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DISSOLUTION BEHAVIOR OF HIGHLY BURNT FUEL

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In order to study the dissolution behavior of a highly burnt LWR fuel, a fuel pin irradiated in the DR3 test reactor in Risoe National Laboratory, has been characterized by microstructural examination and then dissolved under PUREX type conditions. The dissolution behavior was investigated and the residues analyzed by scanning electron microscopy and by ICP–MS and IDMS after dissolution.

For economical reasons, extended burnups of fuel in LWR's are becoming more common. However, dissolution of such a fuel leaves larger amounts of residue than normal.[1] The present study provides data of dissolution characteristics for this type of LWR fuel. The amount of residue as well as its composition have been determined for a well-characterised fuel dissolved under PUREX type conditions on a laboratory scale.

The target fuel pin has been irradiated for about ten years to 70 GWd/tU in the DR3 test reactor in Risoe National Laboratory. Samples taken at 5 positions along the pin (Fig. 1) were dissolved in HNO_3 at concentrations, between 3 and 7M. The residues were separated from the dissolver solutions by centrifugation and dissolved at 200 °C in a mixture of nitric and hydrochloric acids.[2] The solutions were analyzed by ICP–MS and IDMS.

Experimental

Historical data of the fuel: The fuel used for the present study originates from Risoe National Laboratory, Denmark. It was fabriced from UO_2 powder supplied by the UKAEA and was irradiated in the Danish DR3 test reactor from January 3, 1971 to January 15, 1982. The main characteristics of this fuel are given in Table 1.

This fuel has of course to be considered as a target fuel as it has a stack length of only 45 cm and a rather large pellet diameter of 12 mm. Worthy to note, that it has a low initial enrichment of 1.5% ^{235}U.

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Samples preparation: The fuel pieces Nos 3 and 8 were embedded in araldite and polished for optical microscopy and electron microprobe analysis. Samples Nos 2, 5, 7, 10, and 12 were used for the dissolution tests.

The chemical analyses of the solutions (fuel and residues) were done by Inductively-Coupled Plasma – Mass-Spectrometry (ICP–MS) or by Isotope Dilution Mass-Spectrometry (DMS). The main elements forming the residue were analysed by

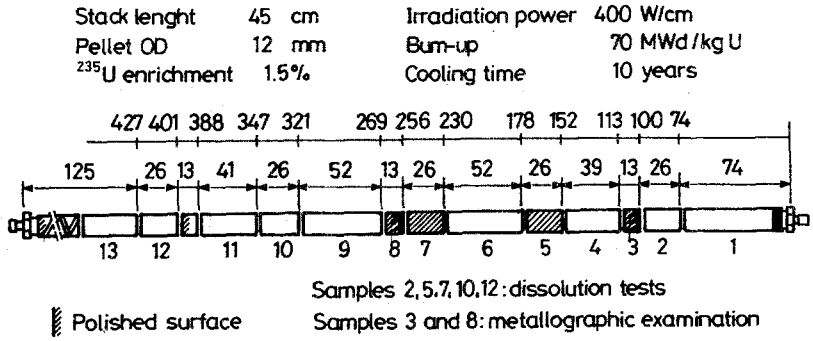

Fig. 1. Cutting plan of the fuel pin

the ELAN ICP–MS from Sciex-Perkin-Elmer, where the elements are ionized in a plasma torch at 800 °C and 10^{-5} torr and analyzed by quadrupole mass spectrometry. The isotopic composition of U and Pu was determined using a Finnigan MAT 262, a single-focussing multicollector mass-spectrometer.

The burn-up was determined by measuring the ^{137}Cs concentration, from which, knowing the fission yield of ^{137}Cs, it was possible to calculate the burn-up of the sample.

For sample No. 7 the burn-up was also determined by means of the ^{148}Nd method. This method requires a time-consuming chemical separation of actinides and fission products. The concentration of ^{148}Nd was determined by IDMS using ^{150}Nd as a spike.[3]

Dissolution procedures: The five samples mentioned above were dissolved under PUREX type conditions. The evolution of the uranium concentration with time is shown in Fig. 2.

The initial volume was always 100 ml. The temperature was kept at close to 98 °C before and after dissolution. During the dissolution, the solution boiled with a maximum temperature of 106 °C for sample No. 7.

At the end of dissolution the solution was heated for further 3 hours. The residues were separated from the dissolver solution by filtration and washed 3 times with 0.1M

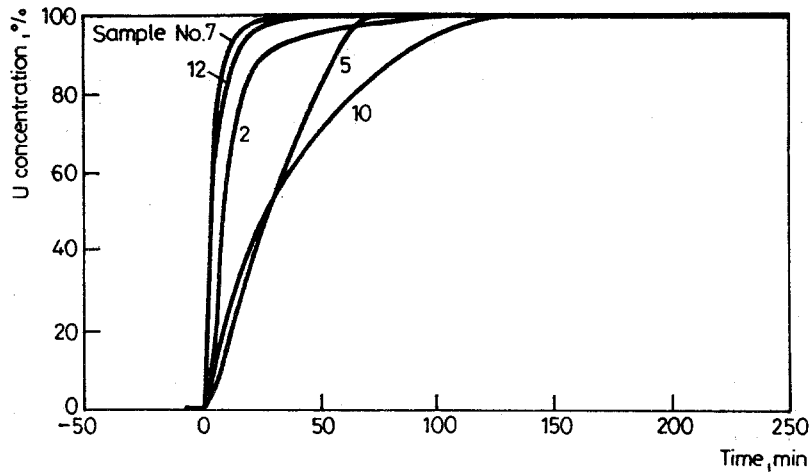

Fig. 2. Evolution of the U concentration as a function of time

Table 1
Fuel characteristics

Green density	55 % TD
Sintering temperature	1700 °C
Density	94.5 % TD
Pellet OD	12 mm
Enrichment	1.5 % ^{235}U
Stack length	45 cm
Irradiation power	400 W/cm
Burn-up	70 MWd/kg U
Reactor power	10 MW(th)
Reactor cycle	23.5 days at full power
	4.5 days shut down
Coolant	70 atm H_2O

HNO_3. The separation from the wash solution was achieved by centrifugation. Finally the residues were dried and prepared for analysis by scanning electron microscopy or dissolved for analysis by ICP–MS or IDMS (Table 2).

About 60 mg of each residue was dissolved in 6 ml of a mixture of HCl/HNO_3 (9/1) at 180 °C for 16 hours in an autoclave. To complete the dissolution the Teflon containers were heated a second time for 16 hours with the same amount of acid mixture.

Table 2
Dissolution results

Sample No.	Dissolution time, min	HNO_3, M	Residue, mg/g fuel	Burn-up at %	ID-MS, g/l	
					U	Pu
2	120	3*	22.5	7.3	90.3	0.865
5	80	5	22.1	6.8	87.1	0.910
7	40	7	16.9	8.5	84.5	0.912
10	110	4	21.5	(7.9**)	87.4	0.898
12	60	6	23.1	7.0	85.9	0.877
				6.8		

*For the dissolution in 3M HNO_3 small amounts of 7M HNO_3 were added (15 ml in total) at different time intervals to keep the acidity close to 3M.
**Measured by the ^{148}Nd method.

Table 3
Concentration of U and Pu in the dissolver solution (g/l)

Sample No.	^{234}U	^{235}U	^{236}U	^{238}U	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
2	0.003	0.001	0.168	90.095	0.018	0.291	0.250	0.055	0.251
5	0.004	0.001	0.157	87.200	0.018	0.300	0.260	0.058	0.274
7	0.002	0.001	0.156	86.906	0.018	0.298	0.260	0.057	0.279
10	0.004	0.005	0.161	85.731	0.019	0.299	0.256	0.057	0.267
12	0.010	0.000	0.147	84.380	0.020	0.302	0.252	0.057	0.246

Results

Analysis of the dissolver solution

The amount of residue decreases with increasing nitric acid concentration and the amount of residue is the lowest for the sample with the highest burn-up. For this sample the highest Pu and the lowest U concentrations in the dissolver solution were also measured.

The volume of the clarified dissolver solution was made up to 250 ml. An aliquot of this solution was diluted 200 times to determine the isotopic composition of uranium and plutonium by isotope dilution mass spectrometry. The results are summarised in Table 3.

As could be expected almost all the ^{235}U has disappeared and neutron capture reactions have led to an exceptionally high ^{242}Pu content in the dissolver solution.

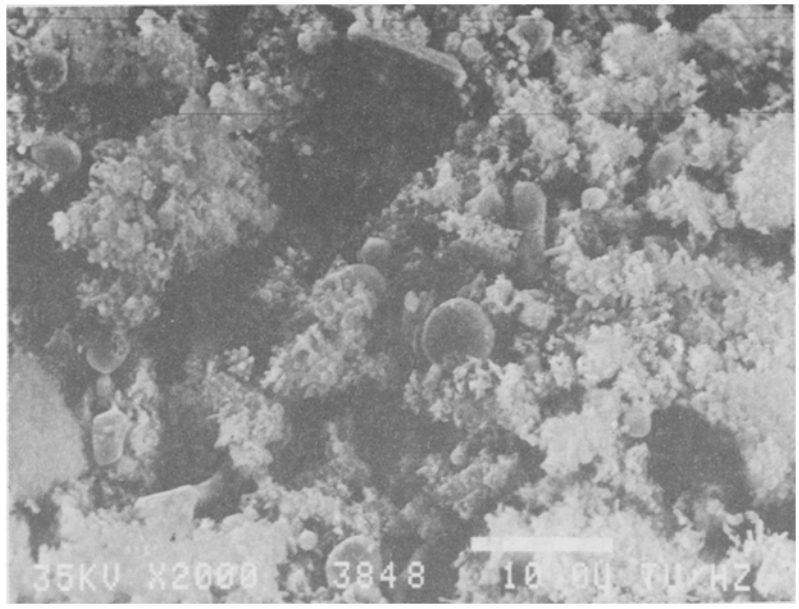

Fig. 3. Microstructure of the residue by SEM (×2000)

Analysis of the residues

The microstructure of the residues after fuel dissolution was analysed by scanning electron microscopy (SEM). Figure 3 illustrates the two phase morphology of the residues (metallic and oxide phases).

The major elements found in the two phases are:

- Oxide phase: Mo, Ru, Zr, Tc, Rh and U, Pu, Pd as traces.
- Metallic phase: Mo, Ru, Zr, Tc, Pd, Rh and U, Pu as traces.

The dissolution of the residues was carried out according to the procedure described above. A qualitative analysis of the dissolved residue was carried out by ICP-MS. The main components of the residue were transition elements such as Zr, Mo, Tc, Ru, Rh, Pd and Ag, a little Te and traces of Pu and U (Fig. 4).

The results of the quantitative analysis are summarised in Table 4. For sample No. 7 from the center of the fuel pin, not only is the total amount of residue the lowest (cf. Table 2) but also the amount of Pu.

Discussion

The high burn-up of the fuel (initially ^{235}U enriched to 1.5%) was achieved by excessive neutron absorption. Hence, this fuel was rather a Pu breeding target than a fuel, where the initial ^{235}U enrichment would have been considerably higher. The fission of ^{239}Pu contributed to a large part to the high burn-up attained. The ^{235}U has almost completely burned out.

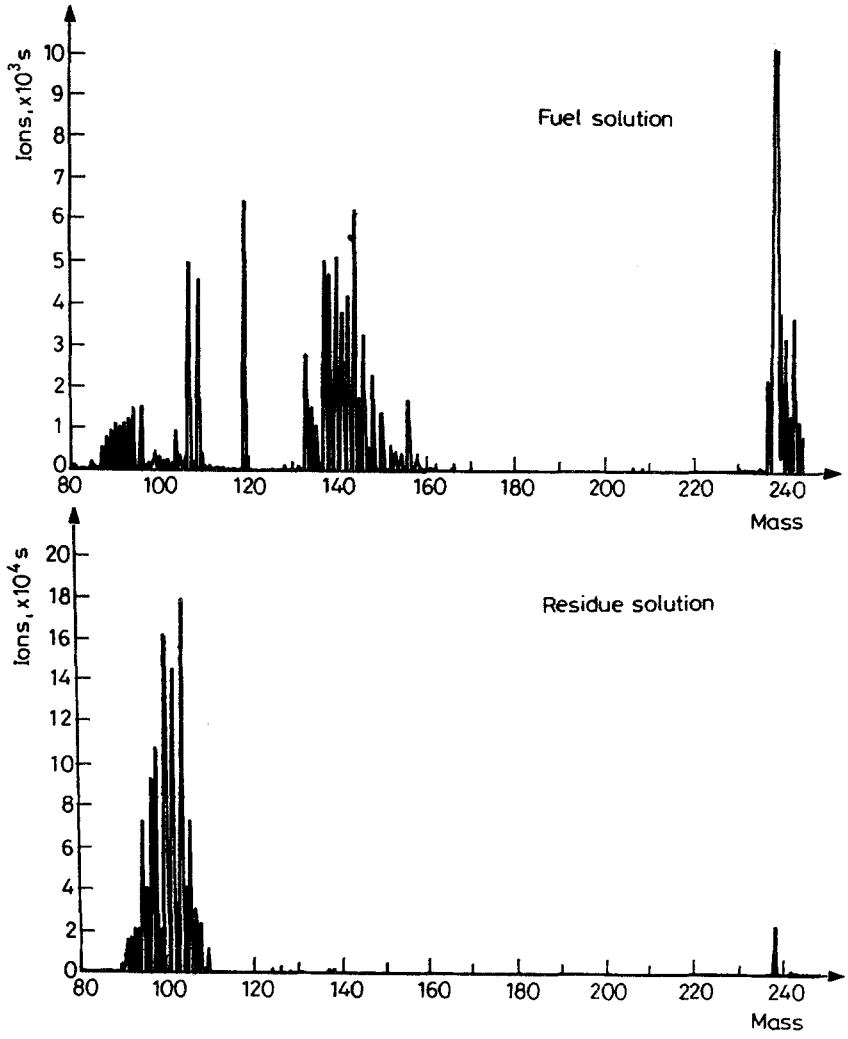

Fig. 4. Mass spectrum of the solutions from sample 5 by ICP-MS

Despite the high burn-up of the fuel, the dissolution went smoothly. Even in 3M HNO_3 the dissolution was complete after 2 hours. The amount of residual PuO_2 was low.

The local burn-up of the fuel determined by using the ^{137}Cs method varied from about 7% at the end to 8.5% in the center of the fuel pin. This last value was found to be only 7.9% if the ^{148}Nd method was used. This may be due to the fact that the accuracy of this method is better, 2% instead of 4% for the ^{137}Cs method, and that the fission yield of the isotopes has contributions from ^{235}U and to a large extent from

Table 4
Results from the analysis of the residue solution

Residue No.	ID-MS, g/l		wt% of initial content in the fuel		ICP-MS, wt %				
	U	Pu	U	Pu	Mo	Tc	Ru	Rh	Pd
2	27.96	6.47	2.9	1.6	39.9	1.8	38.2	2.6	17.4
5	32.48	22.73	3.1	6.5	37.8	2.0	38.4	3.0	18.8
7	35.29	1.17	3.1	0.3	37.1	8.3	34.8	2.7	16.9
10	11.51	11.96	1.1	3.0	38.3	7.2	35.5	2.5	16.6
12	89.84	3.67	8.2	1.0	36.7	7.6	35.3	2.8	17.5

^{239}Pu for this particular fuel. The contributions to the ^{148}Nd yield are very similar (1.69% and 1.70%, respectively) in contrast to those for ^{137}Cs (6.27% and 6.48%, respectively), implying that the value obtained from ^{148}Nd is more precise because it is not effected by assumptions made about the relative contributions to ^{148}Nd from ^{235}U and ^{239}Pu.

Since the ^{239}Pu contributed about 80% of the total fissions, the ^{137}Cs-determined burn-up has a maximum positive bias of 3%. Additional Cs appears to have been deposited in sample No. 2 which comes from the cold end of the pin. This could explain the high apparent burn-up which is not in accordance with the concentrations of U and Pu.

The amount of residue decreased with increasing burn-up, because of the change in the $\Delta G(O2)$ which favored the formation of oxides soluble in nitric acid. However, it should be noted that sample No. 7 with the highest burn-up was dissolved in 7M HNO_3, which certainly contributed to the better dissolution. The isotopic composition of the Pu differs significantly from that of a commercial fuel (high ^{242}Pu content), due to the very specific irradiation conditions. Nevertheless, the isotopic compositions of the dissolved and undissolved Pu are not significantly different.

By microscopic examination, a two-phase morphology was found, i.e., the metallic particles were mixed with an oxide phase, probably partially formed through reprecipitation during or after dissolution.

The content of Pu and U in the residues varied with the dissolution procedure. It is lowest for Pu dissolved in 7M HNO_3 (0.3%) and slightly greater for dissolution with 6M HNO_3. For dissolution carried out in 4M and 5M HNO_3, the amount of undissolved Pu is unacceptably high. During the dissolution in 3M HNO_3 – as explained above – the acidity was kept constant, which somewhat improved the total amount of Pu dissolved. As the oxide phase of the residue is formed through reprecipitation it seems to be worthwhile to study these phenomena so as to be able to avoid losses of Pu which is mainly found in this phase.

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