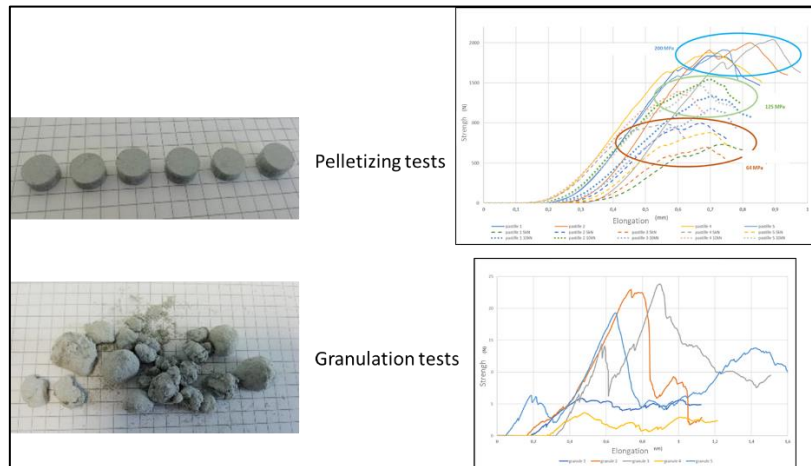

Figure 4.4. Mechanical characterizations of the pellets and granulates

In a second step, these different shaped ashes have been heat treated in a classical lab furnace at eleven hundred degree during three hours. For both shapes, a densified material has been achieved, with a significant densification factor, especially for the pellet (Figure 4.5).
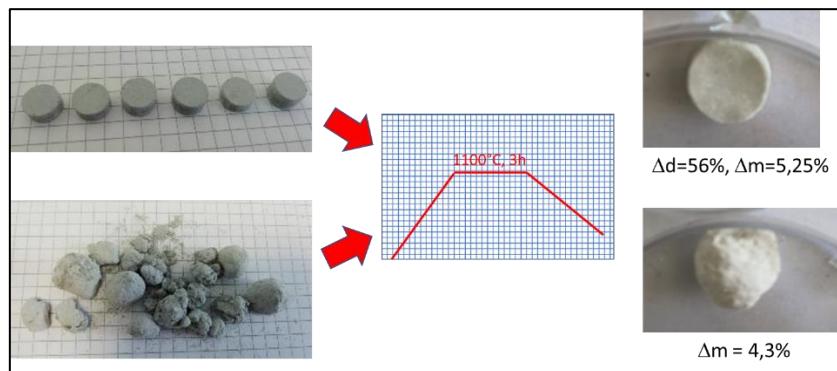

Figure 4.5. Thermal treatment of the pellets and granulates

The next steps will be to realize microstructural analysis to understand the material transformations.

5 National Nuclear Laboratory (NNL)

NNL are tasked with producing scaled up HIP products from the wet oxidation simulant at USFD, to demonstrate the technical ability to upscale this process. This will be directly led by information and data arising from sintered pellets and small-scale HIP trials at USFD.

NNL are in regular communication with USFD regarding progress towards defining a simulant material, and for pre-processing methods to ensure a similar material between both USFD and NNL. Due to the requirement for information feed-in from trials performed at USFD, NNL have not produced larger scale HIPed products at present. The production of these is envisaged as an end-stage outcome of this project, once formulation and processing optimisation has been completed on small products at USFD.

6 National Science Center Kharkiv Institute of Physics and Technology (KIPT)

N.B. This section has been written by Sam Walling (USFD) based on information from KIPT

Due to the invasion of Ukraine by Russia, progress towards KIPT task deliverables has halted for the time being. Several partners from KIPT have left the country, and we understand damage has occurred to buildings at KIPT. The scope of tasks and progress to date towards WP 6.5 goals have been extracted from the KIPT presentation presented at the 2nd Intermediate Workshop in October 14th 2021 by Sergey Sayenko, Vladimir Shkuropatenko, Eugene Svitlychniy, and Alexander Surkov.

6.1 Scope of tasks

6.1.1 Objectives and equipment

KIPT were due to undertake lab scale tests on ash arising from incineration of non-radioactive wood ashes (as simulant material for contaminated wood), encapsulating this within a geopolymer cement. These ashes arise from the treatment of contaminated wood from around Chernobyl Nuclear Power Plant site, using an experimental incinerator built with financial support from the European Commission. The volume of contaminated material is greatly reduced via incineration, but the ash cannot be stored for a long time in this form and requires immobilisation.

After immobilisation of these simulant ashes within a geopolymer cement, these resulting geopolymer-ash materials were due to be densified into crystalline mineral phases through the application of:

- Furnace sintering

- Hot Pressing (HP)

- Hot Isostatic Pressing (HIP)

Materials were to be experimentally characterised and the stability tested using conventional laboratory techniques (XRD, DTA/TGA)

6.2 Progress to date

Good progress was made at KIPT towards the objectives under WP 6.5. Two avenues for investigation were undertaken: using a geopolymer-ash matrix, and formation of fluorapatite from ash.

6.2.1 Geopolymer-ash synthesis and thermal treatment

A geopolymer matrix was produced, using metakaolin, sand, H_2O, KOH, and K_2SiO_3. This resulted in a 70% geopolymer, 30% ash blend being mixed, and left to cure for up to 28 days. The hardened material was then crushed, cold pressed into a pellet, and taken forward for densification *via* sintering, HP, and HIP (Figure 6.1).

Figure 6.1. Crushed geopolymer-ash material (left), and pressed green body of the same material ready for thermal treatment (right).

A simulant ash was produced *via* pyrolytic processing of wood, due to the radioactive nature of the real ashes. The as-obtained particles were photographed and shown in Figure 6.2. Laboratory analysis of the simulant radioactive ash *via* XRD revealed a multi-phase material, including calcite ($CaCO_3$), quartz (SiO_2), hydroxyapatite ($Ca_5(PO_4)_3(OH)$), calcium oxyphosphate ($Ca_4(PO_4)$), and potassium chloride (KCl), as demonstrated in Figure 6.3.

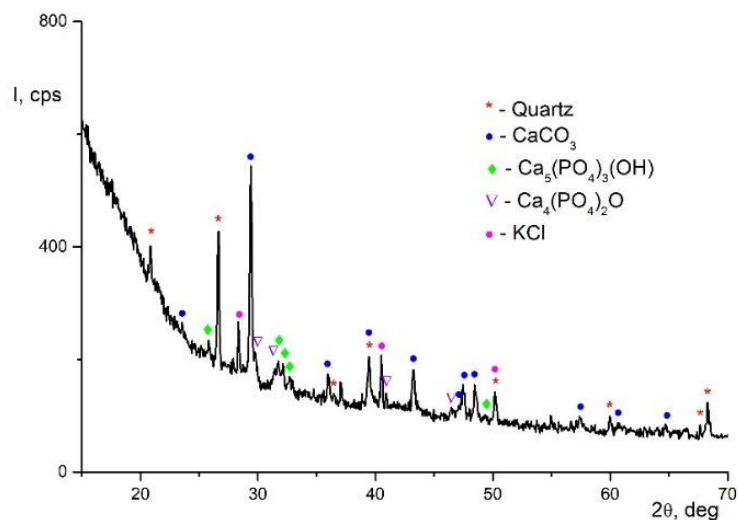**Figure 6.2.** Obtained simulant ash from wood pyrolysis.

Figure 6.3. XRD diffraction pattern of the simulant ash.

The production of a monolithic geopolymer sample both with, and without, this ash was undertaken successfully. XRD analysis of the geopolymers are shown in Figure 6.4, with a 100% geopolymer, and a 70% geopolymer / 30% ash sample analysed. Crystalline phases within the former was determined to be only quartz (SiO_2), while the addition of ash to the geopolymer resulted in the formation of quartz, $CaCO_3$ and KCl. Neither of these materials demonstrated any cracking after 28 days of curing, and both formed solid materials.
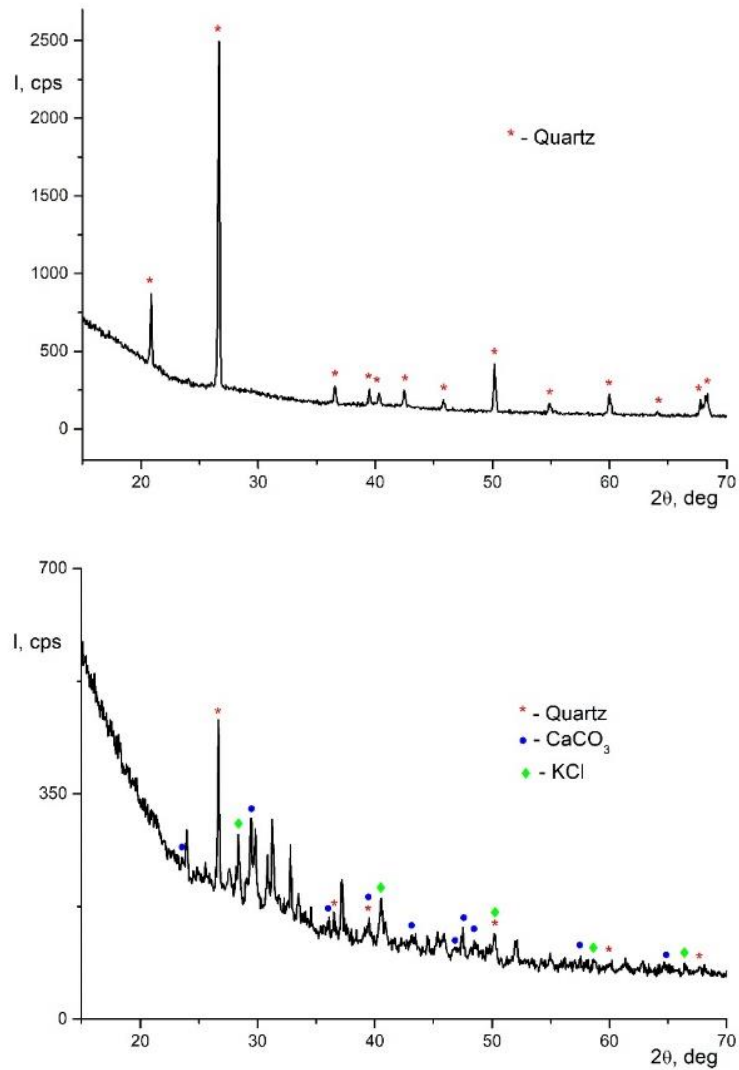
Figure 6.4. XRD reflections for 100% geopolymer (top), and 70% geopolymer – 30% ash (bottom).

The 30% ash-containing sample was taken forward for thermal treatment, by sintering and hot pressing methods. Sintering was undertaken over a range of temperatures from 800-1050 °C, over a 180-minute run, holding at the maximum temperature for 60 minutes. Figure 6.5 shows a pellet of the 30% ash sample after sintering at 1020 °C. Increasing the sintering temperature resulted in higher density (Table 6.1) up to 1020 °C, with an increase to 1050 °C not increasing density any further.
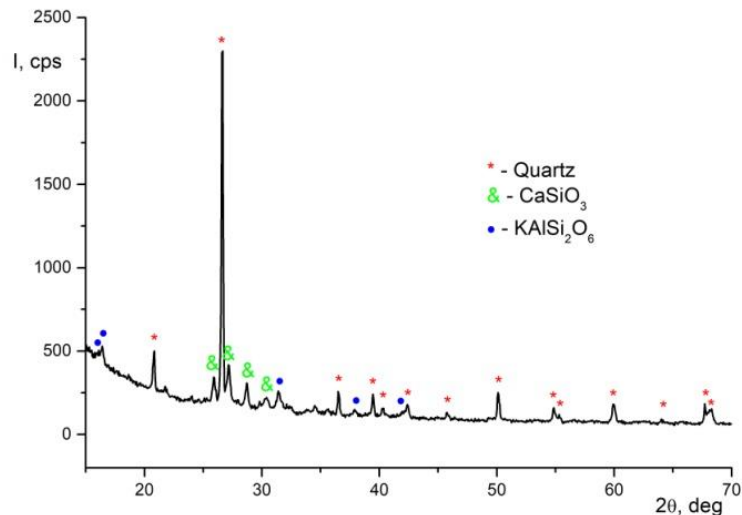

Figure 6.5. Pellet of 70% geopolymer, 30% ash after sintering at 1020 °C.

Table 6.1. Pellet density for 30% ash samples after sintering.

T, °C	Density, g/cm³	% from theor.
800	1,89	70
900	2,10	78
1020	2,30	85
1050	2,30	85

Hot pressing the 30% ash sample was undertaken at 920 °C during a 60-minute run, with 30 minutes at the maximum temperature, utilising a pressure of 40 MPa. Pellets were wrapped in a copper foil to reduce any interaction with the graphite mould. The resulting density of the pellets after HP was 2.57 g/cm³ (95% theoretical density). Figure 6.6. shows pellets after hot pressing, with XRD analysis of these pellets revealed the presence of quartz (SiO_2), calcium silicate ($CaSiO_3$), and leucite ($KAlSi_2O_6$), as per Figure 6.7.

Figure 6.6. Pellets of 70% geopolymer, 30% ash after hot pressing at 920 °C.

Figure 6.7. XRD pattern of the 70% geopolymer, 30% ash sample after hot pressing.

Pellets were then prepared for Hot Isostatic Pressing (HIP) *via* pressing 10 mm x 7 mm pellets (typical mass 1.0-1.1 g), of which multiple pellets were stacked within a cylindrical stainless steel HIP canister, depicted in Figure 6.8.

Figure 6.8. HIP canister prepared with pellets of 70% geopolymer, 30% ash.

6.2.2 Fluorapatite synthesis from ash

An alternative avenue for investigation was the formation of fluorapatite ($Ca_5(PO_4)_3F$) as a stable mineral phase for these ashes, instead of incorporation within a geopolymer matrix. The main phases within the ash include calcite, hydroxyapatite, and calcium oxyphosphate. The addition of some calcium orthophosphate ($Ca_3(PO_4)_2$) and calcium fluoride (CaF_2) in the right stoichiometric amounts, along with sintering at temperature, should drive the system towards the formation of fluorapatite.

The optimal amounts of additives for obtaining fluorapatite from the ash samples has been determined as:

- 50.8 wt.% ash
- 40.4 wt.% $Ca_3(PO_4)_2$
- 8.8 wt.% CaF_2

Thermal treatment of the powder mixture $Ca_3(PO_4)_2$ + CaF_2 + ash was undertaken at 1100 °C in air, for 180 minutes, with 30 minutes at the maximum temperature. XRD analysis of the resulting material after heating is shown in Figure 6.9, revealing the formation of $Ca_5(PO_4)_3F$ alongside $CaSiO_3$.

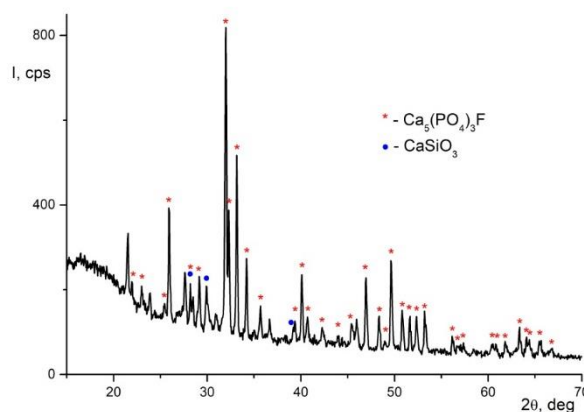**Figure 6.9.** XRD pattern of the $Ca_3(PO_4)_2$ + CaF_2 + ash powder mixture after heat treatment.

Hot pressing of the powder containing fluorapatite was undertaken. Pellets were first prepared by cold pressing and sintering at:

- 1150 °C, 180-minute run (60 minutes at maximum temperature) = 2.56 g/cm^3 density (80%)
- 1200 °C, 180-minute run (60 minutes at maximum temperature) = 2.72 g/cm^3 density (85%)

Hot pressing to increase the density was performed at 1150-1200 °C, for a 60-minute run (30 minutes at maximum temperature), with an applied pressure of 40 MPa. Unfortunately, hot pressing resulted in destruction of the samples (Figure 6.10). This is proposed to be due to the graphite mold, from which carbon is able to

enter the structure of the phosphates, resulting in sample instability and a decrease in thermal stability – with the consequential appearance of cracks and sample destruction. Due to this, it was decided to utilise HIP for future processing, as the pellets will be encapsulated by a stainless steel container, hopefully preventing sample destruction.

Figure 6.10. Pellet after hot pressing.

Future plans for this work package involve Hot Isostatic Pressing of:

- 70 wt.% geopolymer + 30 wt.% ash
- 50 wt.% geopolymer + 50 wt.% ash
- $Ca_5(PO_4)_3F$-containing powder

Along with the associated study and characterisation of the obtained products as a result of the HIP.