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Advanced Gas-cooled Reactor SIMFuel Fabricated by Hot Isostatic Pressing: a Feasibility Investigation

H Ding,¹ L J Gardner,¹ R Mohun,¹ C L Corkhill,¹ M C Stennett,¹ N C Hyatt^{1*}

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

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

Abstract. The manufacture of a simulant UK Advanced Gas Cooled Reactor (AGR) spent nuclear fuel (SIMFuel) was achieved by Hot Isostatic Pressing (HIP). Characterisation of HIP AGR SIMFuels, tailored to burn ups of 25 GWd/t U and 43 GWd/t U (after 100 years cooling) demonstrated fission product partitioning, phase assemblage, microstructure and porosity in good agreement with spent nuclear fuels and SIMFuels, and AGR fuels in particular. A pivotal advantage of the application of the HIP manufacturing method is the retention of volatile fission products within the resultant SIMFuel as the result of using a hermetically-sealed container. This new approach to SIMFuel manufacture should enable the production of more accurate spent nuclear fuel surrogates to support research on spent fuel management, recycle, and disposal, and the thermal treatment of fuel residues and debris.

1. Introduction

The safe management and disposal of spent nuclear fuel is a critical challenge for nation states exploiting civil nuclear energy and the current global inventory of spent nuclear fuels exceeds 300,000 metric tonnes of heavy metal [1,2]. Research involving spent nuclear fuels is challenging and expensive, due to their extremely high dose rate, which requires specialist remote handling facilities. Consequently, there is a need to develop a mechanistic understanding of spent nuclear fuel behavior under conditions relevant to geological disposal, using low activity analogues, which accurately capture the chemistry, phase assemblage and microstructure [3-7]. Such simulant spent nuclear fuels, colloquially referred to as SIMFuels, are also of importance for development of reprocessing flow sheets and thermal treatment processes applied to damaged and degraded nuclear fuels, fuel debris, and fuel residues.

A challenge posed by SIMFuels developed to date is the absence of incorporated volatile fission products, such as Cs, I, Te, and Mo. Cs and I fission products are of critical importance for the early release fraction of spent nuclear fuels in the disposal environment, when infiltrating groundwater encounters a corroded or breached fuel assembly. The typical fabrication process for SIMFuels involves the high temperature (>1600°C) solid state reaction of UO₂ and stable fission product oxides (or alternate reagents), and sintering for several hours, under reducing atmosphere, to give a ceramic body of appropriate porosity. Under such conditions, volatile fission products are completely or partially lost from the phase assemblage [3-7].

Recently, Wangle *et al.* reported the fabrication of SIMFuel material incorporating Cs and I stable fission products, using spark plasma sintering (SPS) [8]. In this approach, an intimate mixture of UO₂ and CsI was subject to reactive sintering in a graphite die, at 1000°C and 10 min under a holding pressure



of 17.7 MPa. The retention of CsI as a separate phase was demonstrated by SEM/EDX and XRD investigation. Nevertheless, some evaporation of CsI from the SPS set up was observed by the authors and the retained CsI was determined to be lower than the initial content. However, this approach has not yet been applied to more complex and realistic SIMFuel chemistries, with a more complete fission product inventory.

We considered that retention of the volatile fission product inventory in SIMFuel materials could be achieved under conditions of Hot Isostatic Pressing (HIP), in which reactive sintering is typically achieved in a hermetically-sealed stainless steel can, under high temperature and pressure (for fabrication of radioactive wastefuels: 1250°C and 200 MPa Ar) [9]. Our development of this technology for the thermal treatment of radioactive wastes has exploited this advantage to contain volatile radionuclide constituents within the product wastefuel. Accordingly, we have undertaken a feasibility study of SIMFuel fabrication, incorporating volatile fission products, by HIP. We focused on the fabrication of SIMFuels for UK Advanced Gas Cooled Reactors (AGRs) for which there exists comparative data for counterparts produced by conventional reactive sintering under reducing atmosphere [10]. AGRs are graphite moderated and CO₂ cooled reactors, which utilize UO₂ fuel, enriched to 2.5-3.5% ²³⁵U clad in stainless steel [11]. Under conventional SIMFuel fabrication conditions, complete volatilization of Cs and Te was observed, and the retained content of Mo, Ru, Rh and Pd was reported to be lower than expected, possibly due to volatilization [10]. For the purpose of this feasibility study, a simplified SIMFuel chemistry was used, with the focus on understanding the retention of Cs, Te and Mo as volatile fission products of interest.

2. Experimental

2.1. Preparation of SIMFuel feasibility samples

This investigation considered fabrication of AGR SIMFuel with a burn up of 25 GWd/t U and 43 GWd/t U, after 100 years of cooling. The estimated stable fission product inventory of such spent nuclear fuels was previously determined using the FISPIN 10.0.1 and reported by Hiezl *et al.* [10]. Based on the published estimated inventory, a simplified SIMFuel composition was established, Table 1, omitting PdO and Rh₂O₃, which are in any case known to form alloy inclusions within SIMFuel and spent nuclear fuels. The depleted UO₂ (>99.9%) powder used in this experiment was purchased from Absco limited (Haverhill, Suffolk, UK) and stable fission product surrogates were purchased from either Alfa Aesar (Heysham, Lancashire, UK) or Sigma Aldrich (Gillingham, Dorset, UK).

Table 1. Target compositions of two SIMFuels after 100 years cooling

SIMFuels composition	25 GWd/t U		43 GWd/t U	
	at.%	wt%	at.%	wt%
UO ₂	97.587	98.193	95.870	97.586
Nd ₂ O ₃	0.483	0.605	0.827	0.364
ZrO ₂	0.369	0.169	0.602	0.279
MoO ₃	0.334	0.179	0.566	0.307
RuO ₂	0.257	0.127	0.454	0.228
BaO	0.244	0.179	0.435	0.323
CeO ₂	0.193	0.124	0.329	0.213
La ₂ O ₃	0.096	0.117	0.160	0.196
SrO	0.032	0.012	0.050	0.019
Y ₂ O ₃	0.041	0.034	0.064	0.054
Cs ₂ O	0.191	0.231	0.309	0.379
TeO ₂	0.044	0.026	0.079	0.047

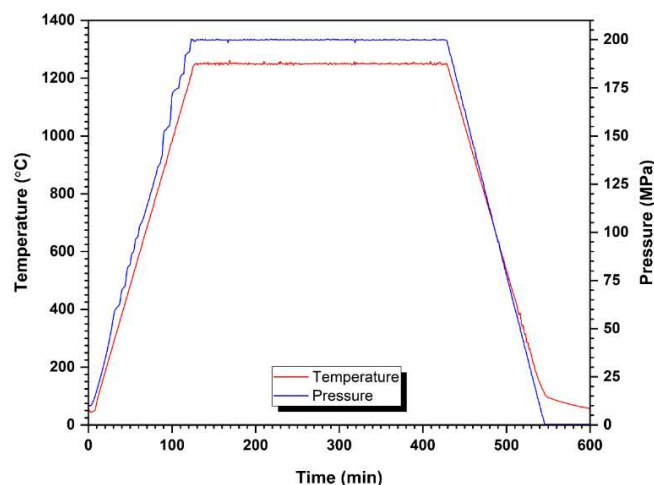


Figure 1. Heating and pressure profile of HIP cycle.

The fission product surrogates were stable oxides except for the use of BaCO_3 and Cs_2CO_3 . A master batch of UO_2 stable fission product oxides / carbonates was produced according to the composition in Table 1 and planetary ball-milled for 15 minutes at rate of 500 rpm. The required quantities of blended stable fission product and remaining UO_2 reagent powders were then planetary milled for 30 minutes at 500 rpm. The homogenised batches were packed into a stainless steel tube (diameter: inner – 3mm, outer – 5 mm) and subject to bake out under 5 Pa vacuum at 500°C for 5 hours. This temperature was selected to be below the decomposition temperature of CsCO_3 to avoid volatilization of Cs (610 °C). The stainless steel tube (Type 316L) was then crimped and welded closed and subject to hot isostatic pressing. The HIP cycle is shown in Figure 1 and incorporated a 5-hour dwell at 1250 °C/200 MPa, with a 10 °C min⁻¹ heating and cooling rate. The ramping pressure was controlled manually and released automatically to match the temperature change as shown in Figure 1. The total volume of SIMFuel produced for each material was approximately 100 mm³.

2.2. Characterisation techniques

Following the HIP cycle, the stainless steel tubes were sectioned to access the HIPed SIMFuel material for characterisation. Powder material was carefully removed from the stainless steel tube, crushed and analysed with a Bruker D2 Phaser diffractometer, using Ni filtered Cu K α radiation (1.5418 Å). All X-ray diffraction patterns (XRD) were collected in the range $10^\circ \leq 2\theta \leq 80^\circ$ with a step size of 0.02°. Unit cell parameters were determined by Rietveld profile analysis using a LaB₆ internal standard. Tube cross-sections were mounted in cold setting resin, polished and characterized by Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM/EDX). Backscattered electron images were acquired using a Hitachi TM3030 SEM with an accelerating voltage of 15 kV, to investigate the microstructure. Images with same magnification were also used to estimate the porosity of the SIMFuel based on the threshold of grey level obtained from ImageJ software. Raman spectroscopy was used to identify changes in the local structure of the UO_2 matrix. Raman spectra were gathered in the range 200-800 cm⁻¹ using a Horiba XploRA Plus Raman microscope with a 523 nm laser and analysed by deconvolution of the band features.

3. Results and Discussion

3.1. Microstructure and porosity

The microstructure of the HIP SIMFuel samples were observed by SEM to exhibit a grain size of ca. 1 μm as shown in Figure 2. The porosity of the SIMFuel determined by image analysis, using ImageJ software, are reported in Table 2, together with that determined for real AGR spent nuclear fuel. It is

apparent that the porosity of the HIP SIMFuels are in good agreement with real AGR spent nuclear fuel and much smaller than the porosity reported for conventionally sintered AGR SIMFuels, typically ca. 20% [12, 13]. The smaller standard deviation in the porosity of the HIP AGR SIMFuel may be due to the homogenised fabrication method, whereas temperature and burnup (and hence composition) gradients exist in the real spent nuclear fuel. It was found that porosity increases for the high burn up composition, which could be attributed to the higher volatile fission product content (because the volatile fission products formed gas bubbles as HIP tube was hermetically sealed).

Table 2. Statistics of area parentage and lattice parameter of HIP AGR SIMFuels.

	25 GWd/t U	43 GWd/t U	Ref
Area Porosity %	2.17 ± 0.32	2.85 ± 0.33	2.19 ± 0.84 [12]
Unit cell parameter a (Å)	5.4721 ± 0.0001	5.4753 ± 0.0001	5.4705 ± 0.0002 [13]

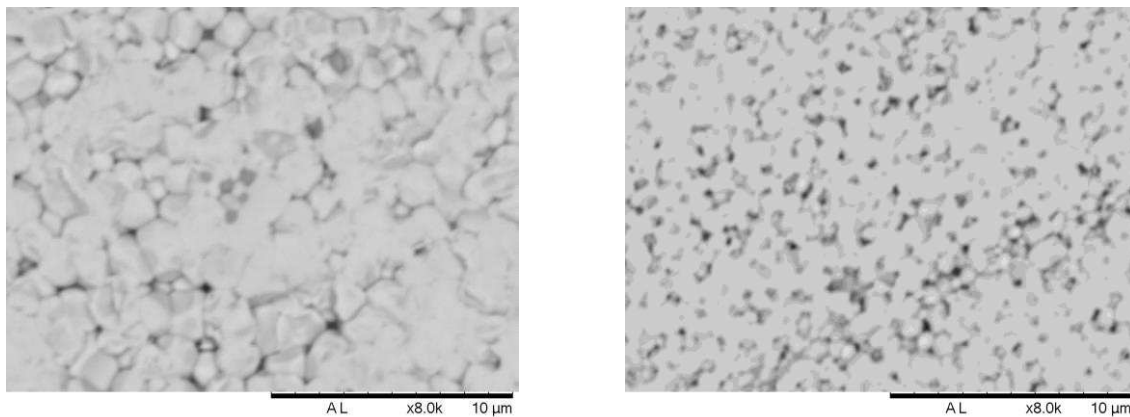


Figure 2. Representative SEM images of microstructure and porosity in 25 GWd/t U (left) and 43 GWd/t U (right) HIP AGR SIMFuels

3.2. UO₂ matrix

The XRD patterns of the 25 GWd/t U and 43 GWd/t U HIP SIMFuel samples exhibited the reflections characteristic of UO₂ (PDF 03-065-028) without additional reflections, as shown in Figure 3. The concentration of additional phases formed by stable fission products was evidently below the level of detection and resolution of the instrument.

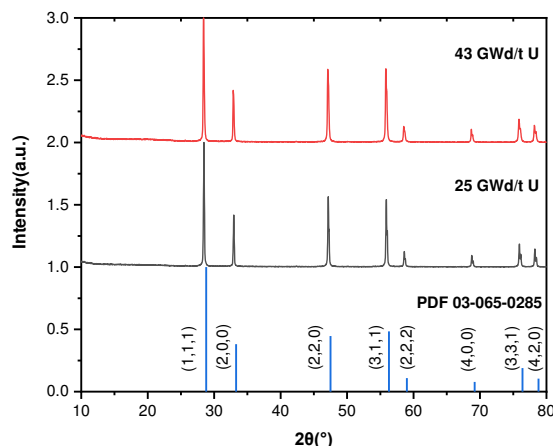


Figure 3. XRD patterns of HIP AGR SIMFuel samples with reference UO₂ pattern.

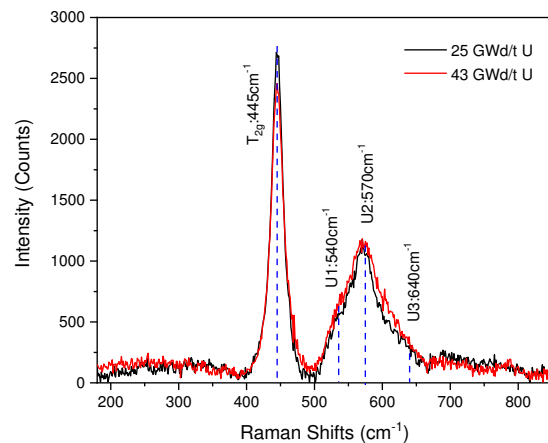


Figure 4. Raman spectra of HIP AGR SIMFuel samples and bands identification.

The refined unitcell parameter (Table 2) showed a slight increase ($0.0320 \pm 0.0001 \text{ \AA}$) from low-doped sample to high-doped sample. It matches well with the typical lattice parameters variations for the intermediate pellet region in real spent nuclear fuel reported in previous study [14,15]. The change is probably due to the fission products (Nd, La, Ce, Zr, Y) dissolved in the UO_2 matrix enlarging the unit cell with a larger average ionic radius. The average ionic radius of dissolved fission products was calculated to be 1.040 \AA and 1.042 \AA for the 25 GWd/t U and 43 GWd/t U HIP AGR SIMFuels, respectively, compared to 1.000 \AA for U^{4+} (all in eight-fold co-ordination). It was found that the change of average ionic radius follows the change of lattice parameter but does not yield a strict linear relationship. The potential cause is the different solubility of fission products as some (e.g. Zr, Ce) were found to be partitioned into oxide precipitates (see below).

Raman spectroscopy analysis, Figure 4, provided further evidence of stable fission product incorporation within the UO_2 matrix, consistent with XRD data. As shown in Figure 4, the sharp T_{2g} band, at 445 cm^{-1} , was observed and assigned to the U-O stretching mode within a symmetric UO_8 cube of the UO_2 fluorite structure [16-18]. The broad feature in the range $500 - 650 \text{ cm}^{-1}$ comprises three bands which are sensitive to defect induced distortion of the UO_2 fluorite lattice, assigned as: U_1 at 540 cm^{-1} , due to oxygen defects; U_2 at 570 cm^{-1} , longitudinal optical mode; and U_3 at 640 cm^{-1} due to oxygen interstitials. The relative intensity of the broad feature comprising the U_1 , U_2 , and U_3 bands increases, relative to the intensity of the T_{2g} band, with increasing burn up. This is consistent with an increased incorporation of fission product species within the UO_2 matrix and hence an increased concentration of lattice defects. The oxygen defect distortion might be induced by fission products dissolved in the UO_2 matrix with an average valence state below U^{4+} , which is consistent with previous Raman analysis of SIMFuel [19].

3.3. Analysis of fission product oxide and metallic precipitates

Fission product oxide and metallic precipitates were formed and observed to be uniformly distributed in the UO_2 matrix. In spent nuclear fuel and SIMFuels, the formation of a perovskite oxide “grey phase” incorporating Zr, Ba, Sr, Mo and Ce, at the boundaries of grains and pores, has been reported [4-7, 10]. Figure 5 shows such a typical grey phase precipitate, a few μm in size. The EDX spectrum of this phase, Figure 5, confirmed a composition consistent with that expected for the grey phase, $(\text{Ba,Sr})(\text{Zr,U})\text{O}_3$ as reported in previous study[10]. Additionally, trace Y, Ce, and Mo were detected within some grey phase oxide precipitates by spot EDX analysis, but the major compositions of these grey phases were similar.

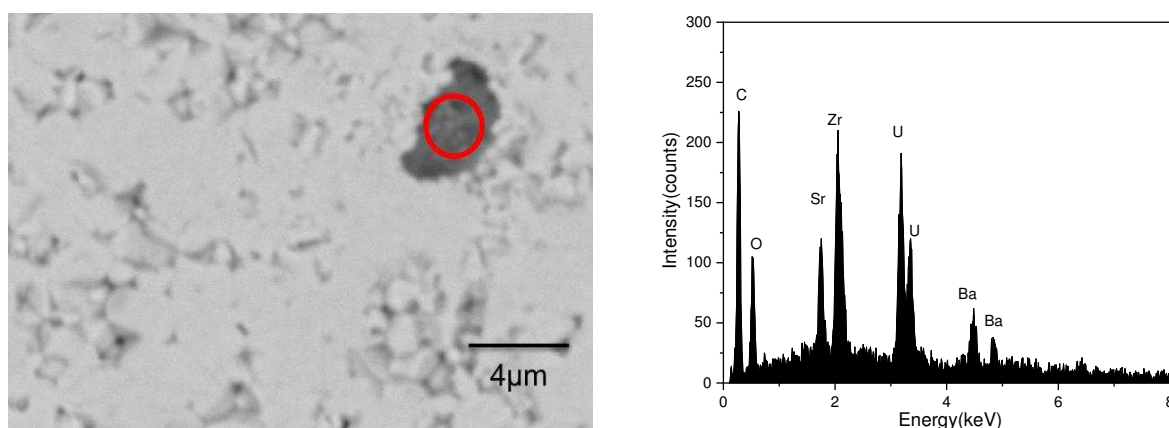


Figure 5. Back scattered electron image and EDX spectrum of typical grey phase oxide precipitate in HIP AGR SIMFuel; in this example 43 GWd/t U.

Metallic precipitates observed in the HIP AGR SIMFuels presented variable morphology and size. EDX analysis of the metallic precipitates revealed that the primary components were typically Mo and Ru.

The elemental compositions were variable but the content of Ru was generally lower than that of Mo, which agrees well with the previous study [4, 10]. Figure 6 shows a typical metallic precipitate with about 64 at. % Mo and 8.7 at. % Ru.

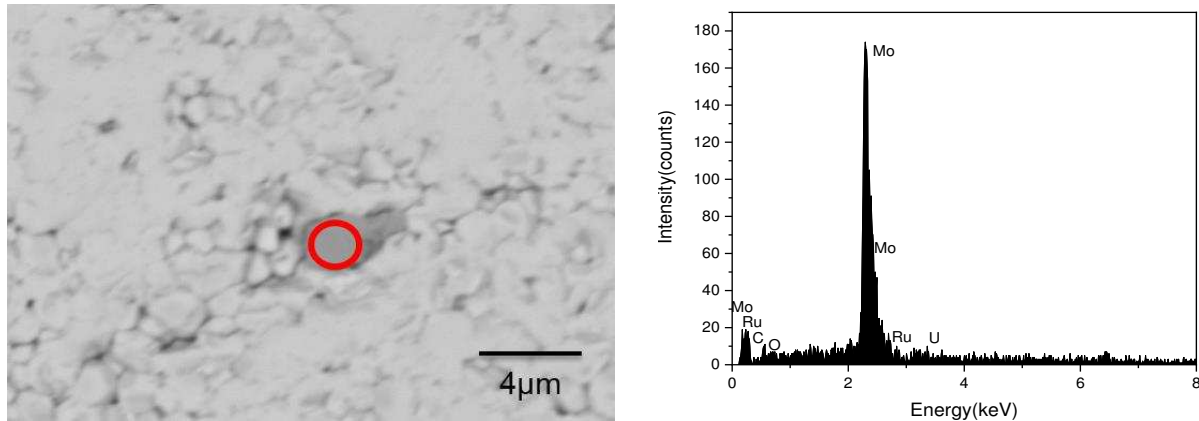


Figure 6. Back scattered electron image and EDX spectrum of typical metallic precipitate in HIP AGR SIMFuel; in this example 43 GWd/t U.

3.4. Analysis of cesium retention

Cs was found to be enriched in the gap between the pellet and stainless steel tube, as shown in the Figure 7, which is consistent with the behaviour observed in AGR spent fuels as well as Boiling and Pressurised Water Reactor (BWR and PWR) spent fuels [1, 20-24]. In the case of AGR fuels, it is hypothesised that Cs is transported as volatile Cs_2MoO_4 , with the formation of Cs_2MoO_4 , CsI or Cs_2Te at the fuel pellet rim [20]. In the present HIP AGR SIMFuels, Cs was found to be associated with Cl, implying the formation of CsCl at the interface between the SIMFuel and stainless steel surface. The formation of CsCl has not been previously reported in post irradiation examination of spent nuclear fuels or characterisation of SIMFuels. However, Cl rich deposits were reported on the internal surface of the Zircaloy cladding, some of which were associated with a high concentration of Cs, although the contribution of other elements to the wavelength dispersive X-ray fluorescence spectra made conclusive identification of the Cl bearing phase difficult [21].

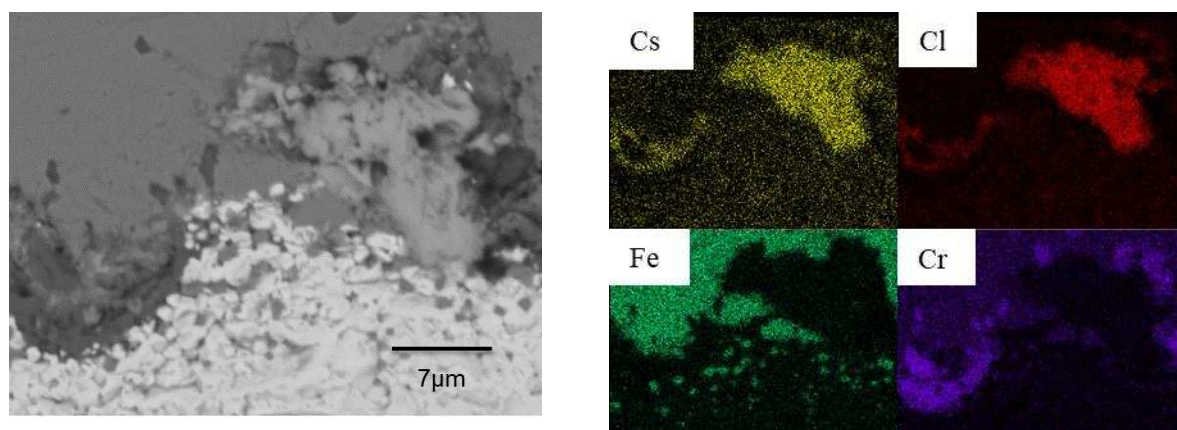


Figure 7. Back scattered electron image and elemental mapping of interface between HIP AGR SIMFuel 43 GWd/t U and stainless steel tube.

The origin of the chlorine in the current observations is uncertain, but could conceivably arise from contamination of reagents, equipment, processes or the stainless steel tubing. The Cl content of UO₂ nuclear fuels is typically trace, for example < 5ppm for CANDU fuel and ³⁶Cl (produced by neutron activation of ³⁵Cl) is of concern for the instant release fraction of spent nuclear fuel [25]. Thus, it is plausible that CsCl is a candidate for rim-enriched Cs species in AGR fuels. However, it is recognised that these species remain poorly characterised in real AGR spent fuels, though it is known that partitioning of Cs into a separate layer on the rim surface does occur.

4. Conclusion

This preliminary investigation has established the potential for production of SIMFuels by HIP, which would enable the detailed microstructural analysis and dissolution behaviour of more realistic fuels to be studied without the need to handle spent AGR nuclear fuel. The fission product partitioning, phase assemblage, microstructure and porosity of the HIP AGR SIMFuels produced were in good agreement with the available data for AGR spent fuels and SIMFuel produced by conventional reactive sintering, as well as the state of the art knowledge of BWR and LWR spent fuels. It was also established that HIP processing of SIMFuels enables retention of volatile fission products such as Cs and Mo, which should enable more accurate surrogates to be developed in future. Cs was found to be enriched at the SIMFuel / cladding interface, as expected. The observed speciation of CsCl is not inconsistent with some available data on spent fuels, but does not agree with consensus predictions of CsI and Cs₂Te formation. However, in this preliminary study I was not incorporated within the SIMFuel composition. Further development and scale up of this promising approach to SIMFuel manufacture is clearly warranted and is in progress.

5. References

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