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**Examination of the surface deposit
on an irradiated PWR fuel specimen
subjected to corrosion in deionized
water**

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EXAMINATION OF THE SURFACE DEPOSIT ON AN IRRADIATED
PWR FUEL SPECIMEN SUBJECTED TO CORROSION IN DEIONIZED
WATER

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

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ABSTRACT

A yellow deposit was observed to form on the surface of a spent PWR fuel specimen exposed to corrosion in deionized water. In a parallel experiment with only groundwater leachant, no such deposit was observed.

The extent and thickness of the deposit appeared to increase over a period of 5 months of air storage. Subsequent examination, including XRD analysis, showed that the deposit consisted of dehydrated schoepite, $UO_3 \cdot 0.8H_2O$.

Approved by

RS Forsyth

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1 INTRODUCTION

In the SKB/STUDSVIK program for the study of the corrosion of spent nuclear fuel in groundwaters, specimens of both BWR and PWR fuel (burnup about 40 MWd/kg U) have been subjected to corrosion tests under both oxidizing and reducing conditions, usually in a bicarbonate groundwater (123 ppm HCO_3^- , pH 8.1-8.2), but occasionally in deionized water.

Results have been reported earlier [1] from corrosion tests on 14 short segments (fuel and clad) from a reference PWR rod, where 6 of the specimens were contacted with oxide groundwater, 6 with mildly-reducing groundwater and 2 with low E_H groundwater (H_2/Pd treated). Two sequential contact periods of 82 and 170 days were used in each case.

On completion of these tests, the segments were contacted with new leachant, in all cases but two using identical conditions as in the first two contact periods. Two segments, 7.1 and 7.2 however, which had been exposed to oxic groundwater previously, were contacted with oxic DIW in order to confirm various observations made on BWR fuel.

Three of the 14 tests were terminated after a third period of 436 days of water contact: 7.1 (DIW-OX); 7.3 (GW-OX)) and 7.7 (GW-RED).

The main interest in these tests was directed to the concentrations of uranium, actinides and fission products in the aqueous phase. Since at

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that time the scanning electron microscope had a large work load, the three fuel/clad specimens, after removal from their leachants, were left suspended by their platinum wire spirals in clean 250 ml pyrex vessels, exposed to normal hot-cell air, until such time when they would be examined further, or sent for disposal.

It was noted on termination of the tests, that whereas specimens 7.3 and 7.7, which had been exposed only to groundwater, oxidizing and reducing respectively, had the same general appearance on visual inspection as that prior to the tests, the open ends of specimen 7.1 showed the presence of a yellow deposit, filling the fuel cracks and fuel/clad gap, and with an irregular zone around the fuel centre.

During the following 5 months of air storage, it was observed that the yellow deposit appeared to gradually spread over the entire open-end surfaces. This report describes the results of an examination of this surface deposit.

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2 EXPERIMENTAL

2.1 SEM examination

A hot-cell periscope photograph of one of the open (cut) ends of fuel/clad segment 7.1 is presented in Fig. 1a, which shows that the yellow deposit completely covers the surface. Details of the surface, including some deposit nodules near a radial crack, are given in Figs. 1b and 1c.

Corresponding photographs of the other two specimens, 7.3 and 7.7, which had been contacted with Allard groundwater (123 ppm bicarbonate) under oxidizing and mildly reducing conditions respectively, are presented in Figs. 2 and 3. No yellow surface deposit could be distinguished on these specimens by periscopic examination.

Since the scanning electron microscope used for subsequent examination of the deposit, a JEOL JXA-840, was only equipped with local shielding (spectrometers), it was necessary to sample the deposit selectively to minimise the amount of active material introduced into the instrument.

This was effected by first scraping the deposit with a scalpel point in an attempt to estimate the thickness of the deposit (Fig. 4) and then by pressing a pre-warmed (about 100^o) plastic tape against the deposit surface, thereby transferring an "image" of the deposit including material from the scrape mark, fuel cracks and general surface (Fig. 5).

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The tape and deposit sample was mounted on a brass specimen holder, introduced into the SEM, and photographs of the deposit were taken at 15 locations. Photographs from three of these locations, which are representative of all locations, are presented in Figs. 6-8.

The surface deposit was seen to consist of roughly orthorhombic crystals about 2 microns in length. Although slight differences in appearance were noted, as exemplified in the figures, no correlation between appearance and location could be made. For comparison purposes, the material is also shown at lower magnification (x1000) in the optical microscope (Fig. 9).

2.2 EPMA examination

Attempts to determine the composition of the crystals at several locations were made using the EDS detector and the WDS spectrometers. No signals over the detection limit from any other element than uranium were obtained. Particular attention was given to the analysis for plutonium, since it is observed during leaching of spent fuel in both bicarbonate groundwaters (pH 8.1-8.2) and deionized water that the ratio of plutonium to uranium in the aqueous phase is always lower than that in the fuel itself (about 0.8 w/o) and, hence, if a uranium-containing precipitate or alteration product is formed at the fuel surface, this could be enriched with respect to plutonium.

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The EPMA results, however, showed no plutonium content in the surface deposit over the estimated detection limit of 0.3 w/o.

2.3 Radiochemical analysis

Three small specimens of the deposit were removed from the surface layer for dissolution and radiochemical analysis. Although efforts were made to obtain specimens free from small fines and grains from the spent fuel matrix, black specks of fuel were clearly seen in two of the specimens, and suspected in the third.

The samples were dissolved in 2N HNO₃ and analysed for uranium, gamma-emitting fission products and actinides.

The results are presented in Table 1. The results for Cs-134 and Cs-137 and the actinides, which were all that could be detected in these small specimens, are expressed as the ratios of the analyzed activities to their theoretical inventories in the determined quantities of uranium, calculated with the assumption that these consisted only of spent fuel particles.

Inspection of Table 1 leads to the conclusion that:

- a) the specimens of yellow deposit were adulterated with fuel particles and
- b) the surface deposits were depleted, probably substantially so, relative to the fuel itself with regard to cesium and the actinides.

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2.4 Fluorescence

In an attempt to determine whether the deposit was fluorescent in UV light, a small specimen was examined outside the cell.

Subsequently, the UV lamp was introduced into the hot-cell, the cell illumination was extinguished, and specimen 7.1 was examined. No fluorescence was observed in these tests.

2.5 Distribution of surface deposit

As mentioned above, both open-end faces of specimen 7.1 were coated with the deposit. In order to determine whether or not all the fuel fragment surfaces were coated in the same way, specimen 7.1 was clam-shelled by cutting two longitudinal slits through the Zircaloy-4 clad. One of the clad halves, with adherent and loose fuel fragments, is shown in Fig. 10.

Perhaps rather surprisingly, it can be seen that the yellow deposit was predominantly located on the open-end surfaces, although some slight traces were seen on some fragment surfaces, and at the interpellet gap. (Fig. 11).

2.6 XRD analysis

Two small samples of the deposit were removed from the open-end surface shown in Fig. 1, mounted on tape and subjected to XRD analysis in a Guinier-Hägg focussing camera.

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Although it had been attempted to sample the deposit without adulteration with fuel particles, the specimens were appreciably radioactive, which increased film background levels. Because of the small specimen size, no internal standard was added.

Exposures of the two specimens were identical and represented one single phase with a good quality diffraction pattern [2]. This corresponded to $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ as reported by Dawson et al. [3]. The measured d values from one of the exposures are given in Table 2 together with Dawson's literature values as comparison.

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3 DISCUSSION

There are two points of interest in the observations reported here: the mode of formation of the deposit, and the fact that the so-called dehydrated form of schoepite was identified and not the tentatively expected fully-hydrated schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) itself.

As noted in the introduction, the deposit formed on the open faces of the fuel/clad segment 7.1 appeared to gradually spread and thicken over an appreciable time period during storage in hot-cell air. The appearance of the crystals also suggests that they were indeed a deposit and not an out-growth from the fuel surface.

The observation after clam-shelling (section 2.5) that the deposit was located predominantly on the open-faces and that the surfaces of the fuel fragments were essentially free from deposit suggests a mechanism of capillary transport from the fuel cracks and subsequent deposition after water evaporation. This hypothesis is being examined in on-going work on both fuel/clad segments and individual fuel fragments.

Periscope examination of the surfaces of specimen 7.3, exposed for all three contact periods to groundwater, showed no significant amounts of yellow deposit. It is, therefore, a reasonable assumption that the deposit found on specimen 7.1 corresponds to the UO_2 matrix which was altered during the corrosion process in the third contact period (DIW), but which could not be held in

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solution because of solubility constraints. (During contact with groundwater, on the other hand, the bicarbonate ligands promote uranium complexing).

This effect is illustrated in Fig. 12 which presents the release fractions for uranium and some key fission product and actinide nuclides for the two specimens during their three contact periods. The release fraction for uranium plotted for the third DIW contact period for specimen 7.1 is a detection limit value. The correct value is probably at least an order of magnitude lower.

Inspection of the figure shows that the release fraction values for the two specimens were very similar during the first two groundwater contact periods. Even during the third contact, the release values for Cs-137 and Sr-90, often regarded as monitors of the on-going corrosion process, are essentially identical. The higher retention of plutonium in deionized water compared with groundwater has been established in previous work (3) and will not be discussed further here.

With the assumption that the Sr-90 release fraction for specimen 7.1 represents the amount of fuel altered during the third DIW contact, with subsequent release of fission products and actinides to the leachant, it can be calculated that 2.4 mg of uranium should be present at or near the fuel surface as secondary phase(s). It was, of course, experimentally unfeasible to quantitatively recover and weigh the yellow

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deposit on the specimen: however, 2.4 mg of uranium, expressed as $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$ with an arbitrarily chosen bulk density of 2 g/cm^3 , would correspond to an even deposit layer over the two open faces of the segment of about $12 \text{ }\mu\text{m}$, a value in reasonable agreement with visual assessment.

There is a small but growing literature regarding the secondary phases formed during the exposure of UO_2 or spent reactor fuel to water. Wadsten [4] identified traces of schoepite in slightly hypostoichiometric UO_2 powder which had been stored for over 15 years in indirect contact with laboratory air at room temperature.

Bates et al [5] have studied the reaction of UO_2 in both powdered and pellet form with dripping groundwater under oxidizing conditions at 90°C . Both schoepite and dehydrated schoepite were identified, together with a number of other secondary phases incorporating cations from the groundwater.

In a study of the alteration under oxidizing conditions of uranite at the Shinkolobwe deposit in Zaire, Finch and Ewing [6] identified a range of uranyl silicates and hydrated oxides including dehydrated schoepite. Some uncertainty existed, however, as to whether dehydration had occurred during specimen storage.

Two other references describing corrosion of CANDU fuel are also relevant to this discussion. Stroes-Gascoyne et al [7] obtained a yellow deposit on the surface of spent CANDU fuel

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exposed to deionized water at 25°C for eight years. XRD and EDX examination of samples of the deposit suggested that it was composed of schoepite or a related hydrate together with a cesium uranate minor phase. The plutonium content of the deposit was below the detection limit of 0.4%.

Taylor et al [8] performed an extensive series of experiment at 200°C and 225°C to study the oxidation of unused CANDU fuel in air-steam mixtures. Under high-moisture conditions (over 50% saturation) both schoepite and dehydrated schoepite were found, detectable quantities being formed significantly earlier at the higher temperature. They suggested that the schoepite was formed by secondary hydration of the dehydrated form during cooling or preparation for examination. In experiments where a significant excess of liquid water was present, such that wetting of the specimen was obtained, large crystals of dehydrated schoepite were formed.

Against this literature background, the identification of the yellow deposit as dehydrated schoepite in the work described in this report is thus somewhat surprising, since the specimen and deposit were never exposed to higher than ambient hot-cell temperatures. Other specimens of spent PWR and BWR fuel are currently being exposed to corrosion in de-ionized water, among them a specimen - 7.2 - which was observed during a recent leachant change to have the same type of initial deposit as was observed for specimen 7.1. After further corrosion, this specimen will be

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examined as soon as possible after termination of the test, and after prolonged storage in air.

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4 ACKNOWLEDGEMENTS

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Table 1

Results of analysis of dissolved deposit specimens

Solution	Weight (g)	U ($\mu\text{g/g}$)	Ratio to inventory			
			Cs-137	Pu-239/ Pu-240	Pu-238/ Am-241	Cm-244
A	9.56	5.5	0.35	0.26	0.24	0.18
B	2.94	4.0	0.17	0.22	0.22	0.18
C	3.74	1.8	0.29	0.16	0.12	0.20

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Table 2

XRD Analysis of yellow deposit

T Wadsten Yellow deposit	J.K. Dawson et al. UO ₃ .0.8H ₂ O
d (Å)	d (Å)
5.1211	5.110
3.4581	3.445
3.4331	3.426
2.8641	2.857
2.5567	2.557
2.4899	2.487
2.1420	2.138
2.0571	2.053
1.9902	1.986
1.9762	1.971
1.8215	1.817
1.7851	1.762
1.7427	1.740
1.7172	1.721
	1.704
1.6423	1.641
	1.632
	1.529
	1.461
1.3853	1.383

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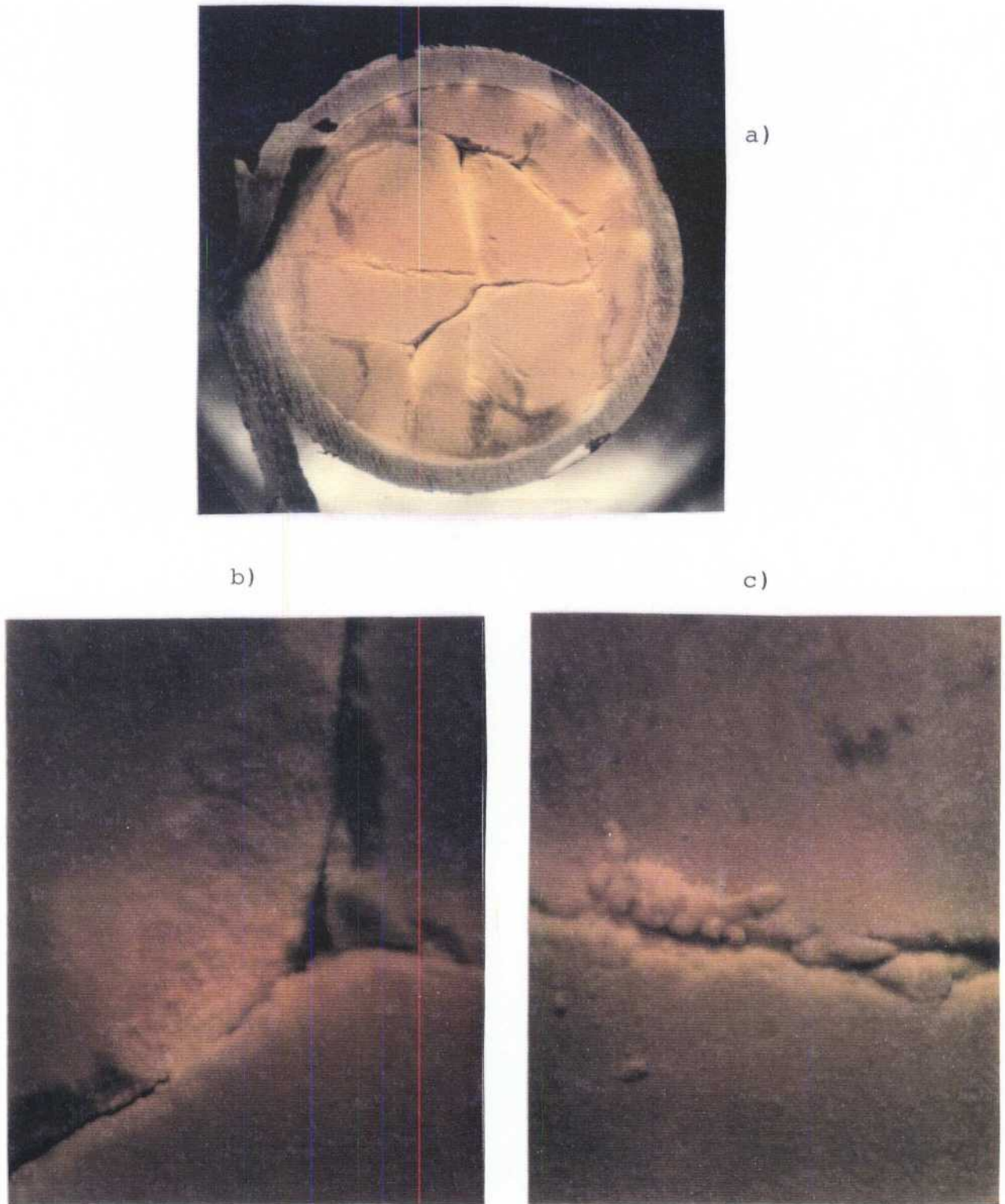


Fig 1. Fuel/clad segment 7.1 after 436 days in deionized water under oxidizing conditions and 5 months of air storage.

a) upper surface (x7) b) and c) details of surface deposit (x50)

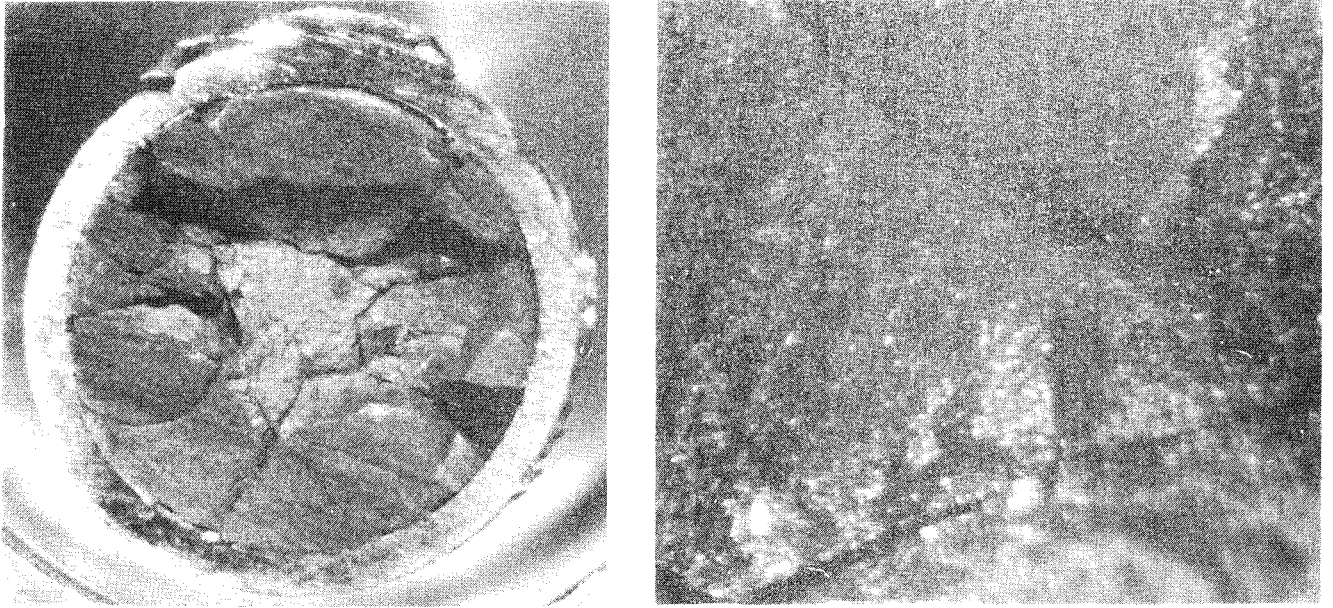


Fig 2. Fuel/clad segment 7.3 after a cumulative contact with Allard GW under oxidizing conditions of 688 days. 5 months of air storage. Upper surface (x7) and detail of fuel surface (x50).

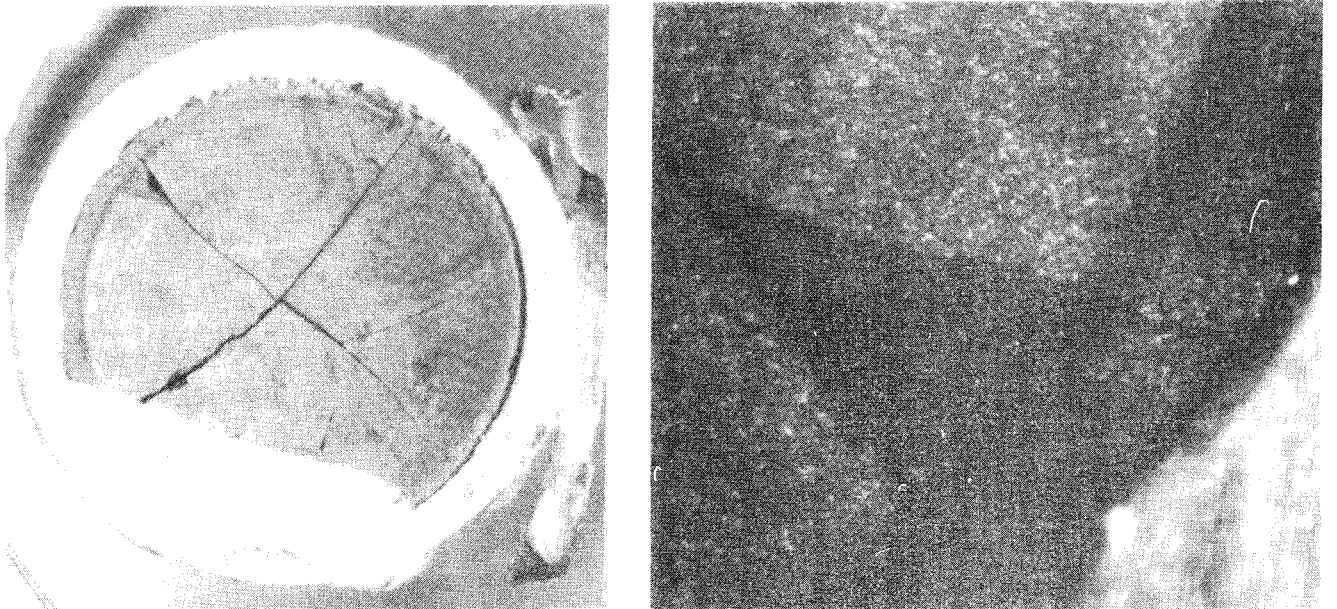


Fig 3. Fuel/clad segment 7.7 after a cumulative contact with Allard GW under slightly reducing conditions of 688 days. 5 months of air storage. Upper surface (x7) and detail of fuel surface (x50). (The white material is silicone grease from the leaching vessel.)

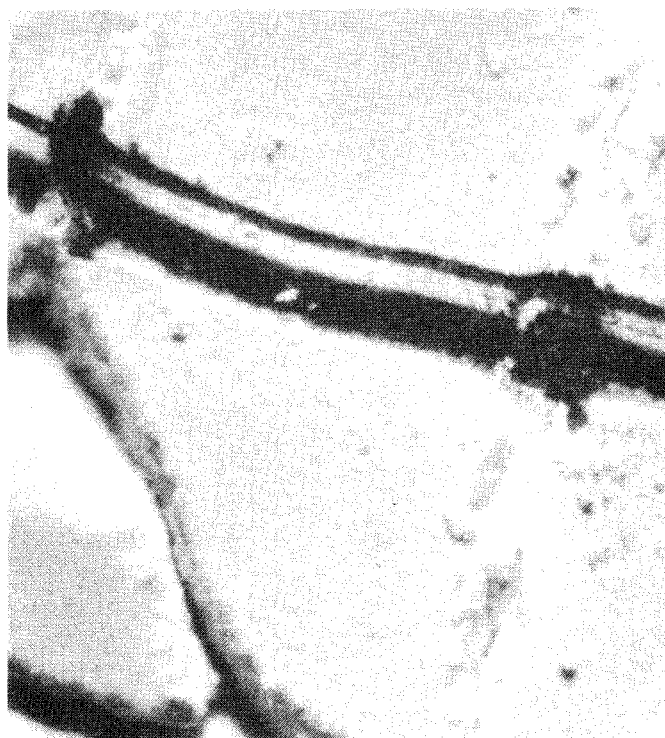
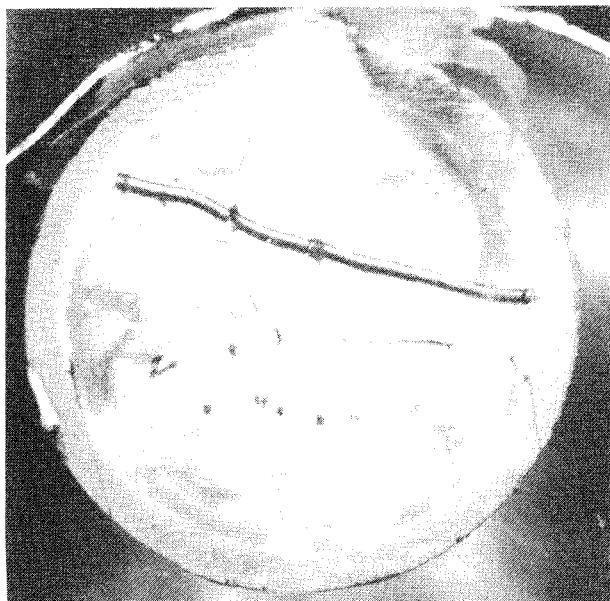


Fig 4. Fuel/clad segment 7.1 after scraping showing position (x7) and detail (x40) of scrape mark.

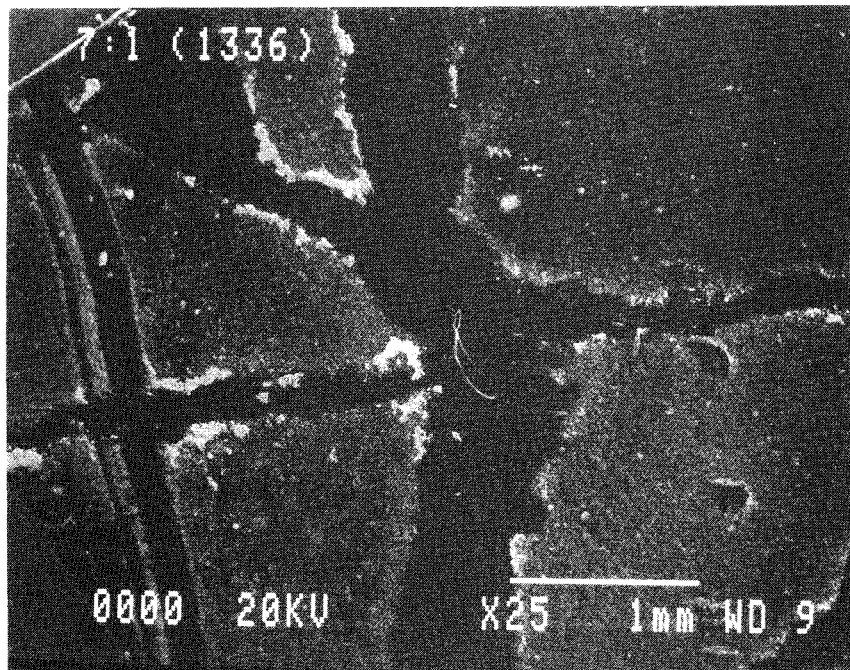
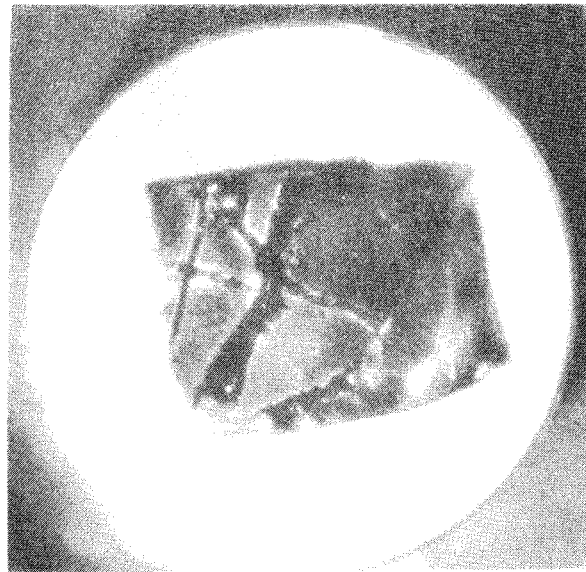


Fig 5. Overview (x6) and detail (x40) of the material transferred to the plastic tape.

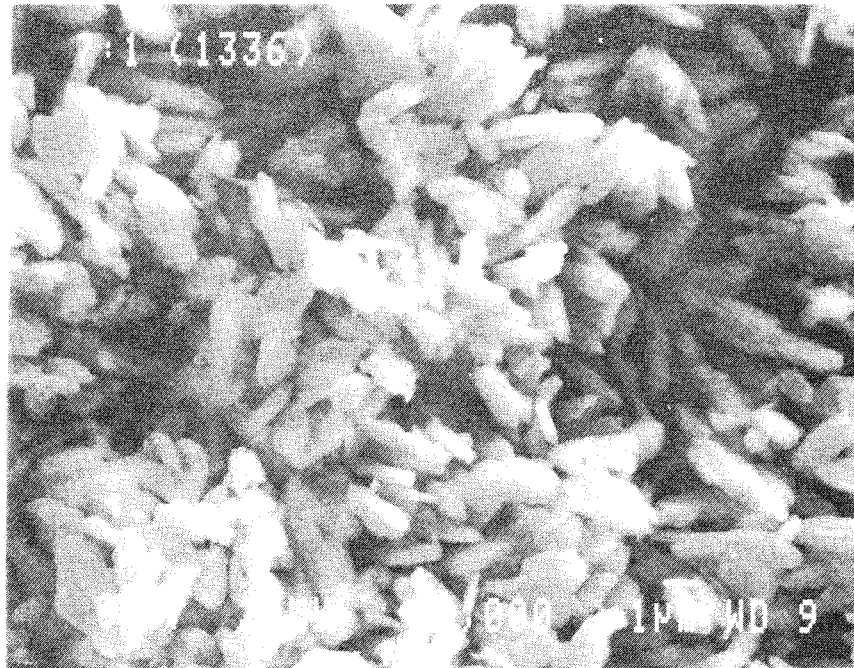


Fig 6. SEM photographs of the surface deposit.

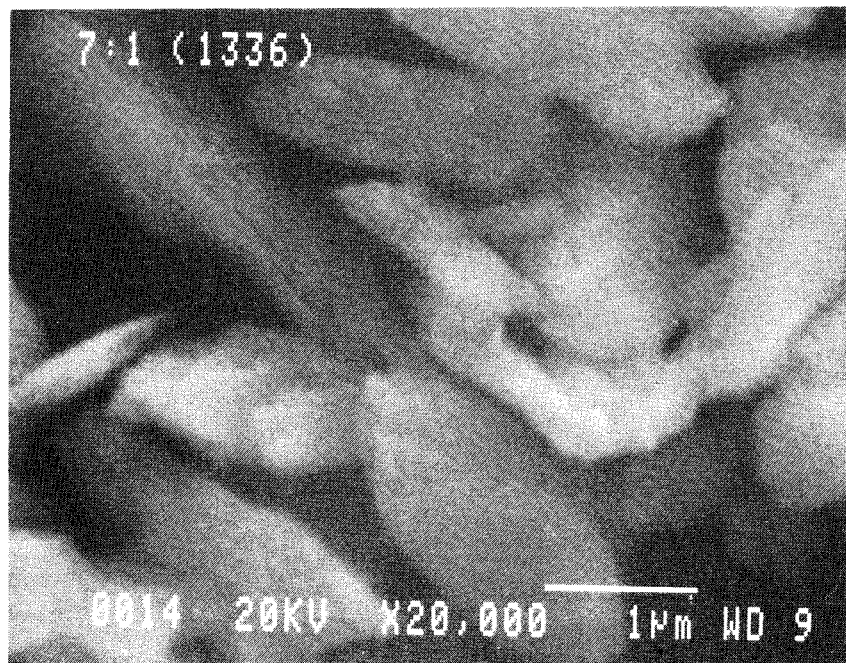


Fig 7. SEM photographs of the surface deposit.

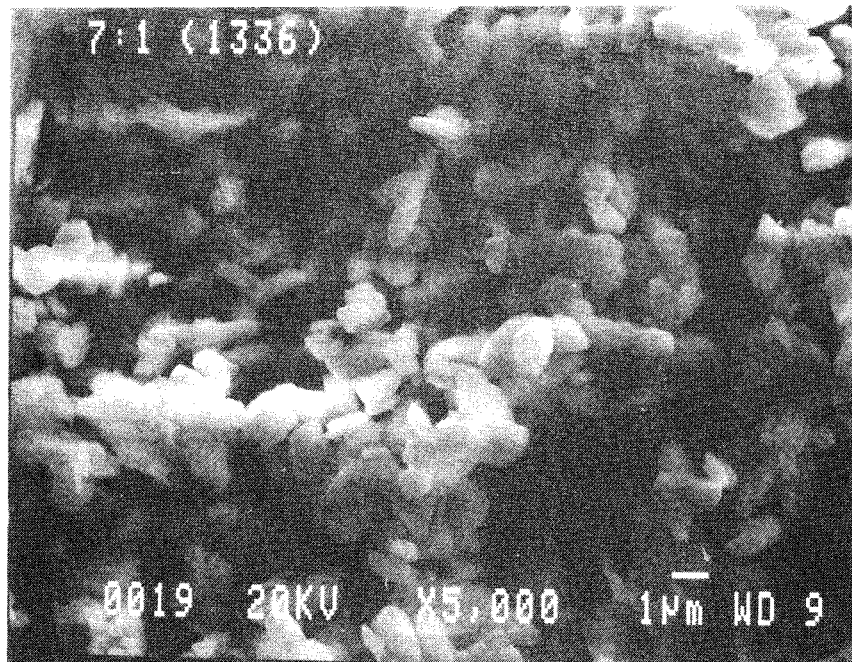


Fig 8. SEM photographs of the surface deposit.

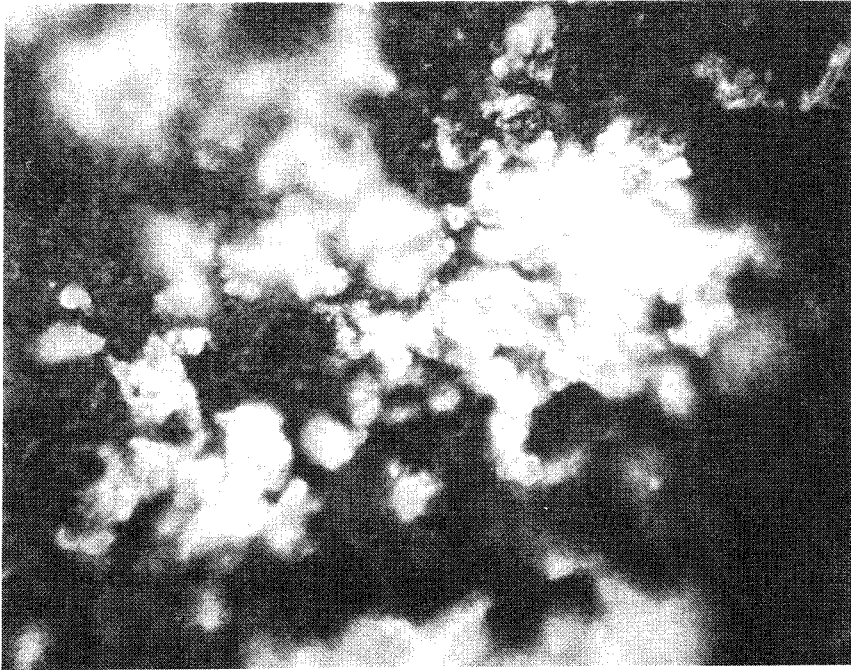


Fig 9. Appearance of the surface deposit in the optical microscope (x1000).



Fig 10. Fuel segment 7.1, clam-shelled to show distribution of yellow deposit.

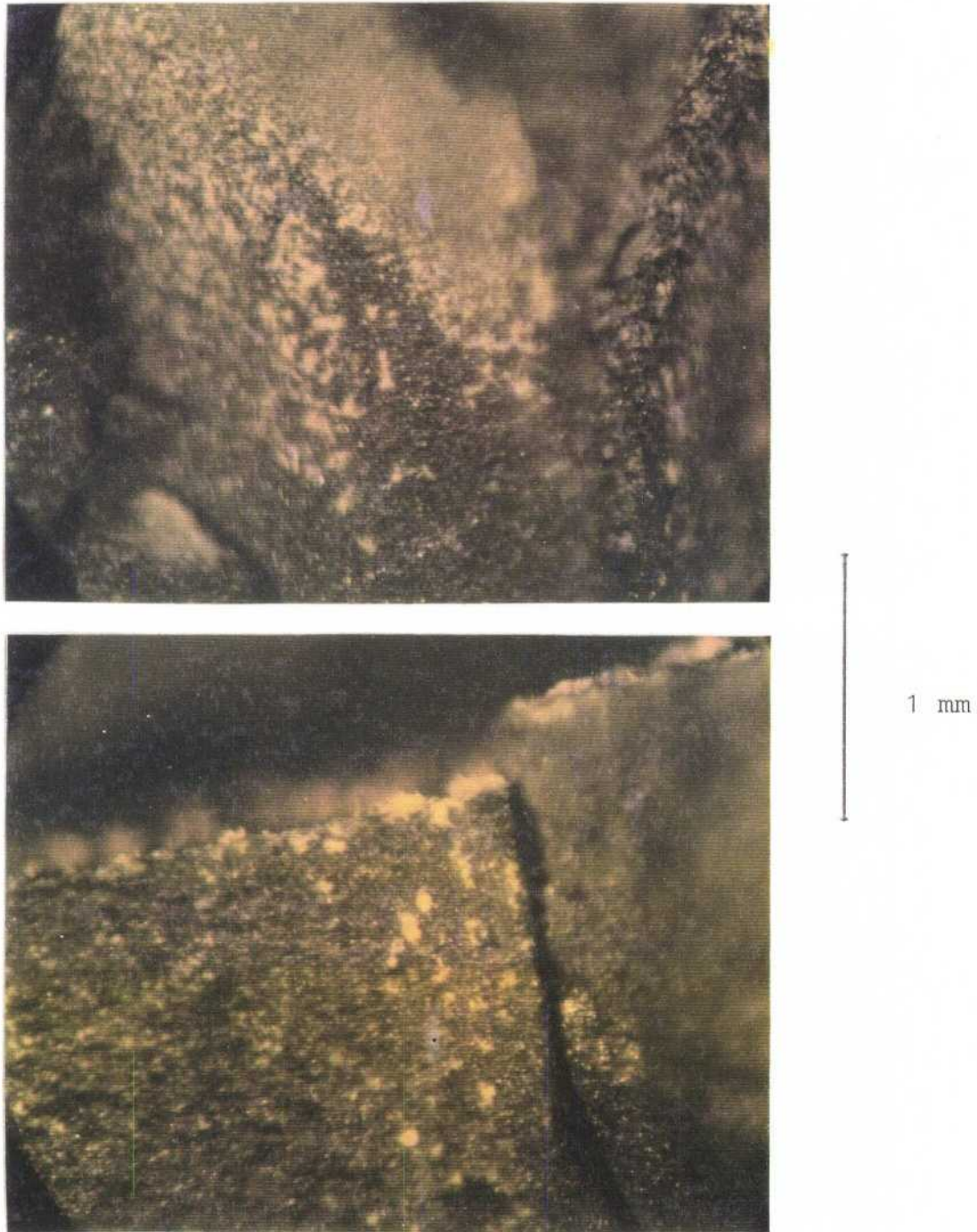


Fig 11. Yellow deposit on fragment (upper) and at edge of pellet dishing (lower).

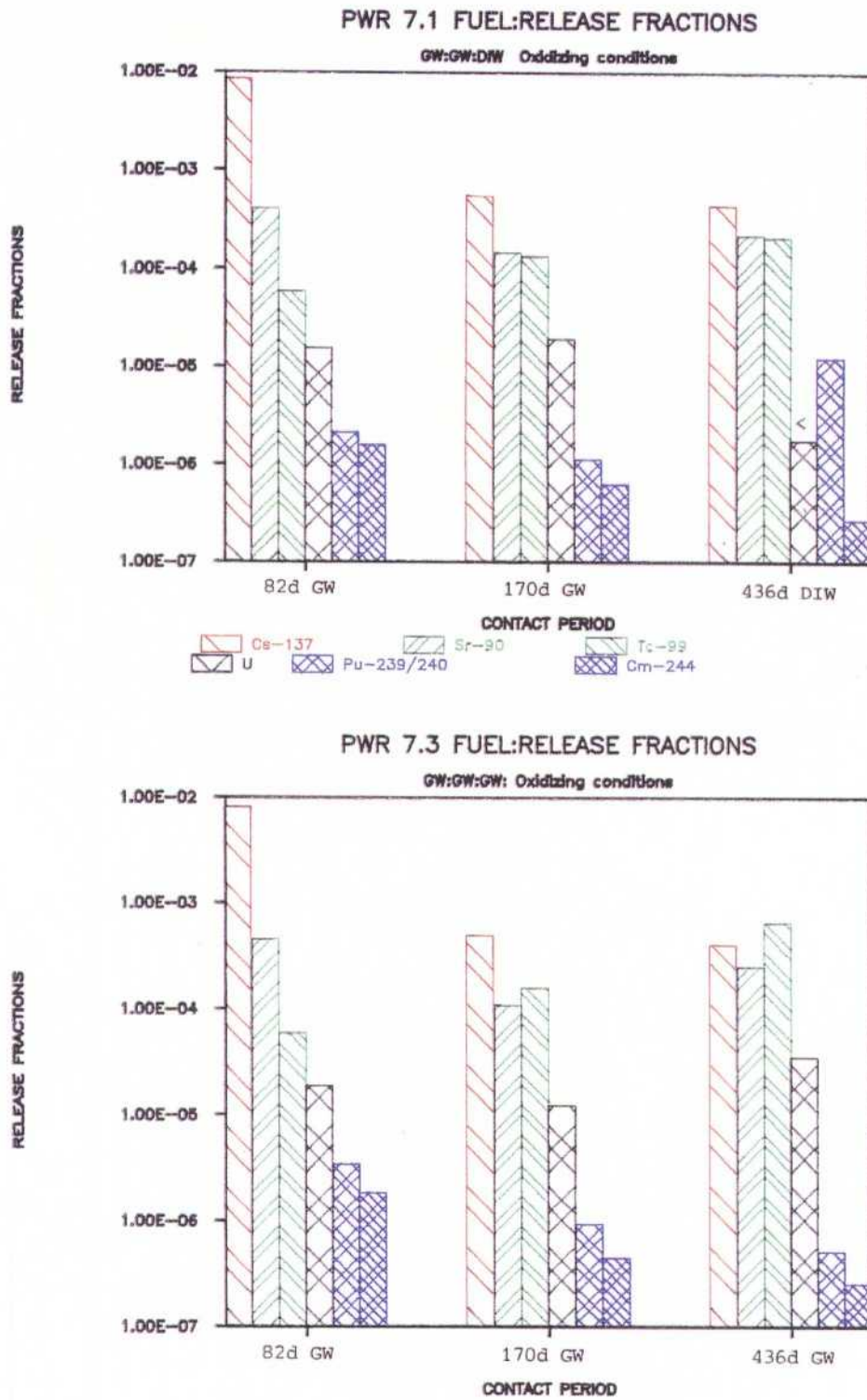


Fig 12. Comparison of release fractions between specimen 7.1 (final contact with DIW) and specimen 7.3 (all contacts with GW).

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List of SKB Technical Reports 1990

TR 90-01

FARF31 –

A far field radionuclide migration code for use with the PROPER package

Sven Norman¹, Nils Kjellbert²

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² SKB AB

January 1990

TR 90-02

Source terms, isolation and radiological consequences of carbon-14 waste in the Swedish SFR repository

Rolf Hesböl, Ignasi Puigdomenech, Sverker Evans
Studsvik Nuclear

January 1990

TR 90-03

Uncertainties in repository performance from spatial variability of hydraulic conductivities – Statistical estimation and stochastic simulation using PROPER

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² SKB AB

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