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DisCo

Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions

DISCO

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Failed fuel report: Characterisation and secondary alteration products

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1 Introduction

The development of robust safety cases for geological disposal of spent nuclear fuel (SNF) requires a solid understanding of its dissolution over very long timescales. Spent fuel dissolution is the main source term for the release of radionuclides under repository conditions and it will control the release of radioactivity in the environment surrounding the engineered barriers (the near field) of a disposal facility once the engineered barrier system (EBS) has degraded and groundwater comes into contact with the spent fuel.

DISCO project represents a logical follow-on from earlier Euratom projects (such as SFS, NF-PRO, MICADO, REDUPP and FIRST-Nuclides) which focused on dissolution and radionuclide release from conventional UO_2 spent fuels. In particular, this project aims to fill the knowledge gap on spent fuel dissolution arising from the development and use of novel types of fuel (Cr/Al- doped and MOX).

Specific objectives of DISCO can be summarized as follows:

- To enhance our understanding of spent fuel matrix dissolution under conditions representative of failed containers in reducing repository environments;
- To assess whether novel types of fuel (MOX, doped) behave like the conventional ones.

As part of the efforts to address the first of the specific objectives, work has been undertaken to characterise some UO_2 SNF that had been stored inside steel cans in the presence of water for a period of approximately 4 decades. The understanding of fuel corrosion is based on a large body of testing, of which that associated with SNF which has been largely conducted for exposure times of 1-2 years. Examination of the fuels described below provide an opportunity to compare the impart of much longer term exposure to water under conditions relevant to disposal in order to compare the results with expectations from shorter term testing.

The Windscale Advanced Gas Reactor (WAGR) began operation in 1962 and an extensive Post Irradiation Examination (PIE) campaign was carried out to examine the behaviour of fuel pins under a wide range of operating conditions. The remains of fuel that had been subjected to destructive examination was placed into 5” diameter screw top cans and transferred into a storage pond at Sellafield. It was anticipated that this fuel would be reprocessed after a relatively short period and consequently the cans were never designed to provide long term containment. It has been shown that this fuel is likely to have become wetted within a short period and, since reprocessing of this fuel was not completed, some fuel was stored in a wetted condition for in excess of 40 years until a repackaging programme began in 2012.

There is little reported post leaching examination of uranium dioxide fuel available. Of the available data, optical microscopy (Figure 1) suggests that enhanced leaching takes place at the fuel surface however this sample image was taken from a sample of fuel used in a controlled leaching trial and it is not entirely clear how representative it would be of fuel that had leached in actual conditions found inside a steel container. It was therefore felt that the WAGR fuel provided an opportunity to examine fuel which was more likely to represent the bulk of pond stored fuel and as a result NNL retained a number of fuel pins for future examination. The EU Horizon 2020 Research and Training programme has taken advantage of this and examination of this fuel has been funded as part of the Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions (DisCo) project.

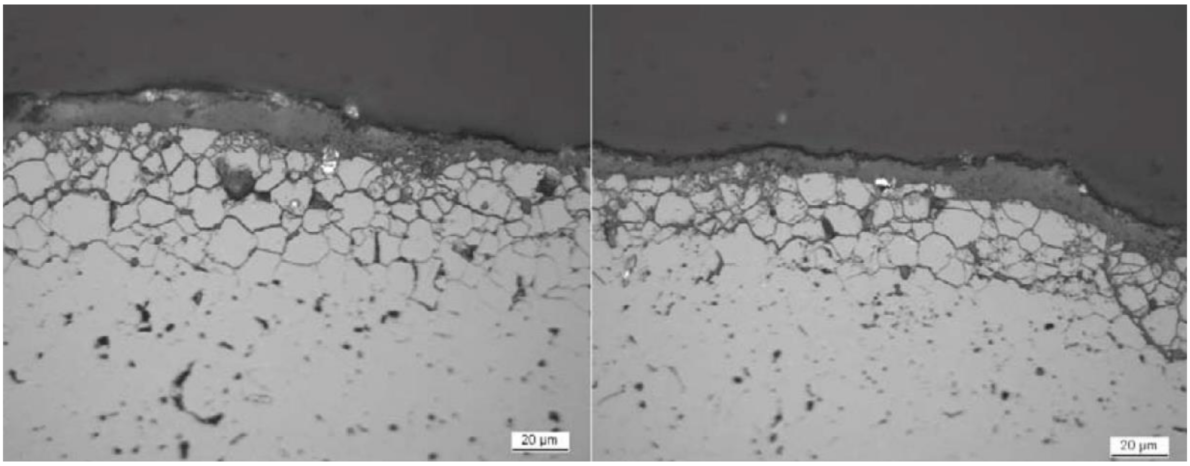


Figure 1. A cross sectional image through an irradiated fuel fragment exposed to simulated ground water (Zwicky, Low, & Ekeroth, 2011).

The retained fuel came from a range of irradiation experiments. Following a study of records two sections of fuel were identified as being of particular interest as part of the DisCo project. The following report presents the results of gamma spectroscopy measurements carried out to positively identify the fuel of interest as well as the results of the subsequent metallographic examination.

2 Fuel identification

As a prototype reactor, WAGR was used to test a wide range of fuel characteristics under a range of operating conditions. As a result, fuel was removed regularly for PIE, resulting in examination of fuel with a wide range of burnups. The fuel pin sections retained had burnups ranging from 2 to 21 GWd.teU^{-1} and different geometries: narrow (10mm diameter) solid pellets, wide (14 mm diameter) solid pellets and wide (14 mm diameter) annular pellets (with a 4 mm diameter bore). The fuel burn-up is low compared to that typical for most power reactors[1], therefore the fuel selected for examination was that which had the highest burnup. However there was also interest in examination of both solid fuel, because of its similar geometry to LWR fuel and annular fuel, which is similar to current gas-cooled reactor fuel.

Interrogation of the records indicated that the highest burnup fuel was from IE 221B stringer 4 (221B/4), which had 10mm diameter, solid fuel pellets. The storage can that had contained

[1] With the notable exception of CANDU reactors.

this fuel also contained remnants from an early IE 221B stringer which had a burnup of only ~5 $GWd.teU^{-1}$ and was visually identical. Gamma spectroscopy was carried out to identify the high burnup fuel from 221B, the results of which are shown in Figure 2. The pins highlighted in dark blue are those from 221B/4.

The retained fuel included two annular sections with a hollow bore. A section of annular fuel was also selected for examination because a number of reactors, including the UK's Advanced Gas-cooled Reactors (AGRs) have annular fuel, and there is little data on annular fuel. Both sections of annular fuel were from irradiation experiment (IE) 424, stringer 4 (424/4) and had a low burnup of around 8.9 $GWd.teU^{-1}$. These sections of fuel are shown in the light blue box in Figure 2.

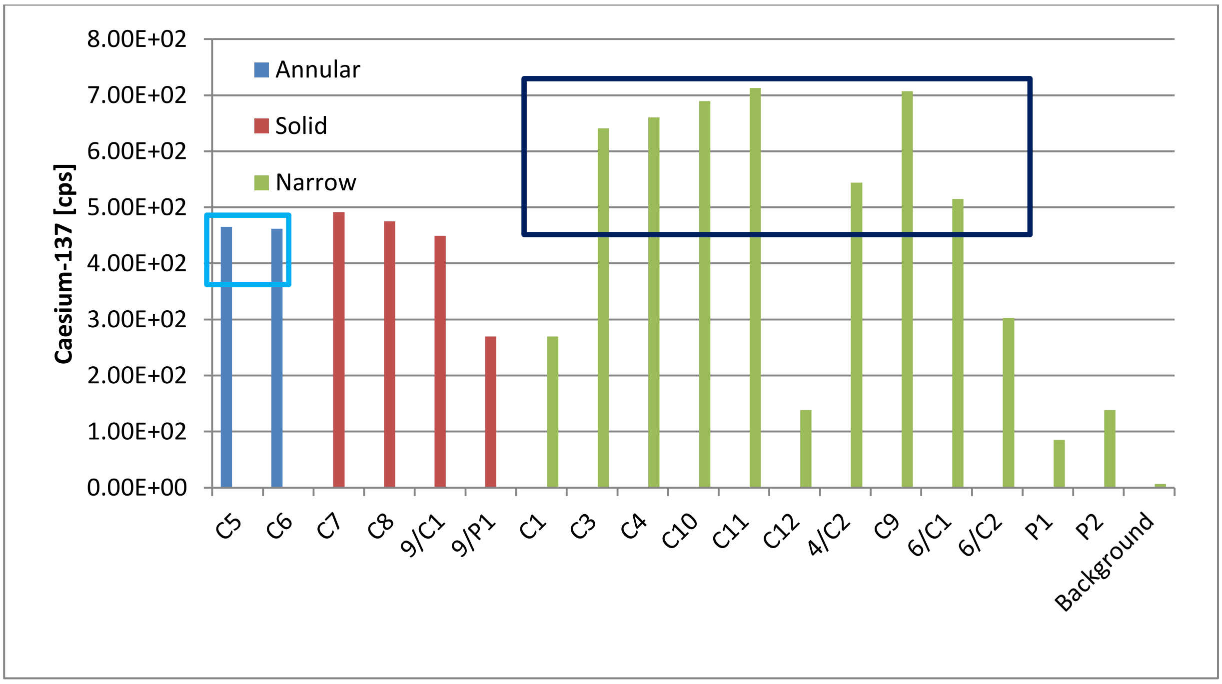


Figure 2. Spot gamma scan results for retained fuel pins

Axial gamma scans of the most promising candidate fuel sections were carried out to look for evidence of fuel that may have been leached or oxidised due to extended contact with pond water (e.g. Figure 3, region A) and to identify suitable positions for sample extraction. The gamma scans identified normal features expected in SNF, such as pellet-pellet interfaces (PPI) and insulator pellets. The gamma scan also indicates a decrease in caesium towards the ends of the solid fuel section from 221B/4, whereas that from the annular fuel section from 424/4 did not show a decrease in caesium at the ends. This is most likely to be due to the presence of an annulus, which allowed greater water penetration along the whole length of the fuel section pin leading to roughly equal axially leaching of caesium.

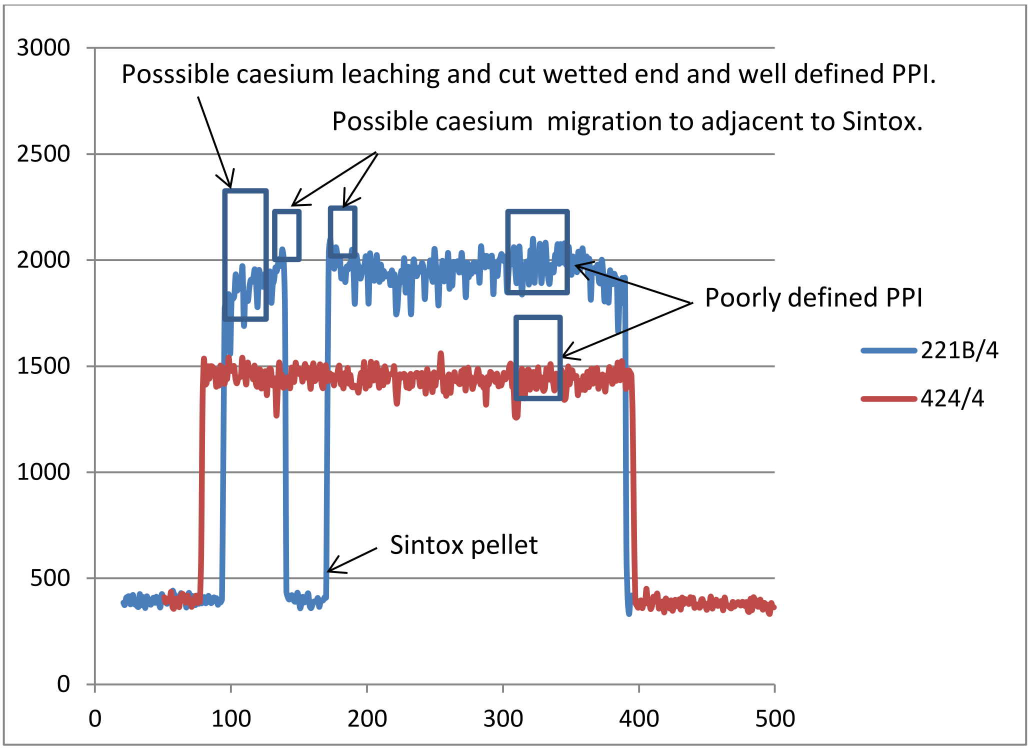


Figure 3. Axial gamma scan of pin sections examined.

A summary of the key information relating to the two samples identified is given in Table 1.

Table 1. Key characteristics of the fuel examined

Irradiation Experiment	Stringer Mean Irradiation [GWd.teU^{-1}]	Pin Irradiation [GWd.teU^{-1}]	Average Rating [W.cm^{-1}]	Enrich-ment [%]	Discharge date	Date to pond	Retrieval date
221B/4	21.2	27.1	152	2.9	19-Sep-68	5-Dec-69	29-Sep-14
424/4	6.21	8.89	304	2.7	12-Jun-69	5-Dec-69	29-Sep-14

3 Fuel Examination

Longitudinal samples, approximately 25mm long, were cut from the exposed end of pin sections from both IE 221B/4 and 424/4 and also from a non-exposed section of 221B/4. The samples were mounted in resin and were polished using consecutively finer grades of polishing media. The samples were initially examined in the as polished state and then again following an etch with a mixture of hydrogen peroxide and sulphuric acid, to bring out the fuel microstructure.

3.1 As-polished Observations

Since the principle aim of the metallography examination was to assess the effect of long term exposure to water, particular attention was paid to regions potentially facilitating the ingress/assess of water to the fuel. These regions included:

- Fuel-clad gap
- Fuel cracks/microcracks/intersections of sintering defects with pellet surfaces
- Pellet-pellet interface (PPI)
- Interlinked fission gas bubble network
- The "wetted" end and the "non-wetted" end

The observations from the examinations of IE 221B/4 and IE 424/4 are presented below.

3.1.1 IE 221B/4

Figure 4 shows an overview of the solid fuel section, with the wetted end to the right of the image. The nominal outer dimension for this solid fuel sample is ~10.16 mm (0.4").

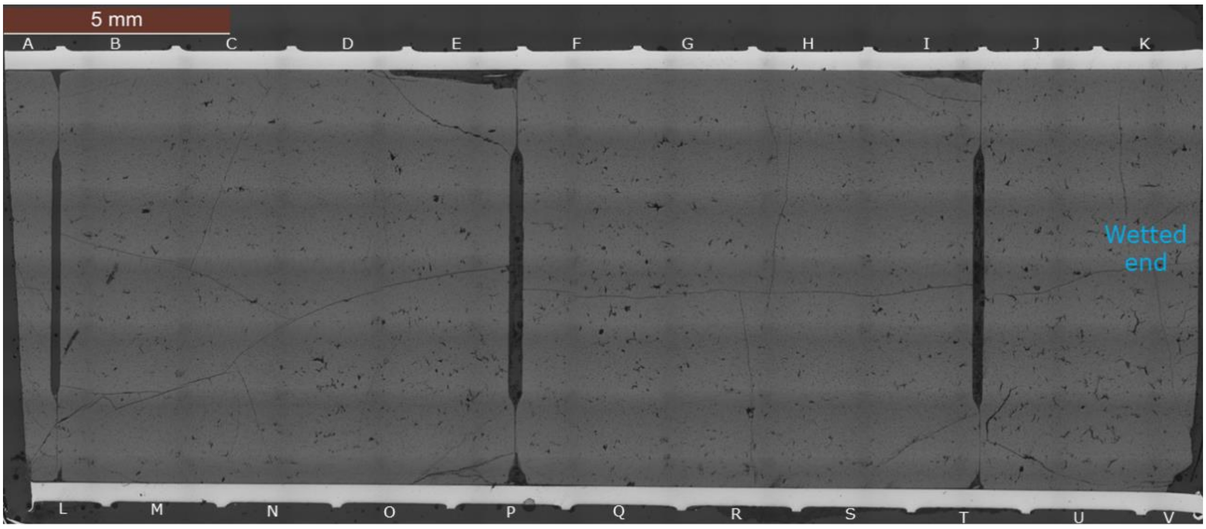
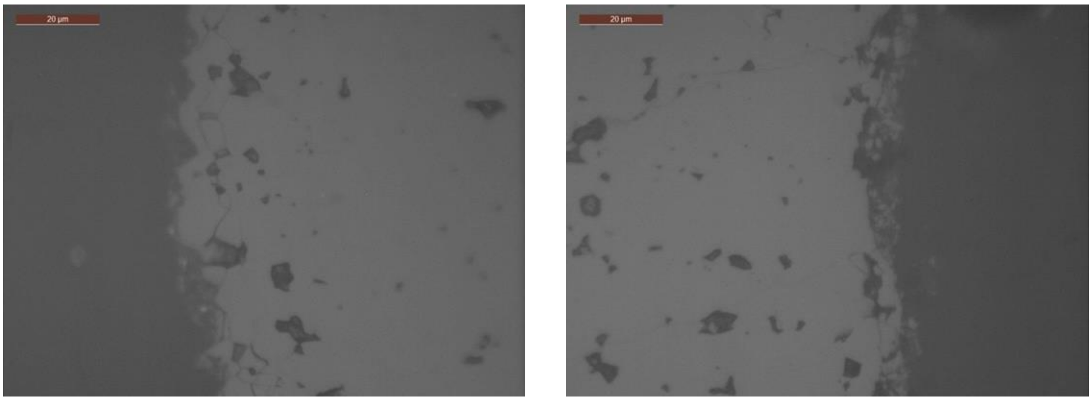


Figure 4: A macrograph of IE 221B/4

There appeared to be very little microstructural difference between the fuel at the wetted and non-wetted ends of the samples, as shown in more detail in Figure 5. No intergranular porosity was observed within the fuel of IE 221B/4. The grain size within this fuel is small making it somewhat difficult to differentiate between as-manufactured porosity and "pull out[2]" as a result of sample preparation.

[2] Pull out refers to loss of small part-grains that are pulled out of the fuel matrix during preparation as a result of poor adhesion between the grains and the matrix.

There was no evidence of any higher oxides or corrosion products within the fuel, with particular attention paid to cooler edge regions of the fuel and areas where water exposure was more likely, such as the wetted end, fuel cracks, fuel-clad gap and the PPI regions.



(a) Non-wetted end (b) Wetted end

Figure 5: As-polished condition of the ends of the fuel section from IE 221B/4

Examination of the cladding showed a continuous fuel-clad gap which matches with historic examination (Figure 6). The outer oxide layer appears to have been lost in all but one location at a rib root (Figure 7) and a similar observation was found for the carbon deposit.

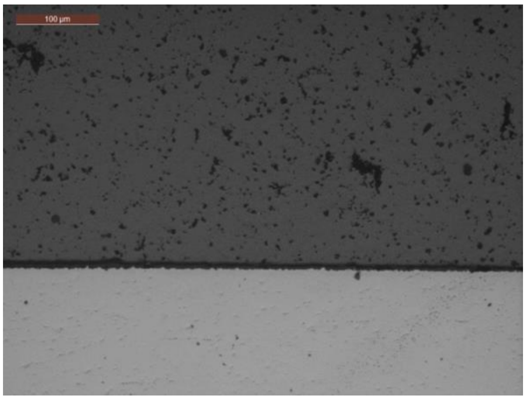
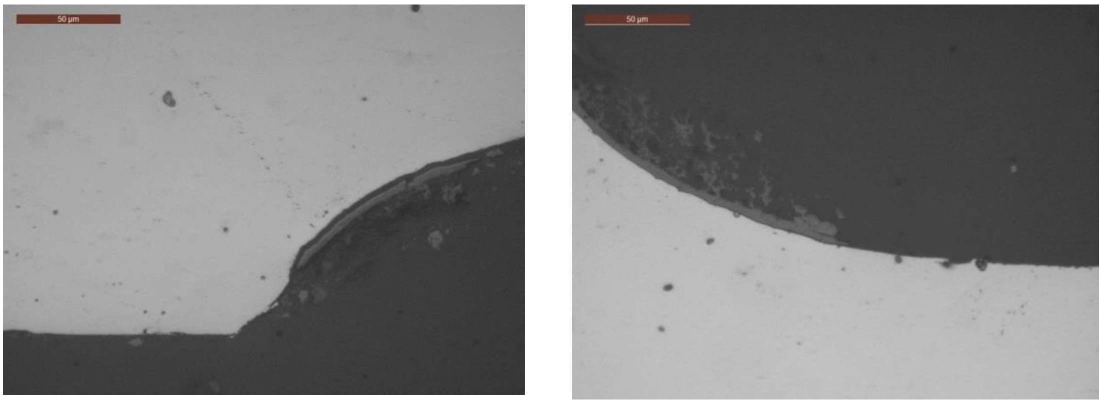


Figure 6: As-polished micrograph showing the continuous fuel-clad gap found on 221B/4.



(a) Oxide (b) Carbon deposit

Figure 7: Rib roots showing the remains of oxide and carbon deposit (221B/4).

3.1.2 IE 424/4

Figure 8 shows an overview of the sample from the end of IE 424/4 the nominal outer dimension for this annular sample is ~14.48 mm (0.57”). The black globules seen around the cracks are due to non-aqueous polishing media seeping out of the sample during examination.

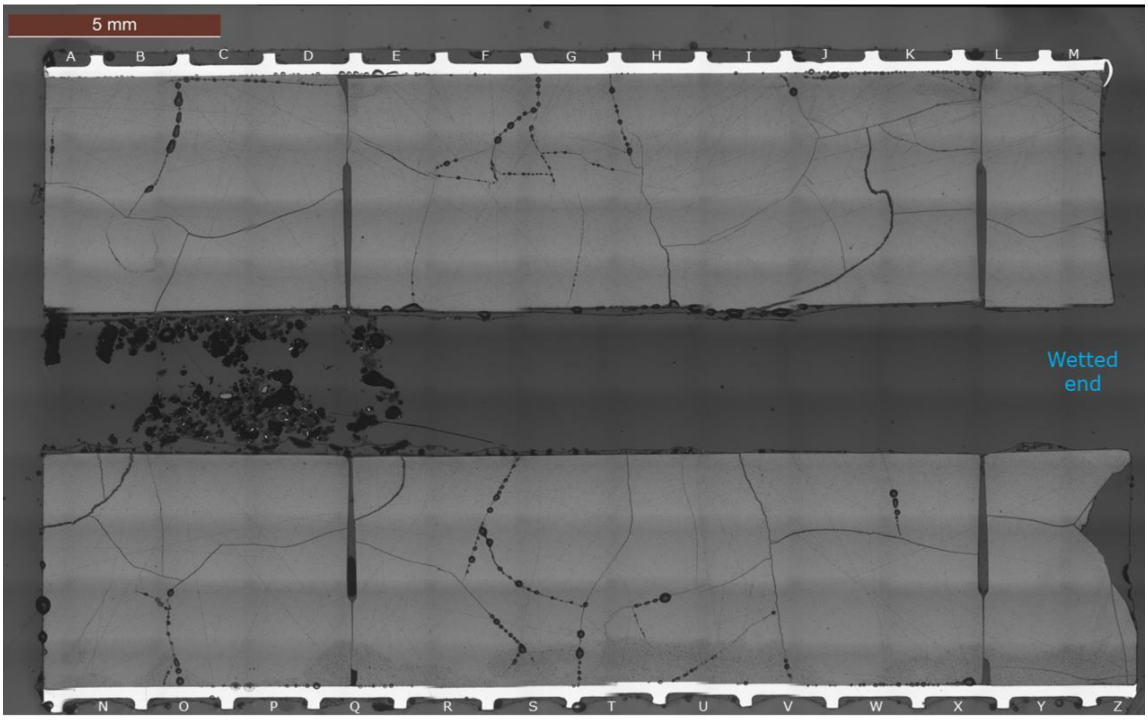
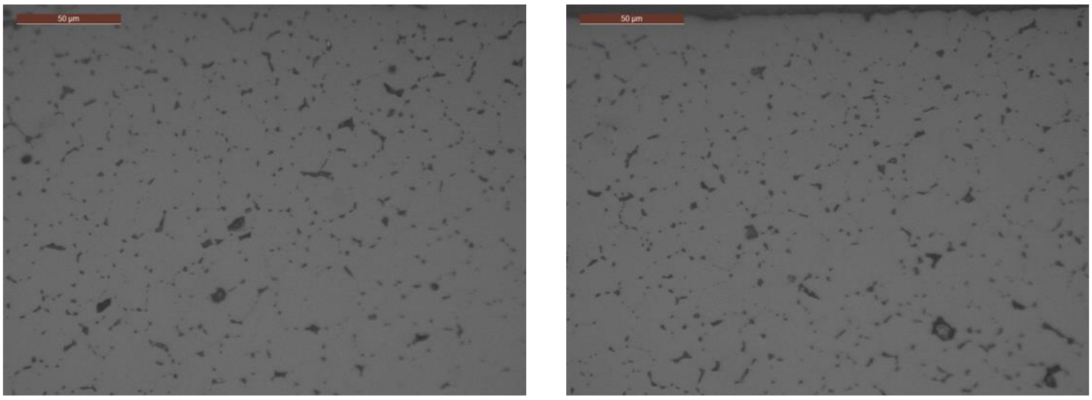


Figure 8: A macrograph of IE 424/4

Intergranular porosity was observed within the fuel on either side of the bore and at both the wetted and non-wetted ends of IE 424/4 (Figure 9). No intragranular porosity was visible, which is not uncommon for fuel from WAGR. Large amounts of as-manufactured porosity were observed in the fuel near the clad. Towards the middle of the fuel this porosity appeared to have sintered up, with the development of intergranular porosity within the hotter regions of the fuel near the bore. Figure 10 shows higher magnification image of the near interlinkage of intergranular porosity within one dimple region at the pellet end. This is another potential pathway for the ingress of water.

In the as-polished condition there appeared to be very little microstructural difference between the fuel at the wetted and non-wetted ends of the samples (Figure 11) and there was no evidence of any higher oxides or corrosion products within the fuel.



(a) Non-wetted end (b) Wetted end

Figure 9: As-polished micrographs showing the intergranular porosity within IE 424/4

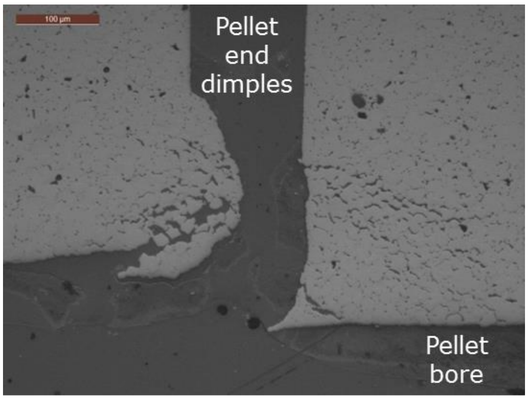
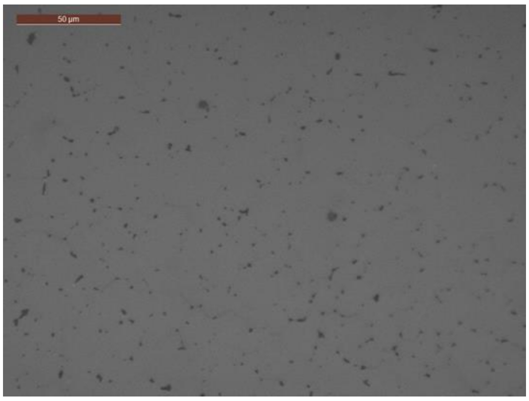
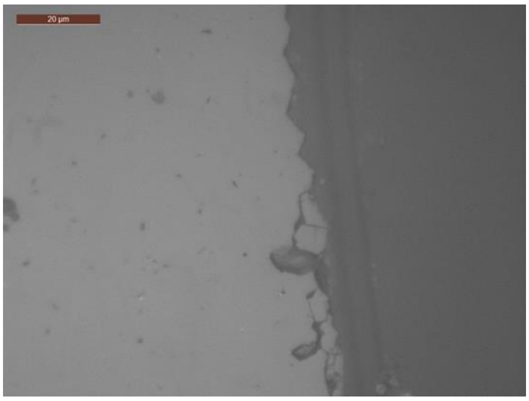


Figure 10: IE 424/4 - As-polished micrograph of the swollen region of the dimple showing near interlinkage of intergranular porosity.



(a) Non-wetted end

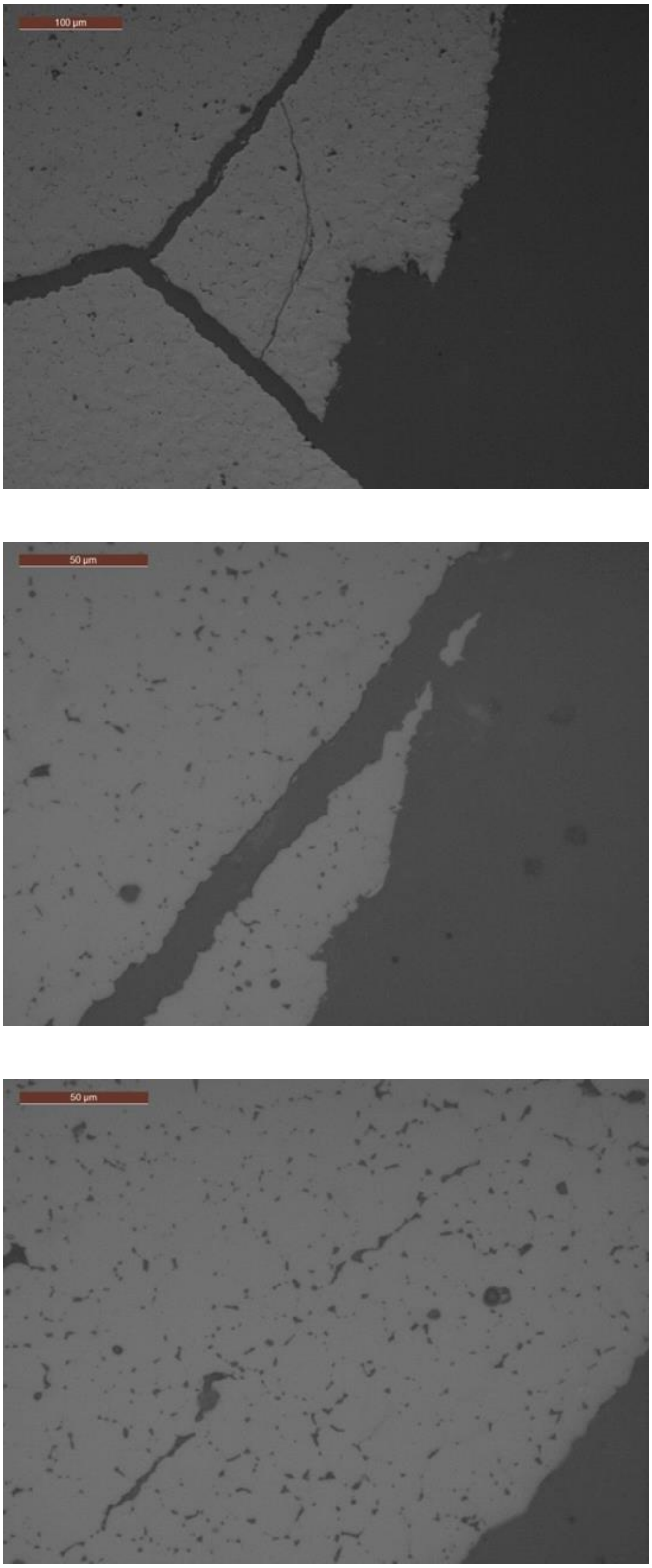


(b) Wetted end

Figure 11: As-polished condition of the ends of the fuel section from IE 424/4.

As can be seen in the macrograph of IE 424/4 (Figure 8) a piece of fuel appeared to be missing from the bottom fuel at the wetted end of the sample. Figure 12 shows as-polished micrographs of the region. There appears to be a large fuel crack running around this area. The high magnification micrographs (Figure 12 (b) and (c)) show there was plentiful intergranular porosity with some possibly interlinking. However the area of fuel exposed to the water and around the cracks showed no evidence of any fuel oxidation or loss of material.

As with 221B/4, a fuel-clad gasp was found throughout 424/4 (Figure 13). However, unlike 221B/4, the cladding oxide layer had been retained, although was found to have lifted in places (Figure 14). Minor intergranular attack (IGA) was noted in places (Figure 15) but is consistent with non-penetrating surface corrosion associated with silicon intrusions.



a) Low power micrograph of the area adjacent to where the fuel is missing.

b) High magnification of the area around the fuel crack.

c) High magnification micrograph showing plentiful intergranular porosity, with some interlinking.

Figure 12: As-polished micrographs of the region around the missing fuel area at the wetted end of the fuel section from IE 424/4

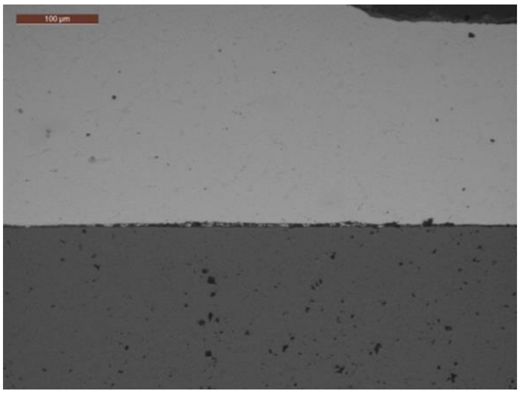
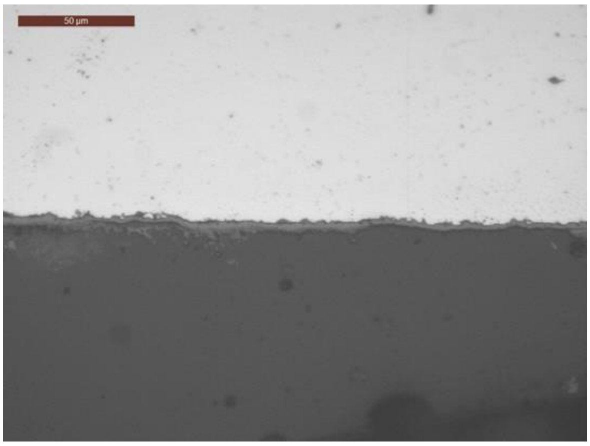
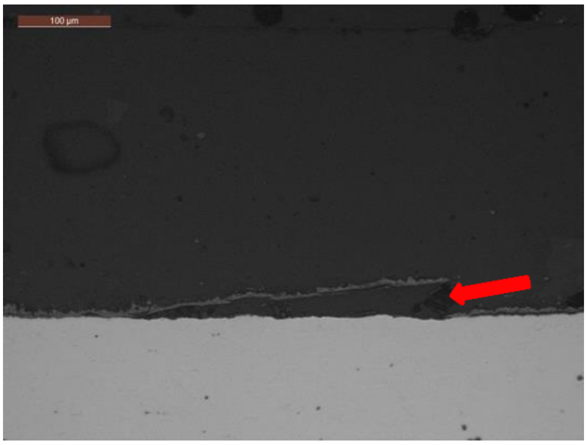


Figure 13: As polished image showing the fuel-clad gap in 424/4.



(a) Typical clad outer surface oxide layer



(b) Area where the oxide layer had lifted.

Figure 14: As-polished micrographs showing the condition of the outer surface oxide layer around IE 424/4.

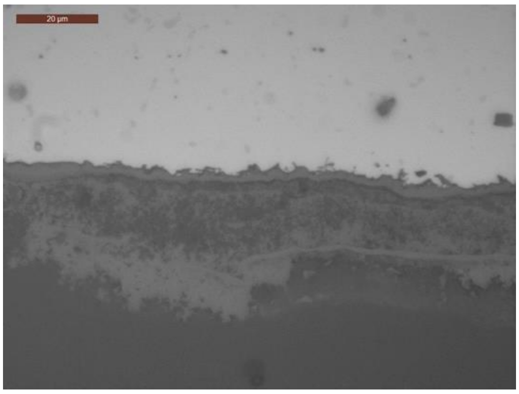


Figure 15: As-polished image showing limited IGA in 424/4.

3.2 Fuel Etch Observations

A mixture of 9:1 hydrogen peroxide and sulphuric acid was used to etch the fuel within the samples, highlighting the grain boundaries and microstructures within the fuel. The observations after the fuel etch are summarised below.

3.2.1 IE 221B/4

A macrograph of the fuel etched sample 221B/4 is shown in Figure 16. During the examination particular attention was paid to areas where water was potentially more likely to penetrate, i.e. in the fuel-clad gap, PPI regions and fuel cracks.

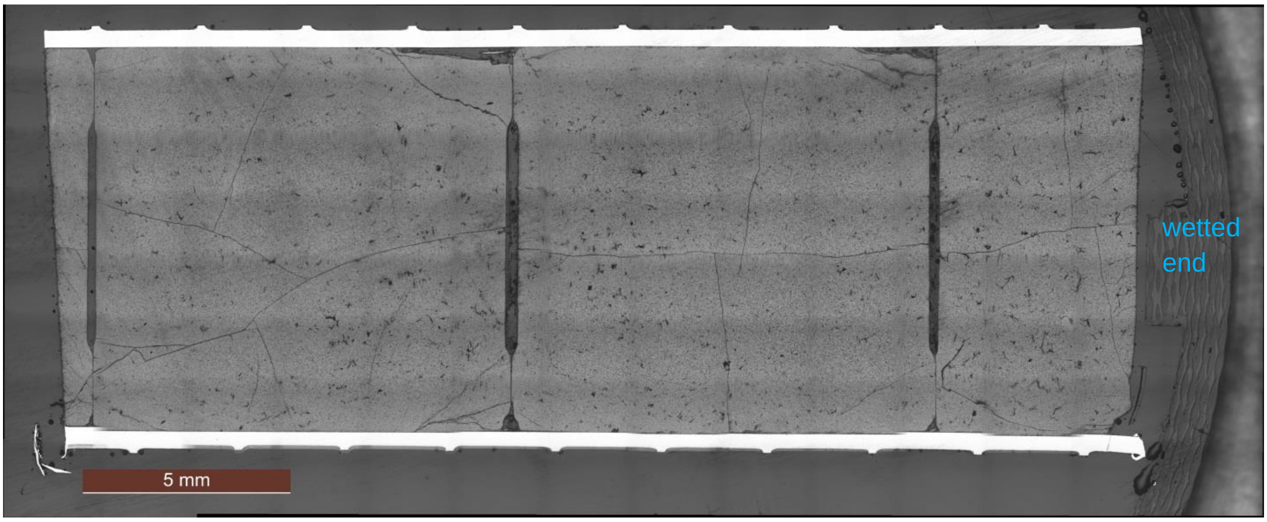


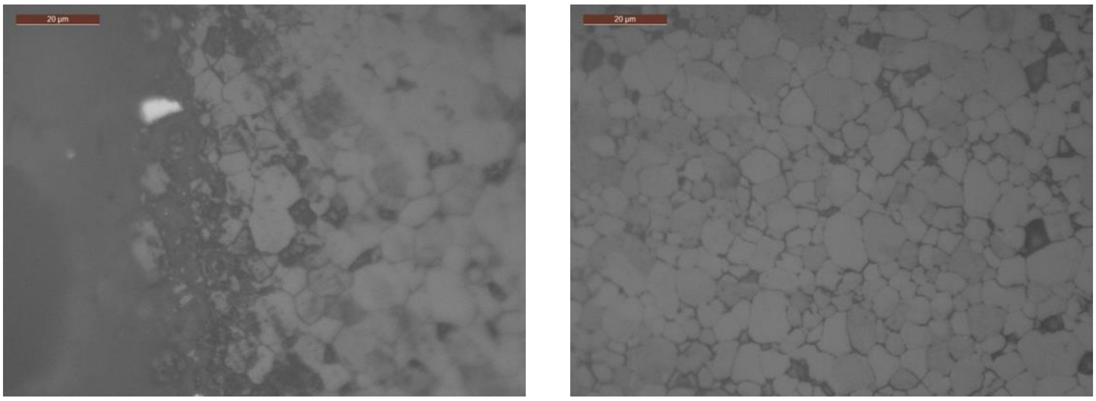
Figure 16. Macrograph of sample 221B/4 following etching

Figure 17 shows the fuel at the non-wetted end of the sample; this should represent the fuel structures most like the original sample (>40 years ago).

Figure 18 shows the fuel at the wetted end of the sample, including areas of cracking and microcracking which originate at the wetted fuel end. Comparing Figure 17 to Figure 17 (non-wetted fuel) there is no obvious difference within the fuel between the two ends. They also show that there was no discernible microstructural evidence of fuel oxidation both at the wetted end and within the fuel around these cracks.

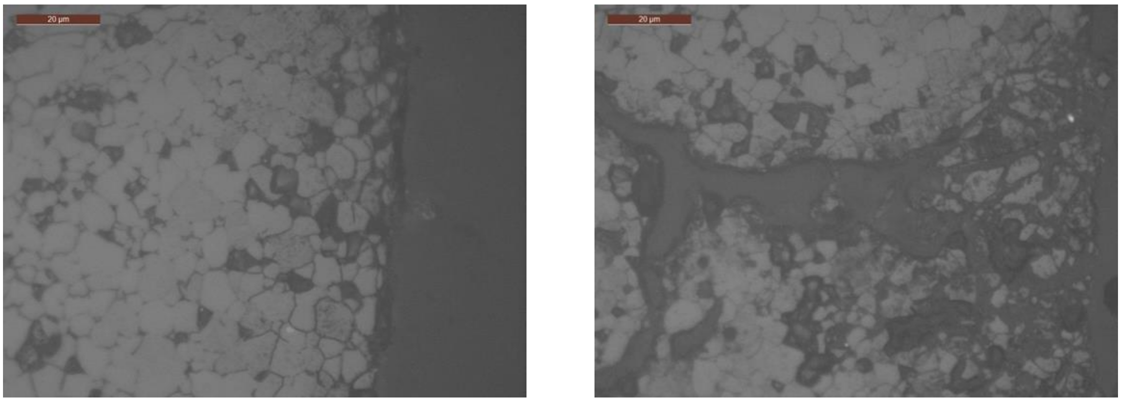
An example of the fuel adjacent to the fuel-clad gap on both the top and bottom sides of the samples is shown in Figure 19(a) and (b). Figure 19 (c) shows the region around the PPI within rib space T (see Figure 4), near the wetted end of the sample. As these micrographs show, there is very little evidence of any microstructural changes within the fuel along the fuel-clad gap or at the PPI.

Figure 20 provides a comparison between the fuel microstructure in the current investigation and that reported in the original PIE (Nairn, Skinner, & Bradshaw, 1970). There is clearly no significant change observable at this level of resolution.

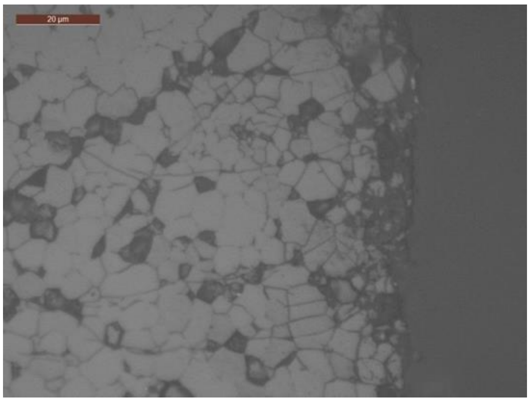


(a) Fuel surface (b) Bulk fuel microstructure

Figure 17: IE 221B/4 – Etched micrographs of the fuel at the non-wetted end of the sample

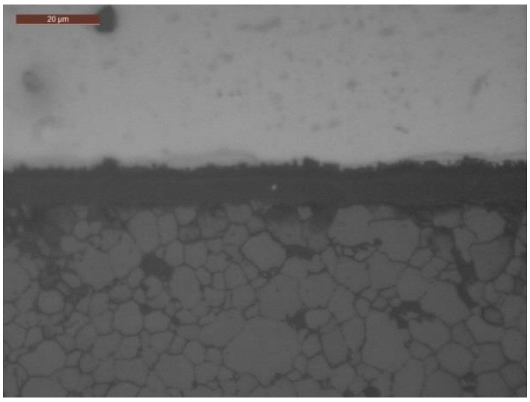


(a) Fuel surface (b) Sintering defect

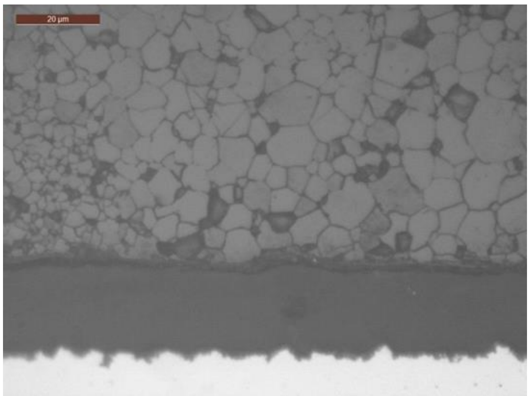


(c) Microcracks running from the wetted surface

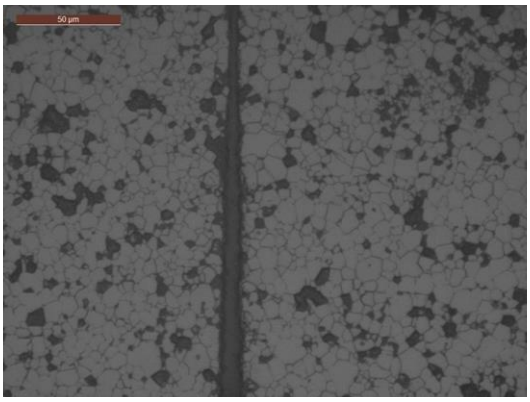
Figure 18: IE 221B/4 – Fuel etched micrographs showing the fuel at the wetted edge of the sample.



(a) Fuel-clad gap at the top of the sample

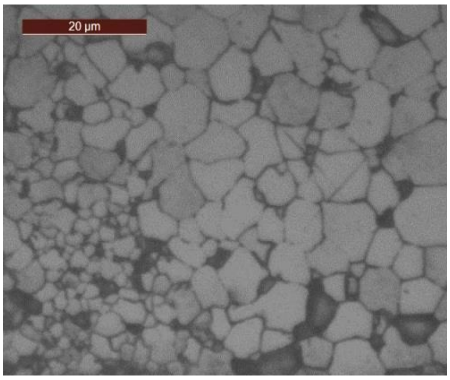


(b) Fuel-clad gap at the bottom of the sample

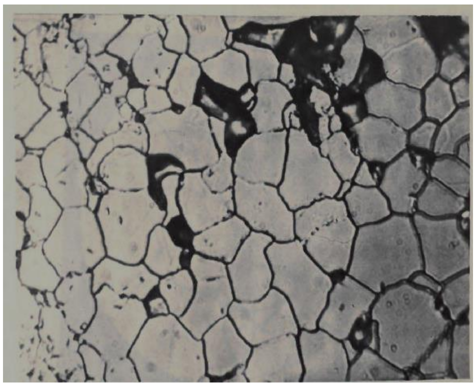


(c) Fuel around the PPI

Figure 19: IE 221B/4 – Fuel etched micrographs of regions susceptible to the ingress of water.



(a) Current



(b) 1960's

Figure 20. Comparison of recent and historic ((Nairn, Skinner, & Bradshaw, 1970)) examinations of the fuel microstructure.

3.2.2 IE 424/4

In IE 424/4 the bore provides another route for water to migrate freely through the sample, allowing rapid access to the PPI's, fuel-clad gap and fuel cracks throughout the fuel stack. Therefore during the examination particular attention was paid to these regions. A macrograph of the sample following the fuel etch is shown in Figure 21.

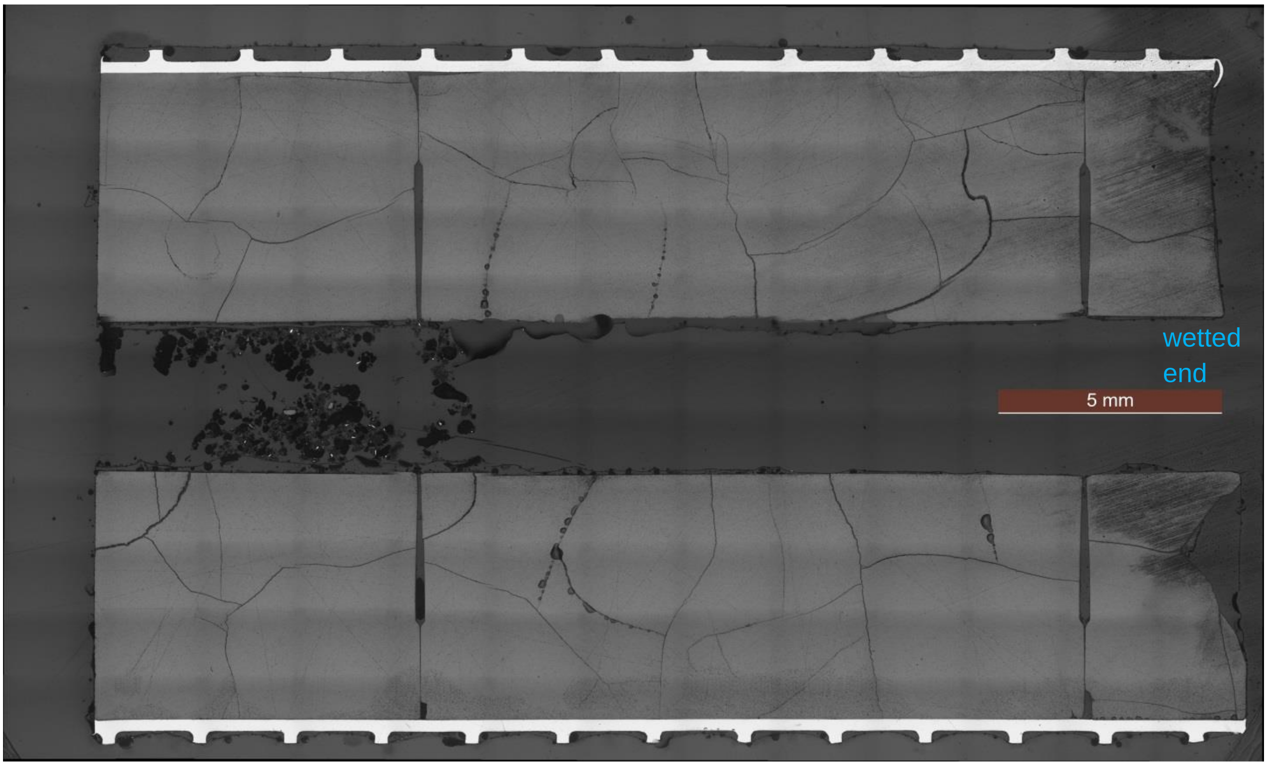


Figure 21. Macrograph of sample 424/4 following etching

Figure 22 shows the fuel at the non-wetted end of IE 424/4 and Figure 23 shows the fuel at the wetted end. When examining both these regions there was little evidence of any microstructural differences and also no evidence of any fuel oxidation.

Figure 24 shows fuel etched micrographs of the area where the fuel was missing at the wetted end of the sample. These micrographs show that there was fuel cracking and intergranular porosity around this region. However there was no evidence of any microstructural differences within this region compared to areas of fuel around the rest of the sample.

Particular attention was paid to the fuel next to the fuel-clad gap (Figure 25), around the PPI regions (Figure 26), on either side of the bore and also around the fuel cracks. As the images show, there was no obvious fuel oxidation within these fuel regions or any evidence of any microstructural changes.

The intergranular porosity within the fuel around the bore region was continuous along the fuel from the wetted end to the non-wetted end. As mentioned in the as-polished observations, interlinked intergranular porosity was observed at the dimple within rib space L (see Figure 8). Figure 28 shows this region in the etched condition. As can be seen, this interlinkage could provide another possible pathway of water ingress to the fuel. Examinations around this area show no obvious signs of fuel oxidation.

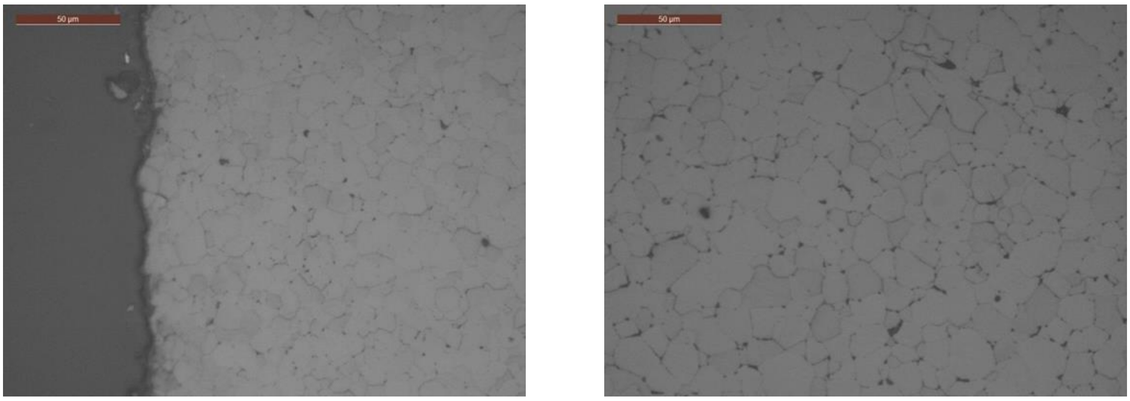
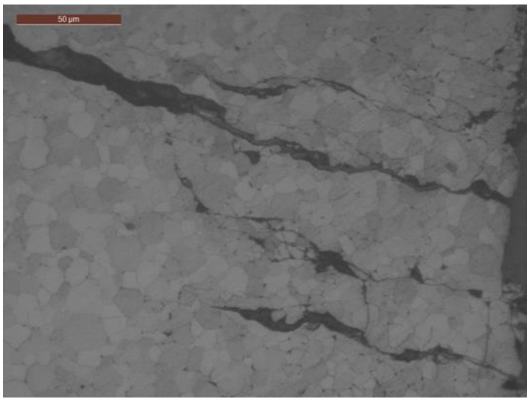
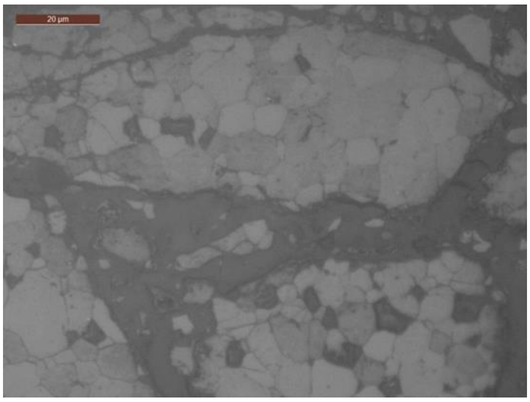


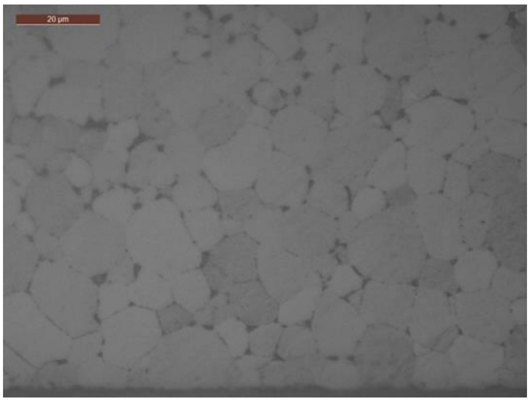
Figure 22: IE 424/4 – Etched micrographs of the fuel at the non-wetted end.



(a) Fuel cracking

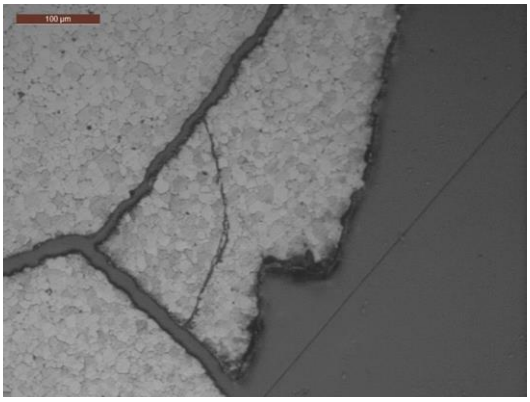


(b) Fuel near the clad at the top of the sample

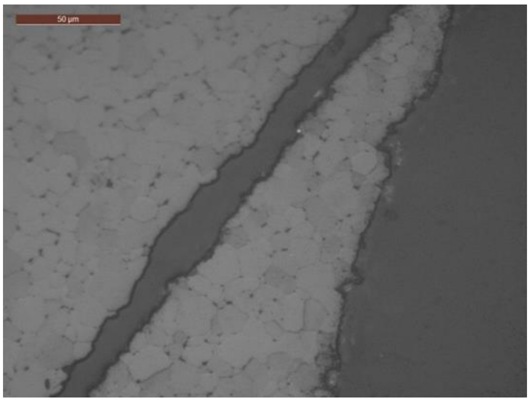


(c) Intergranular porosity

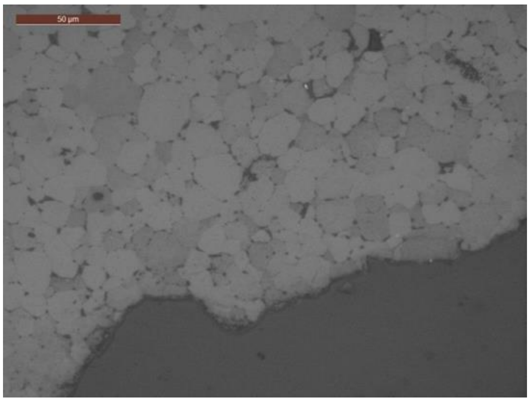
Figure 23: IE 424/4 – Etched micrographs of the fuel at the wetted end.



(a) Overview of the area next to where the fuel was missing

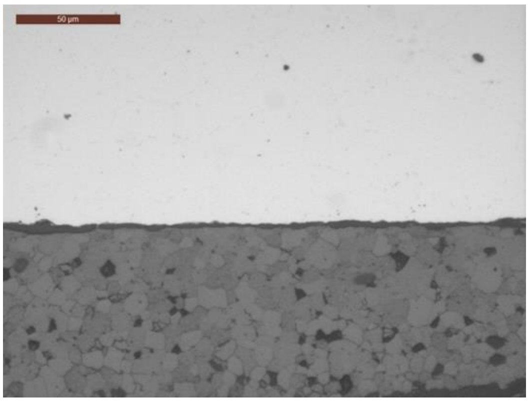


(b) Fuel crack within the region where the fuel was missing

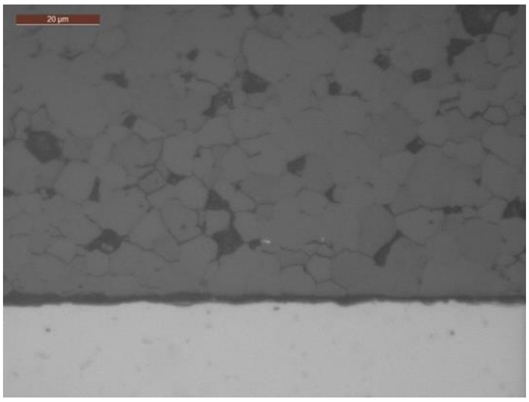


(c) Intergranular porosity within the fuel

Figure 24: IE 424/4 – Etched micrographs around the missing fuel region, at the wetted end.



(a) Top side



(b) High magnification of the fuel at the bottom side

Figure 25: IE 424/4 – Etched micrographs showing the fuel condition around along the fuel-clad gap.

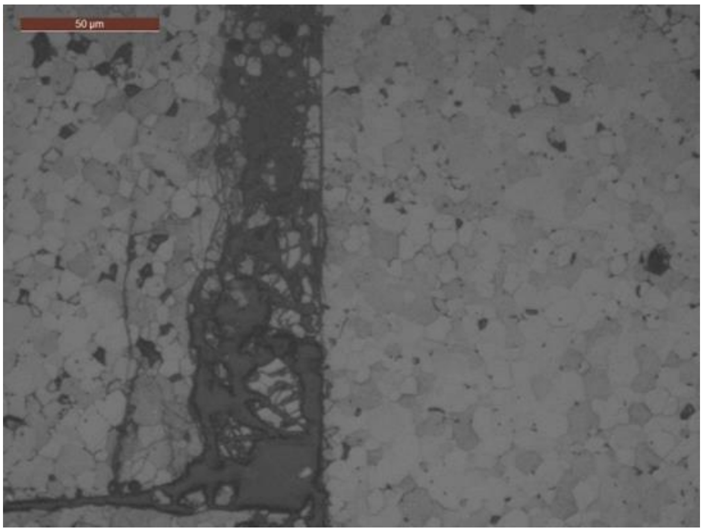
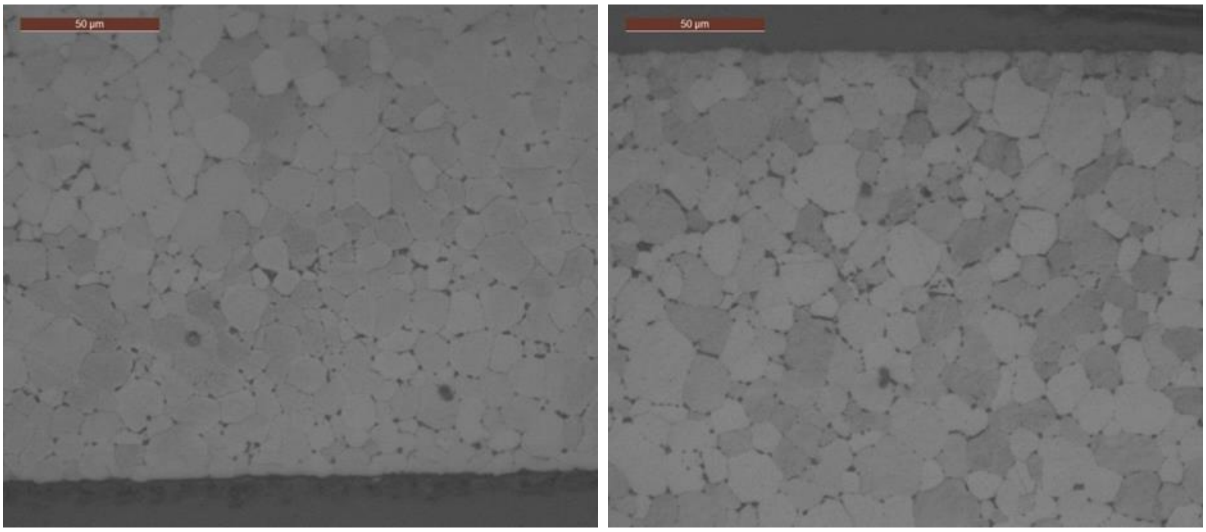


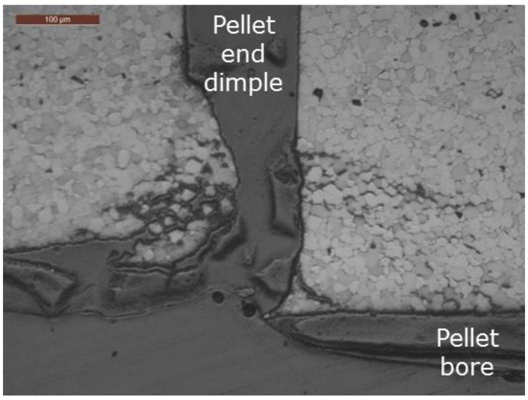
Figure 26: IE 424/4 – Etched micrograph of the PPI within rib space L.



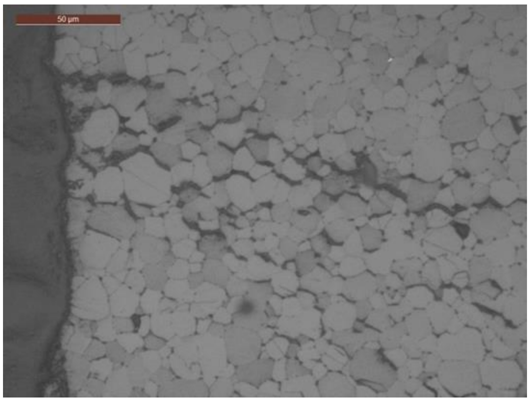
a) Top side

b) Bottom side

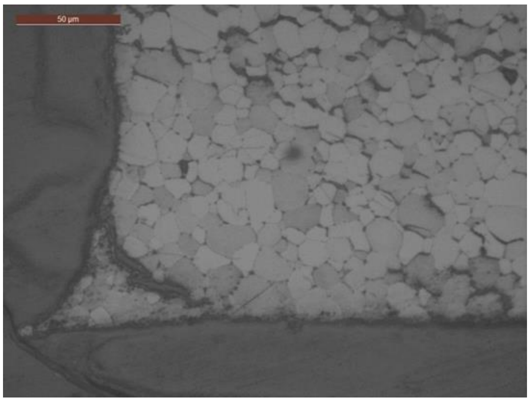
Figure 27: IE 424/4 – Etched micrographs showing the fuel condition around the bore.



(a) Overview of the swelled dimple at the PPI/bore



(b) Interlinked intergranular porosity



(c) Interlinked intergranular porosity

Figure 28: IE 424/4 – Fuel etched micrographs showing the interlinked intergranular porosity at the dimple.

4 Summary & Conclusions

Through record interrogation and gamma spectroscopy it has been possible to identify sections of fuel which have spent in excess of 40 years in a wetted condition during pond storage. A sample of solid pellet fuel (221B/4), which is geometrically similar to LWR fuel, and a sample of lower burnup annular fuel (424/4), which is geometrically similar to AGR fuel, have been examined to enable a comparison between:

- Their overall microstructures now (after storage) and those observed in the original PIE examination >40 years ago.
- The wetted and the non-wetted regions within each sample to seek evidence of any deterioration in the integrity of the UO_2 fuel pellet and the 20/25/Nb cladding.

Particular attention was paid to fuel microstructures at or near potential water access or leak paths. The condition of the cladding, particularly evidence of any enhanced corrosion or sensitisation was also of importance.

The key observations are summarised below:

- There was no detectable difference between the fuel microstructure in the wetted and non-wetted regions of the fuel.
- There was no microstructural evidence of the formation of higher oxides in the fuel, such as intergranular veinous U_3O_7/U_3O_8. It is the volume change associated with the progression of U_3O_7 to U_3O_8 that can potentially lead to the disintegration of the fuel; of which there was no discernible evidence.
- There is no significant difference in fuel microstructure today as compared with original PIE images (see Figure 20).
- The results contradict those seen in previous examinations of leached fuel however, it should be noted that the LWR fuel seen in Figure 1 was part of a controlled leaching study in known conditions and was also of significantly higher burn up than the WAGR fuel examined here.
- The oxide layer was almost entirely missing from the higher burnup sample, 221B/4.

Overall, both the fuel and cladding appear to be in remarkably good condition after >40 years water exposure during pond storage. Further electron-optical work is to be undertaken as part of the DISCO programme, which will complement the optical metallography results.

5 References

1 Nairn, J. S., Skinner, J., & Bradshaw, K. A. (1970). *Post-Irradiation Examination of Windscale AGR Fuel Elements - Progress Report No. 42.* Prog. Rep. 42: UKAEA.

2 Zwicky, H.-U., Low, J., & Ekeroth, E. (2011). *Corrosion studies with high burnup light water reactor fuel-Release of nuclides into simulated groundwater during accumulated contact time of up to two years.* Tr-11-03: SKB.