

SKB

**TECHNICAL
REPORT**

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**The SKB spent fuel corrosion programme
Status report 1988**

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THE SKB SPENT FUEL CORROSION PROGRAMME
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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.

Information on SKB technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20), 1986 (TR 86-31), 1987 (TR 87-33) and 1988 (TR 88-32) is available through SKB.

ABSTRACT

The results of the Swedish spent fuel corrosion programme from 1982 to 1988 are reviewed. Areas where additional research will be required are identified.

The major findings and conclusions after the first six years of the programme are that uranium attains relatively rapidly a constant solution concentration of about 1 mg/l. This is probably solubility controlled. Also plutonium, after initially higher concentration appear to reach a constant concentration of about 0.3 $\mu\text{g/l}$ in groundwater. In DI water, the normalized Pu release is higher than the U release, indicating ongoing fuel oxidation-/alteration after the leachant has been saturated with U.

Under reducing conditions, the absence of fuel oxidation and the very low U solubility lead to a stronger tendency towards congruent releases, controlled by the solubility of the fuel matrix.

The fission products Cs, Sb, Tc and Mo appear to selectively leached, probably from inclusions or from fuel cracks, fissures and grain boundaries.

**The SKB Spent Fuel Corrosion Programme.
Status Report 1988**

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BACKGROUND

The intention with this report is to summarize the findings from the past six years of the on-going SKB programme for spent nuclear fuel corrosion. It will be a part of the background material for identifying areas where additional studies, experimental as well as theoretical, will be required during the next six years' period of the SKB research programme. Most of the reviewed data has been published elsewhere and the complete publication list of the spent fuel corrosion programme can be found at the end of this report.

The spent fuel corrosion programme started in 1982 with experimental work using irradiated nuclear fuel. Later, the programme has been expanded to include also basic studies of uranium chemistry and the dissolution kinetics of uranium oxides under reducing and oxidizing condition aiming at modelling the corrosion behaviour of spent fuel under laboratory as well as repository conditions.

INTRODUCTION

The experimental programme, which started at the beginning of 1982, was formulated on the basis of the quick-look experiments performed at Studsvik in 1977 [1] as part of the support for KBS-2, a survey of the very limited literature (essentially Katayama's work at Battelle PNL [2] and Vandegraaf's at AECL, WNRE [3]) and a visit to these laboratories in 1981. The programme was presented

and discussed in the autumn of that year at the first Spent Fuel Workshop, initiated by SKB and held at Studsvik.

Faced with a multi-parameter problem, a relatively restricted budget compared with the USA and, particularly, Canada, and a very small working area (one concrete cell 2x2 m), the programme was structured initially around:

- 1) one fuel type (BWR) but from different locations in the fuel column to take into account probable irradiation effects which were indicated in the 1977 work.
- 2) a standardized groundwater (Allard synthetic GW, pH 8.2, 123 ppm bicarbonate).
- 3) a standardized straightforward experimental set-up (the 250 ml Pyrex flasks used in the 1977 experiments) -- cheap, transparent and un-instrumented to facilitate in-cell manipulation and to permit an early start for the programme.
- 4) the division into three fractions of possible material release after each corrosion exposure:
 - material retained on a membrane filter, apertures 1.5 to 1.8 μm as a measure of the "colloidal" fraction
 - material in the centrifugate after such filtering
 - a vessel strip solution as a measure of precipitated and/or adsorbed species.

It was anticipated that each of these fractions would contribute to the measured total release, but some difficulties in data interpretation for the results from the strip solutions were expected, due to possible random loss of fuel particles and fragments from the open-ended fuel specimens during the experiments.

- 5) an analytical scheme in which each fraction in each corrosion experiment would be analysed for U, the actinides by direct deposition alpha spectrometry, Sr-90 by separation and beta counting, and by gamma spectrometry (Ru-106, Sb-125, Ce-144 and Eu-154).

Although the release of these fission products is not significant for safety analysis considerations, it was hoped that their determination would help to identify release mechanisms.

In the cost/benefit choice between duplicate analyses and an increased number of corrosion experiments, the latter was selected in order to widen the statistical base and to increase flexibility later in the programme.

- 6) a nominal corrosion temperature of 20 - 25°C, the ambient temperature in the hot cell. The temperature(s) in the fuel cracks, of course, would be somewhat higher.

As mentioned above, the fuel used in the initial part of the programme was from a high burnup (42 MWd/kg U) BWR fuel rod. Later, when results from tests under reducing conditions (H₂/Pd reduction) showed that although release rates were lower than under oxidizing conditions, they were appreciably higher than those predicted theoretically for reducing conditions in the absence of radiolysis effects, leaching tests were performed on a low burnup (0.5 MWd/kg U), short-cooled rod to examine corrosion rates in the near-absence of alpha radiolysis. Results from these experiments together with detailed descriptions of the experimental procedures have been reported earlier [4-11].

Concurrently with continued experiments on the high burnup BWR fuel, extending the integrated contact times, experiments are also in progress since early 1986 on a PWR fuel rod of about the same burnup (43 MWd/kg U) [12, 13].

EXPERIMENTAL

The specimens used in most of these experiments consisted of 20 mm long segments of fuel and clad corresponding to about 16 g and 12 g of UO₂ for the BWR and PWR rods respectively. Each specimen was suspended in a platinum wire in 200 ml of the leachant in a 250 ml Pyrex flask. In some of the experiments, also selected fuel fragments have exposed to water. All leach tests were performed at 20 to 25°C, the ambient temperature of the hot cell. After removal of the leachant from the flask the pH was measured on one aliquot and then two 10 ml aliquots were centrifuged through membrane filters with apertures of 1.5 to 2.0 nm. Both membrane filters and centrifugates were subjected to analysis. The empty flask was exposed for a few days to 5M HNO₃/0.5M HF. This rinse was also analysed.

In one experimental series, the leachant was deionized water while a synthetic groundwater was used for the other experiments. The composition of the groundwater is given in Table 1.

Table 1. Composition of the synthetic groundwater

Species	HCO ₃ ⁻	SiO ₂	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺
ppm	123	12	9.6	70	18	4.3	3.9	65

pH: 8.0-8.2, ionic strength: 0.0085

PROGRAMME

A schematic summary of the spent fuel corrosion programme is given in Figure 1:

- a) Series 3.1 to 3.3: oxidizing conditions.
In experiment series 3.1 (distilled water) and 3.2 and 3.3 (groundwater) three specimens were corroded according to a modified IAEA procedure, the same specimens being successively exposed to new leachant after each sample time. This series is still going on.
- b) Series 3.4 and 3.5: oxidizing conditions, static leach test.
In this series, after an initial 14 days pre-leach to remove most of the gap inventory, separate specimens were corroded statically during a pre-set contact time.
- c) Series 3.6 and 3.7: reducing conditions.
In this series, six specimens were included. Each specimen was first pre-leached under oxidizing conditions for two periods of 91 days and 27 days respectively to remove most of the gap inventory of cesium. In the third stage of leaching, reducing conditions were imposed on the system by bubbling 6 % H₂/Ar through the leachant in the presence of a Pd catalyst. Two specimens were leached for 28 days and two specimen were leached for 55 days.
- d) Series 5: bentonite interaction series.
In this series, four fuel/clad specimens were pre-leached under oxidizing conditions for two periods of 91 and 27 days respectively and then contacted with new groundwater containing 1.5 % of crushed and sieved bentonite. Two specimens were leached for 27 days and two specimens were leached for 266 days.
- e) Series 3.13 to 3.18: Replenishment series.
In this series, six specimens were leached in groundwater under oxidizing conditions. Details of the experiments are given in Table 2. After initial filling, the flasks were allowed to stand for 27 days, following which 20 % of the leachants were removed and immediately replaced by fresh groundwater. This was repeated four times after different contact periods.

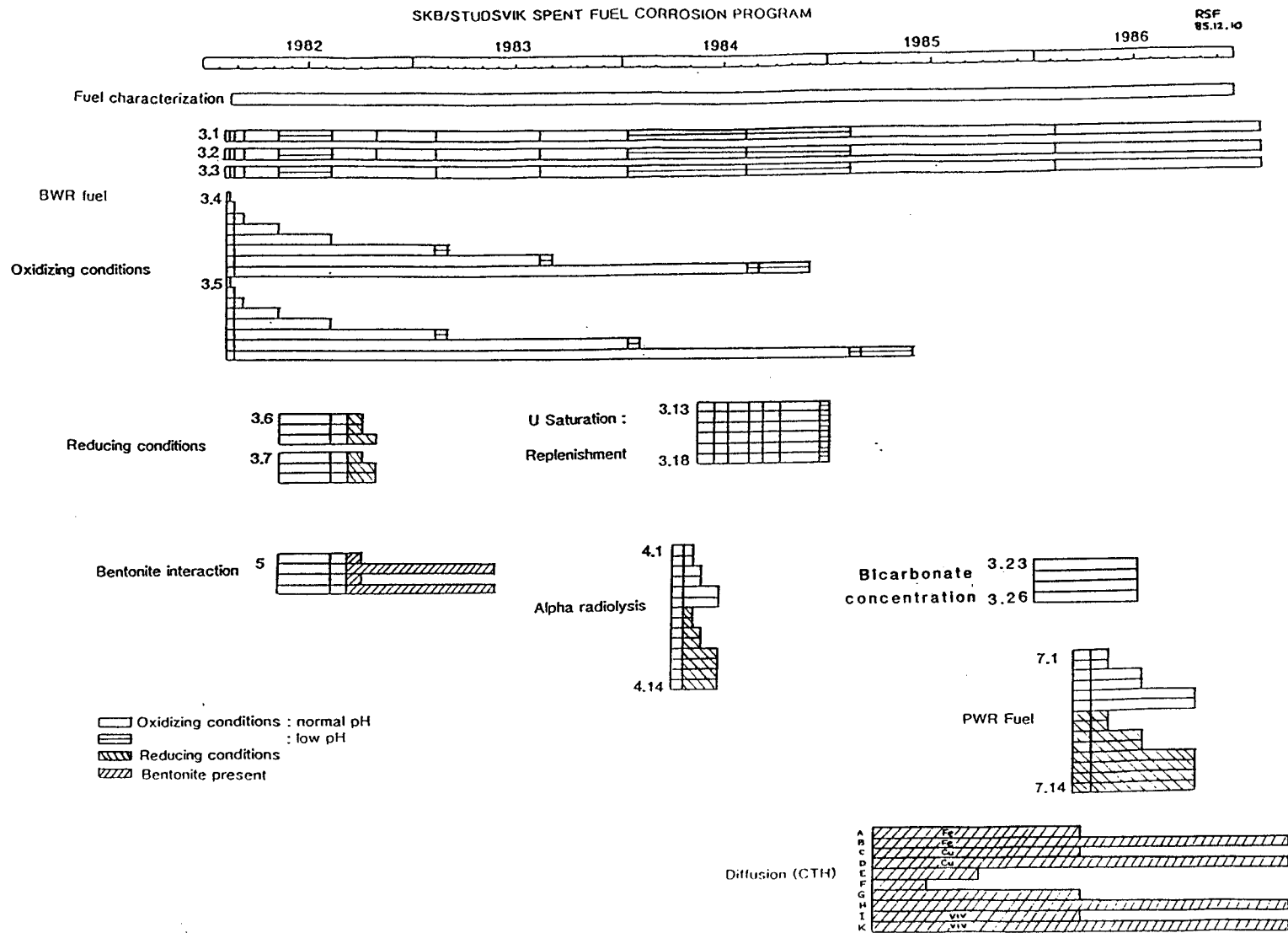


Figure 1.

Graphic presentation of the SKB/Studsvik spent fuel corrosion programme.

Table 2

Replenishment experiment: Summary of test conditions

Experiment	Flask	Fuel Specimen	Wt UO ₂ (g)
3.13	Polypropylene	Fuel/clad segment	16.6
3.14	"	Fuel fragments >4 mm	5.7
3.15	"	"- 3.15-4 mm	5.7
3.16	Pyrex	Fuel/clad segment	16.6
3.17	"	Fuel fragments >4 mm	5.8
3.18	"	"- 2-3.15 mm	3.9

f) Series 4.1 to 4.14: alpha radiolysis.

The purpose of this experiment was to study the effects of alpha-radiolysis by leaching specimens from a low burnup fuel rod (0.5 MWd/kg U, 22 kW/m linear power). This fuel had an alpha activity of less than one percent of that of the high burnup fuel. The gamma and beta activities were comparable. In this series 14 segments specimens were pre-leached in oxidizing groundwater for 3 weeks. Six of the fuel specimens were then, in pairs, leached again under oxidizing conditions for periods of 2, 4 and 6 weeks. The remaining 8 specimens were leached, under the reducing conditions described in c) for the same periods.

g) Series 3.23 to 3.26: bicarbonate concentration dependence.

In this series, four specimens were leached under oxidizing conditions in distilled water and in sodium bicarbonate solutions (1,2 and 4 mM) respectively. This experiment is still going on.

h) Series 7.1 to 7.14: PWR fuel leach test.

In this series, experiments were included where the fuel is contacted with groundwater reduced under more realistic conditions. In a closed system, the groundwater is circulated continuously over rock cores from deep bore-holes. When a low E_h was attained, the reduced groundwater was transferred by

means of an in-cell manifold to the leaching vessels which prior to the transfer had been flushed with nitrogen and evacuated. After groundwater transfer, the vessels were placed under water in stainless steel cans to minimize in-leakage of air. Experiments were also carried out under oxidizing conditions and under reducing conditions as described in c). The experimental parameters are summarized in Table 3.

Table 3

Experimental parameters: PWR fuel tests.

Fuel specimens	Experimental conditions
7.1 - 7.6	Oxidizing
7.7 - 7.12	Reducing: rock cores/GW
7.13 - 7.14	Reducing: H ₂ /Pd/GW

i) Diffusion experiments

In this series, ten specimens of spent fuel, ca 3 g each are corroded in the presence of highly compacted bentonite in diffusion cells. The experiment parameters are given in Table 4.

Table 4.

Diffusion experiments: experiment conditions.

Diffusion medium	Duration
Bentonite	101, 197, 365 and X days
Bentonite + 0.5 % Cu	386 and X days
Bentonite + 0.5 % Fe	386 and X days
Bentonite + 1.0 % Vivianite	386 and X days

These experiments are currently being analysed and to date only preliminary cesium results are available [21].

DEFINITION OF RELEASE

Dissolved, adsorbed and colloidal species

The experimental procedure described above, involving analysis of three fractions - centrifugate, vessel strip and membrane filter - is based on the assumption during experiment design that adsorption (vessel strip) and colloid formation (membrane filter) could be significant in these solutions with very low concentrations of highly-charged species. It was also expected that small fuel fragments and fines could be lost from the suspended open-ended fuel/clad specimens and later be included in the amounts found in the vessel strip and on the filter.

Considerable attention has been paid to evaluation of the experimental results in order to assess the size of such contributions.

The problem is illustrated by the set of results shown in Table 5, which refer to the 350 day static leaching in groundwater under oxidizing conditions of a BWR fuel segment.

Although the results refer to the total leachant volume of 200 ml, it should be noted that the aliquots actually analysed were over two orders of magnitude smaller.

It can be seen that, except for the selectively-leached or readily soluble elements cesium, strontium and antimony, the total amounts recovered from the leaching vessel are predominantly due to the vessel strip and membrane filter fractions. For experiments performed under reducing conditions, when the amounts of uranium, lanthanides and actinides found in the centrifugates are considerably lower than in the case of oxidizing conditions, this effect is even more pronounced.

Table 5. Experiment 3.5.6. Analytical results on centrifugate, vessel strip and membrane filter.

	Centr.	Strip	Filter
	Bq/200 ml		
Cs-137	8.60 E07	4.70 E06	2.80 E06
Sr-90	1.50 E07	4.60 E05	1.60 E06
Sb-125	6.00 E04	ND	5.60 E03
Ce-144	ND	2.20 E05	ND
Eu-154	ND	2.00 E04	2.00 E03
Pu-239/240	2.00 E02	4.70 E03	3.90 E02
Pu-238/Am-241	8.20 E02	2.30 E04	1.20 E03
Cm-244	2.40 E01	2.20 E04	1.90 E03
	$\mu\text{g}/200 \text{ ml}$		
U	1.40 E02	1.00 E02	4.80 E01

Use of the sum of the measured amounts found in the three fractions gives a conservative value for release from the fuel. Unfortunately, however, this may lead to conclusions regarding release mechanisms which are erroneous. This is illustrated in Table 6, which presents the sums of the three fractions from experiment 3.5.6 (Table 5) expressed as fuel inventory for each nuclide. The table also includes corresponding release fractions from an experiment performed under reducing conditions, where centrifugate concentrations of lanthanides and actinides were one or two orders of magnitude lower than in the centrifugate in experiment 3.5.6.

Clearly, although there is some scatter in the results, it can be concluded that the lanthanides and actinides are released congruently with uranium under both oxidizing and reducing conditions, while cesium, strontium and to some extent antimony are released preferentially. Indeed, it appears that the total release fractions are similar in magnitude in the two experiments in spite of large differences in contact times and redox conditions. These conclusions are, of course, largely invalid if it can be shown that the vessel strip and membrane filter fractions mainly represent fuel fines and fragments under the experimental conditions employed, i.e. with leachants over a pH range of 7 to 8.2, room temperature, and Pyrex vessels. This will be discussed in the following.

Table 6 Total release fractions (centrifugate, vessel strip and membrane filter) for experiments performed under oxidizing and reducing conditions

Experiment	Release Fraction	
	3.5.6	3.7.1R
Conditions	Oxidizing	Reducing
Contact time (d)	350	28
Cs-137	1.5 E-03	1.7 E-03
Sr-90	4.9 E-04	2.3 E-05
Sb-125	4.3 E-05	3.8 E-06
Ce-144	7.6 E-06	2.8 E-06
Eu-154	7.2 E-06	5.3 E-06
Pu-239/240	9.0 E-06	6.1 E-06
Pu-238/Am-241	9.4 E-06	3.8 E-06
Cm-244	9.1 E-06	4.0 E-06
U	2.0 E-05	<9.8 E-06

Vessel strip solutions

An evaluation of the vessel strip results in the BWR fuel experimental series was published two years ago [8] with the conclusion that the solutions represent with a high degree of certainty the dissolution of fuel fragments and fines. Now, when additional results are available, this conclusion still holds. The results for the entire BWR fuel series are summarized in Table 7. Uranium contents of the vessel strip solutions ranged between 3 and 640 $\mu\text{g}/200\text{ ml}$, with no correlation with experimental parameters other than a not unexpected tendency to higher values during the initial contact with the leachant. The ratios to inventory given in the table are normalised to the corresponding uranium values. The results for Pu-239/240 are also presented graphically in Figure 2. Clearly, when allowance is made for measurement scatter and possible bias, the results strongly support the hypothesis of fuel fines dissolution.

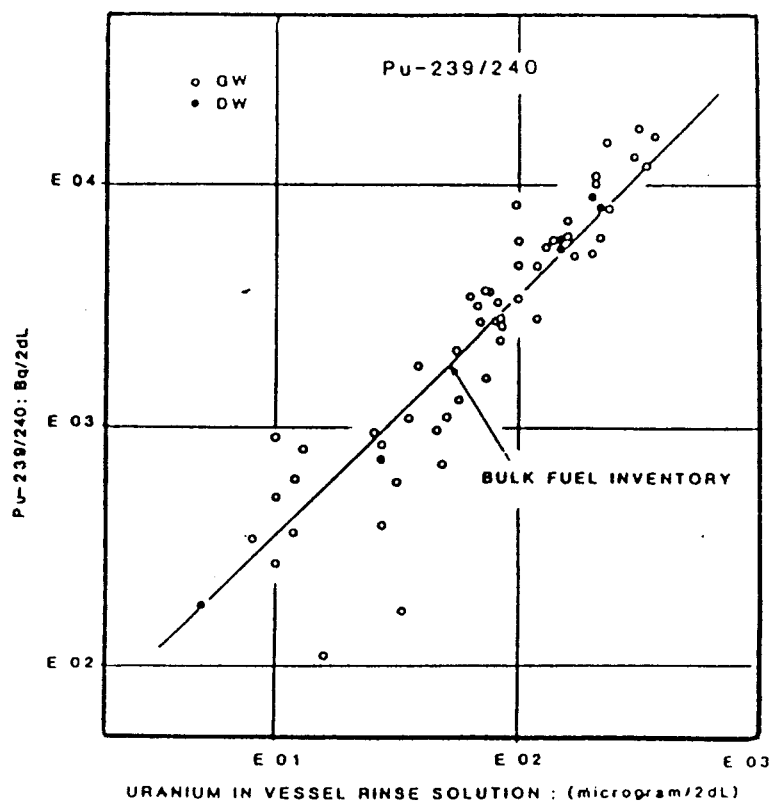


Figure 2. Correlation between Pu-239/40 and uranium in vessel rinse solutions.

The results of vessel strip analysis for 28 experiments on PWR fuel under both oxidizing and reducing conditions have also been reported [13] and support the same conclusion.

Membrane filters

For the BWR fuel series, the quantities of uranium found on the membrane filters were usually below the detection limit of 20-40 μg (calculated for 200 ml leachant). In only 11 experiments of over 70 performed was a discrete value for uranium reported. The average composition (ratio to inventory) of the material found on the filters in these experiments is listed in Table 8.

Apart from Sr-90 (and Cs), which is clearly over-represented, the analyses lend little support to any other assumption than that even the membrane fraction is most likely dominated by fuel fines.

Reporting units

Because of the difficulty in defining the surface area of highly-cracked spent UO_2 fuel, the experimental results are expressed as fractions of the initial inventory of each radionuclide. For the leach fraction, the term "Fraction of Inventory in Aqueous Phase" (FIAP) is used. As was discussed above, only the centrifugate fraction of the solution is considered as leached material, with the exception of Sr and Cs which are clearly over-represented on the membrane filters. For these nuclides, the term "Corrected FIAP" is used.

Table 7. Composition of vessel rinse solutions (ground-water and deionized water leachants)

U Content	($\mu\text{g}/200 \text{ ml}$)
Range:	3 - 640
Mean:	101
Standard Deviation	110

Ratio to inventory

Nuclide	Mean	Stand. dev.
Sr-90	1.3	0.9
Ru-106	0.9	0.5
Ce-144	1.8	0.5
Eu-154	1.2	0.6
Pu-239/240	1.2	0.6
Pu-238/Am-241	1.2	0.5
Cm-244	1.3	0.7

Table 8. Composition of material on membrane filter
(groundwater and deionized water leachants)

U-Content		
(µg/200 ml)		
Range:	7 - 200	
Mean:	47	
Standard Deviation:	56	
Ratio to inventory		
Nuclide	Mean	Stand. dev.
Sr-90	11.0	9.4
Ru-106	0.6	0.7
Ce-144	0.9	0.5
Eu-154	0.7	0.4
Pu-239/240	0.4	0.4
Pu-238/Am-241	0.3	0.3
Cm-244	0.7	0.5

RESULTS

The purpose of the experiment programme is to study the corrosion behaviour of spent UO₂ fuel and the release of fission product and actinides under different, but repository related conditions. Some experiment parameters, such as redox conditions and water chemistry (DI water vs. groundwater) have a large influence on the fuel corrosion, the redox conditions being by far the most important one. For other parameters, the results of the high burnup fuel series have shown that the individual behaviour of uranium, actinides and fission products is to a large extent independent of the applied conditions. In the following, the results will therefore be discussed by elements, for oxidizing and reducing condition respectively, rather than by individual experiment series.

OXIDIZING CONDITIONS

Uranium

High burnup fuel

The concentrations of uranium in groundwater from the series 3.2 to 3.7, series 5 and series 7.1 to 7.6 leachant centrifugates are typically in the range 0.5 - 2 mg/l (see Figure 3). Most of the BWR data shown in the Figure 3 has been published before [8]. Concentrations measured in the ongoing BWR fuel studies as well as the PWR fuel studies agree well with the earlier observations within the relatively large scatter in the data.

At 482 days contact time, the groundwater series showed increased concentrations. These data were obtained from the 12th contact period in the series 3.2 and 3.3. However, the 13th contact period for these two series (238 days) did not show these unexpectedly high uranium concentrations.

For comparison, concentrations measured in deionized water (series 3.1) are also shown in the figure. The deionized water concentrations for earlier contact times (shorter than 200 days) are in

most cases below the analytical detection limit and are plotted at the respective "less than" value. For the more recently obtained longer contact times, improvements in the analysis techniques have lowered the detection limits, but "less than" values are still recorded in some experiments. The uranium concentrations found in deionized water are generally in the range of a few $\mu\text{g}/\text{l}$.

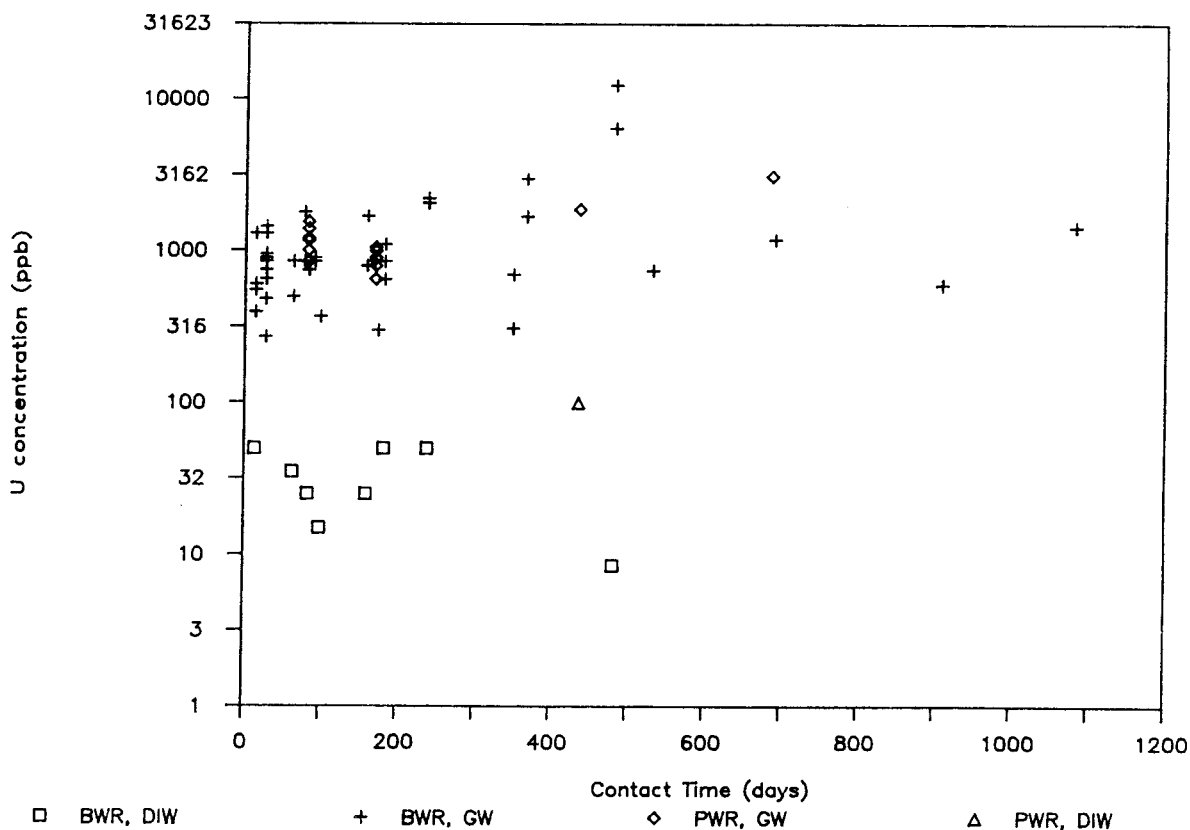


Figure 3. Uranium concentrations in centrifugate for high burnup BWR and PWR fuel.

In experiments 3.13 and 3.16 in the replenishment series, higher uranium concentrations were measured. However, both these specimens were fuel segments cut about two years prior to the start of the experiment. A tentative explanation for the higher uranium concentrations is that those two segments had experienced some surface oxidation during the air storage preceding the leaching.

Successive replenishments lowered the uranium concentrations to those normally found for the high burnup fuel. The corresponding replenishment experiments with fuel fragments did not show initially high uranium concentrations.

Uranium

Low burnup fuel

The uranium results from the low burnup fuel (0.5 MWd/kg U, 22 kW/m) have not been included in Figure 3, but the concentrations were much higher as can be seen in Table 9.

Table 9. Uranium concentration (ppb) in centrifugate, low burnup fuel.

Contact time (d)	22*	15	28	55
Oxidizing conditions	6380	3700	6250	8250
Reducing conditions		34	37	21

*Pre-leach

The uranium concentrations also appear to increase with time and even after 55 days may not have attained saturation. It seems unlikely that alpha radiolytical effects, presence or absence, could have caused these effects. The explanation is probably to be found in differences in fuel morphology, microstructure and stoichiometry between the high burnup and the low burnup fuel types.

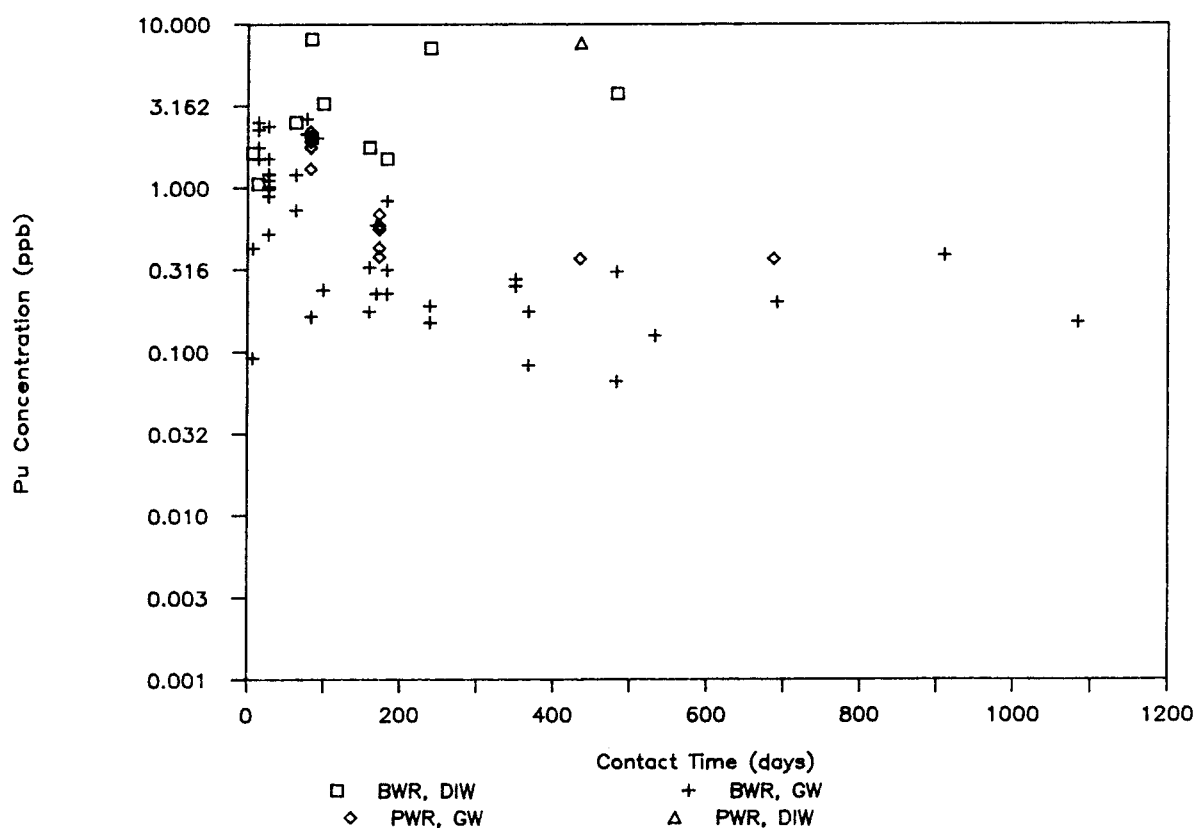
Plutonium

The concentrations of plutonium in groundwater and deionized water solutions are shown in Figure 4. The PWR fuel data seem to follow the previously observed trend for BWR fuel, i.e. the concentrations observed for shorter contact times drop by about one order of magnitude at longer contact times. As for uranium the scatter in measured concentrations is appreciable, but seems

to level out at 0.2 to 0.3 ppb after about 200 days contact time.

It is also worth noting that the unexpectedly high uranium concentrations at 482 days contact time (12th contact, 3.2 and 3.3 series) are not reflected in a corresponding increase in plutonium concentrations.

Contrary to what was found for uranium, the deionized water leachants have consistently higher plutonium concentrations than the groundwater. Based on the relatively few measurements available, the initially observed concentrations of about 3 ppb seem to remain also at longer contact times.



Cesium and strontiumHigh burnup fuel

Cesium, iodine and the fission gases Kr and Xe are the most mobile fission products in operating reactor fuel and there is convincing evidence that they are released from the fuel matrix with about the same fractions of inventory. The measured fission gas release fraction for the PWR rod was $1.06 \cdot 10^{-2}$ [12] and the corresponding value for the high burnup BWR rod was $7 \cdot 10^{-3}$. Hence, the Cs-137 releases during leaching should approach these value.

In the PWR experiments under oxidizing conditions, the mean FIAP during the first 82 day contact period was $7.7 \cdot 10^{-3}$, with an apparent difference of about 10 % between specimens from the two parts of the fuel column sampled. In the BWR experiments substantial differences in Cs-137 release behaviour were noted between different parts of the rod [8]. This is probably due to their different irradiation histories, since the axial power profile in a BWR rod varies during operation because of control rod movements.

The mean Cs-137 FIAP for the PWR fuel during the second 172 day contact period was $5.8 \cdot 10^{-4}$, giving a mean cumulative FIAP value of $8.3 \cdot 10^{-3}$ for a cumulative contact time of 254 days. The individual results together with the BWR results are presented in Figure 5. The PWR values are seen to be somewhat lower.

The mean strontium FIAP values for the first 82 day contact for the six PWR experiments was $4.0 \cdot 10^{-4}$, again with the same spread between specimens as observed for the Cs-137 results. For the second, 172 day, contact the mean FIAP was $1.2 \cdot 10^{-4}$, giving a cumulative 254 day value of $5.2 \cdot 10^{-4}$. The individual results are presented in Figure 6 together with the BWR results for comparison.

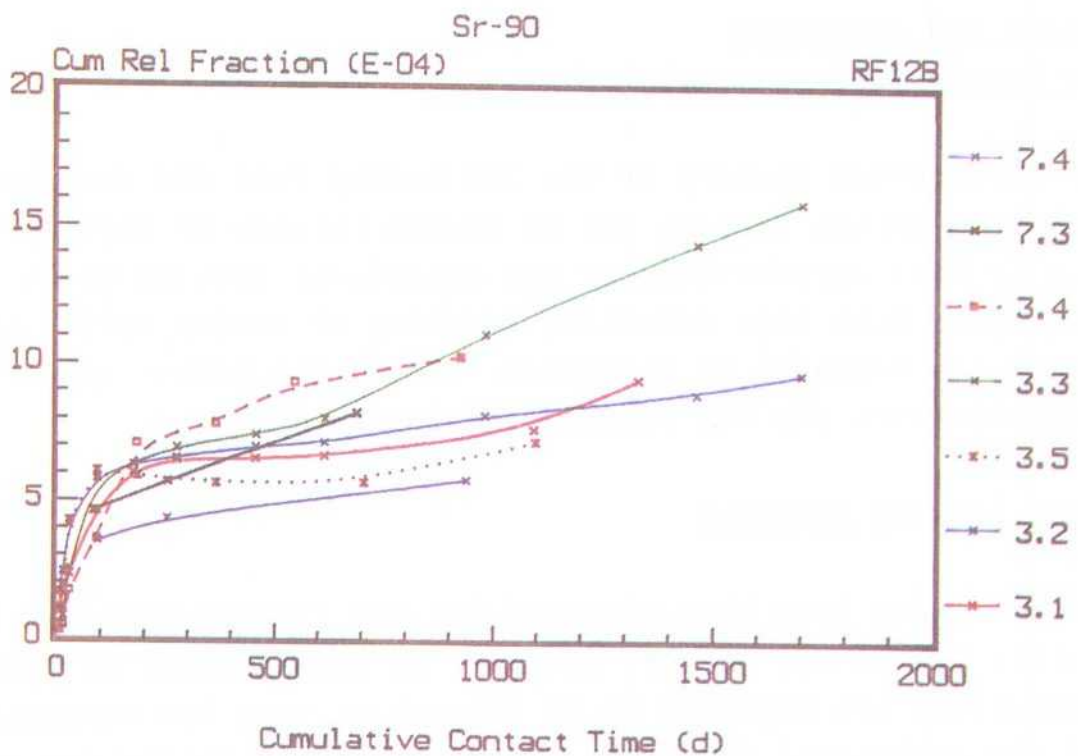
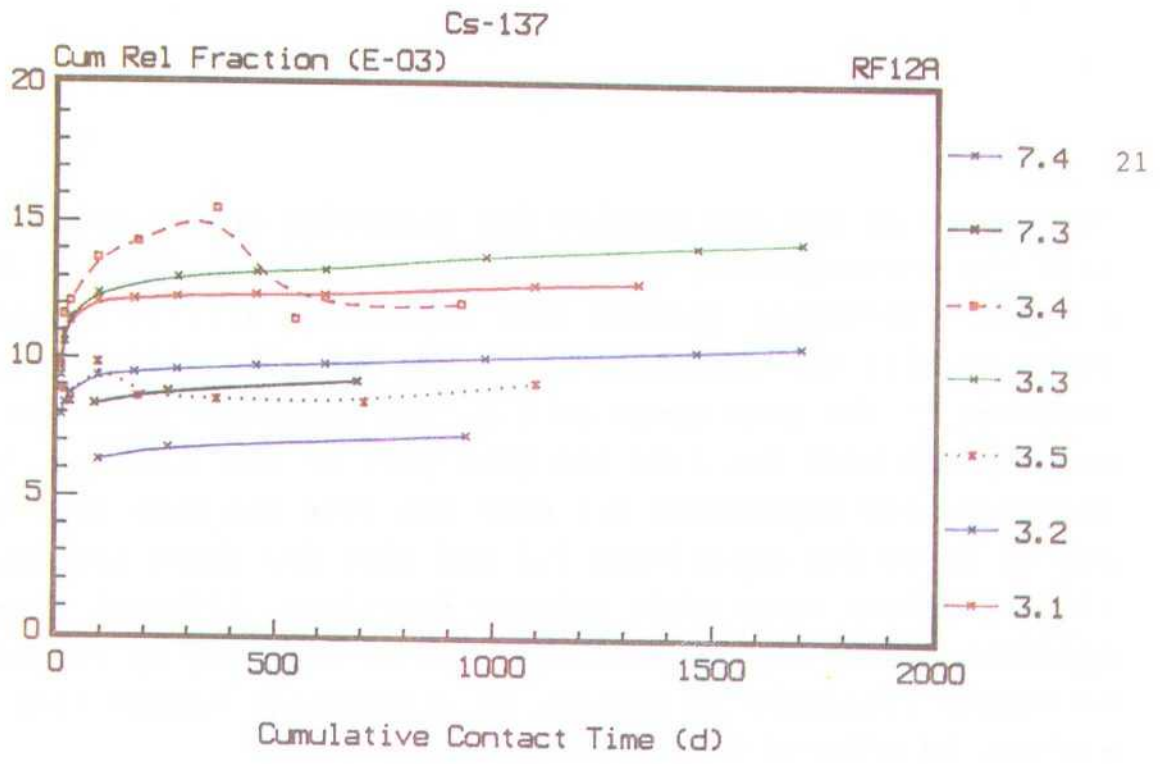


Figure 5. (Top) Cesium, cumulative fractional releases in sequential leaching of BWR and PWR fuel. 3.1 refers to sequential leaching of BWR fuel in deionized water. 3.2 and 3.3 refer to sequential leaching of BWR fuel in groundwater; 3.4 and 3.5 to static leaching of BWR fuel in groundwater. The 3.1, 3.2 and 3.5 specimens are cut from one section of the fuel rod. The 3.3 and 3.4 specimens are cut from a different section of the fuel rod. 7.3 and 7.4 refer to PWR fuel.

Figure 6. (Bottom) Strontium, cumulative fractional releases from leaching of high burnup BWR and PWR fuel. The notations are the same as in Figure 5.

The trends in the BWR results for strontium appear to correlate with the corresponding cesium results, i.e. experiment 3.3 giving a higher fractional release than experiment 3.2. It should also be noted that the experiments 3.1 and 3.5 also give fractional releases in the same range as 3.2. The specimens for these experiments were cut from the same part of the fuel rod. The specimens for experiment 3.4 were cut from the same part of the rod as those for experiment 3.3 and also for these two experiments, Figure 6 shows comparable release fractions. Although there is no apparent reason why strontium should be affected by control rod movements similarly to cesium, no alternative explanation can at present be offered to this observation.

Cesium and strontium

Low burnup fuel

The irradiation history of the low burnup fuel rod does not give reason to expect fission gas or cesium release of any importance. This is also corroborated by the experiment results which show that apart from some selective leaching of cesium during the pre-leach, the releases of strontium, iodine and barium appear to be congruent with the UO₂ matrix dissolution.

Other fission products

All specimens have been analysed for the fission products Ru-106, Sb-125, Ce-144 and Eu-154. However, at near neutral pH the lanthanides are expected to be present at very low concentrations and the analytical detection limits prevented collection of complete sets of results. Also Ru-106 was in many cases found to be below the detection limit. Only for Sb-125 a more complete set of data could be collected (Figure 7.).

When the PWR fuel test series started, the analytical programme was expanded to include also Mo and Tc-99. These data are, however, at this time incomplete.

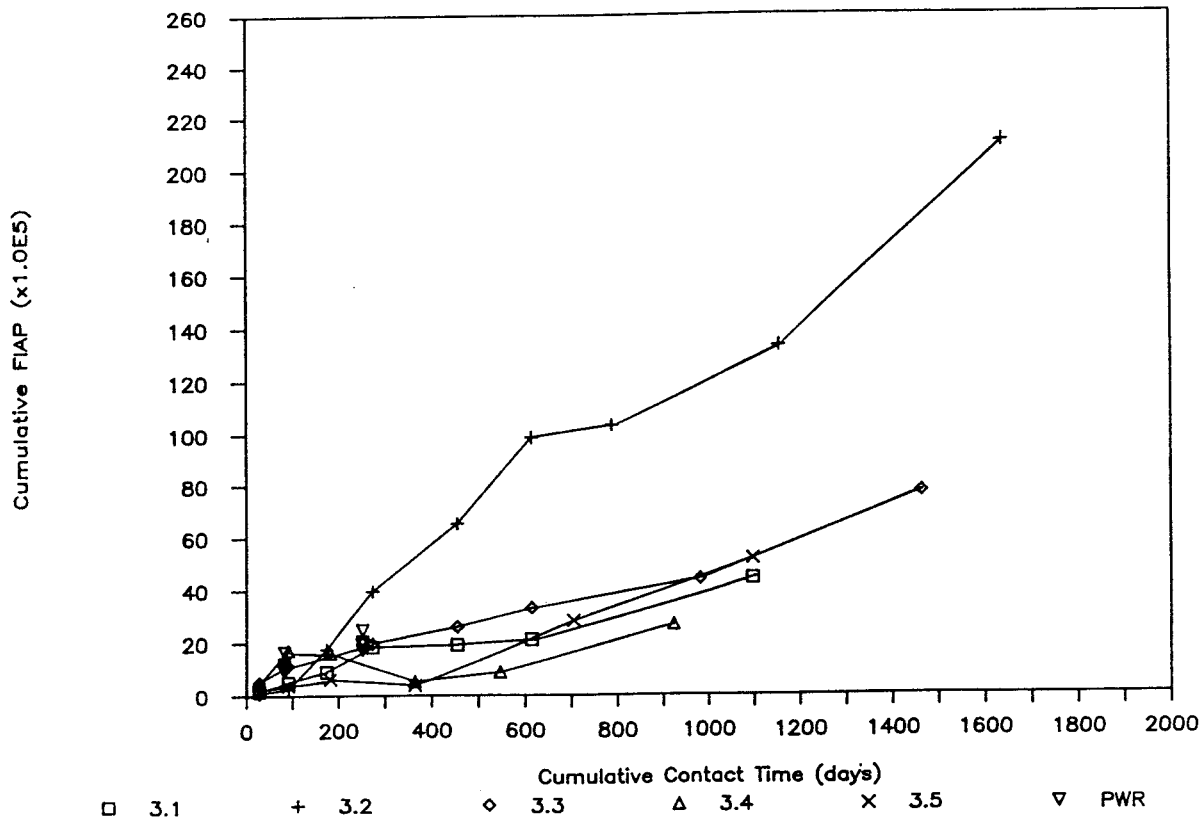


Figure 7. Antimony, cumulative fractional releases from leaching of high burnup BWR and PWR fuel. 3.1 refers to sequential leaching of BWR fuel in deionized water. 3.2 and 3.3 refer to sequential leaching of BWR fuel in groundwater; 3.4 and 3.5 to static leaching of BWR fuel in groundwater. The 3.1, 3.2 and 3.5 specimens are cut from one section of the fuel rod. The 3.3 and 3.4 specimens are cut from a different section of the fuel rod.

Low pH tests

A contamination incident occurred during the programme for the series 3.1 to 3.3 and also for the 91 days preleaches in the series 3.6 and 3.7. At the end of the contact times, it was found that the pH had decreased to between 2.3 and 5. Not unexpectedly, the fractional releases of radionuclides in these leachants were markedly higher than those measured during the preceding contact periods with normal pH. However, an interesting feature of the low pH exposures results was that the substantial differences in release fractions between different elements observed at higher

pH, and which could be caused by either preferential dissolution or by saturation/readsorption almost disappeared, indicating congruent dissolution.

In subsequent tests, shorter (20 days) low pH exposures were included in the test programme (see Figure 1) to follow a long exposure at high pH. It was expected in these tests that if the redeposited material or alteration products were soluble, the ratios of actinides and lanthanides to strontium (and uranium) would be enhanced compared with those in the fuel itself. Examples of results are shown in Table 10.

The results for curium appear to show some enhancement, but this is thought to be a combination of experimental error and variation in local curium inventories. Thus, it can be concluded that the experiments give no support to the hypothesis of appreciable adsorption or precipitation of actinides and lanthanides on the fuel/clad surfaces. An interesting observation is that at low pH, the strontium release fraction exceeded the cesium dissolution fraction, indicating, perhaps, different attack sites on the fuel surface than those at high pH.

Table 10. Normalized release in low pH tests.

pH	2.0	3.2	3.4	4.0	4.1	5.5
Sr-90	100	100	100	100	100	100
U	100	80	120	90	40	4
Pu	100	130	12	100	60	40
Cm	260	90	230	170	140	60
Ce-144	150	120	110	180	100	65
Eu-154	110	80	100	130	100	65
Cs-137	70	90	80	80	60	70

Bentonite scoping tests

The preliminary study of spent fuel/bentonite interaction (series 5) has shown no significant changes in the uranium concentrations, no indications of increased corrosion due to changes in solution, or due to sorption. The measured uranium concentrations were the same as in the experiments where no bentonite was present. This has been attributed to a very low sorption of anionic uranylcarbonate species onto bentonite. The concentrations of plutonium and cationic fission products in the aqueous phase were lowered considerably, by up to two orders of magnitude in the case of plutonium due to sorption onto the bentonite.

REDUCING CONDITIONS

Uranium and plutoniumHigh burnup & low burnup fuel

For the three fuel types discussed in this paper, a series of tests at reducing conditions was performed, where the reducing conditions were imposed on the system using 6% H₂/Ar gas in the presence of a palladium catalyst. The results for uranium and plutonium are presented in Table 11. In the tests performed under reducing conditions, the uranium concentrations in solution drop by up to three orders of magnitude. The corresponding drop in plutonium concentrations are about two orders of magnitude.

Table 11. Average concentration of uranium and plutonium in tests performed under reducing conditions.

	High burnup BWR	Low burnup BWR	PWR
U ($\mu\text{g/l}$)	40*	30	1.5**
Pu ($\mu\text{g/l}$)	$2 \cdot 10^{-3}$ *	$6 \cdot 10^{-3}$ *	$6 \cdot 10^{-3}$ *

* "Less-than" values included in calculating the average value.

** Same as in *, but lower detection limit due to improved analytical techniques.

Cesium and strontiumHigh burnup & low burnup fuel

In general, the release of fission products appear to be less influenced by the redox conditions in the tests. For high burnup fuel, both BWR and PWR, the cesium releases are virtually un-

affected by the redox conditions, indicating that at the early stages of leaching under reducing conditions, cesium release is essentially independent of UO_2 matrix attack.

For low burnup BWR fuel a reduction of cesium release by about a factor of ten was observed.

Under both oxidizing and reducing conditions, the fractional release of Sr-90 was always higher than the corresponding value for uranium for both BWR and PWR fuel. However, the Sr-90 release fraction decreases under reducing conditions, even though the effect is relatively small, about an order of magnitude.

DISCUSSION

General

For long-term predictions of releases from a spent fuel repository, it is essential to understand the mechanisms through which the radionuclides are released from the waste form. Radionuclides in solid solution with UO_2 or otherwise encapsulated in the UO_2 grains will be released as the UO_2 -matrix dissolves. For radionuclides segregated to grain boundaries, cracks and fissures in the fuel, the release may be largely independent of UO_2 dissolution. Although some efforts have been devoted to studying fission product and actinide distributions in reactor fuel (see e.g. ref [14]), very little has been done with reference to the leach behaviour of the fuel. It is therefore important to relate the present spent fuel corrosion data to dissolution mechanisms and establish which radionuclides are most likely released through some type of preferential leaching and which ones are released through UO_2 -matrix dissolution or breakdown.

An important step in this analysis is to establish what is fraction of material released through leaching/corrosion. As was discussed previously, we have concluded that only the centrifugate fraction represents chemically released material. (With some corrections

for sorption of elements such as Sr and Cs.)

Uranium and plutonium

The present data support our previous conclusions that uranium and plutonium concentrations in oxidizing groundwater seem to be solubility controlled [8]. For uranium this was also supported by calculations assuming schoepite to be the solubility controlling solid [8]. However, it must be borne in mind that a number of assumptions has to be made when calculating the solubilities of spent fuel. Parameters, such as E_H , oxidation state of the fuel before leaching, precipitating solid phases, etc., are not determined in the experiments. Thus, agreement between calculation and experiment must be taken with some caution. Factors, such as fuel morphology and fuel surface oxidation seem to influence the initial release of uranium from the fuel specimens [8]. Furthermore, a recent redetermination of the solubility of amorphous and crystalline schoepite [16] have shown that the observed uranium concentrations in the spent fuel leach experiments are about a factor of 20 lower than predicted. In addition to this redetermination of schoepite solubility, the thermodynamic database of uranium for EQ3/6 geochemical codes has also been validated [22].

In Figures 8 to 10, the fractional releases of uranium, plutonium and some fission products are compared for different fuel types and leach conditions. In groundwater under oxidizing conditions, the plutonium release is lower than the uranium release by one to two orders of magnitude. Although the plutonium is expected to be dissolved in the fuel matrix and, consequently, released congruently with uranium, an apparent incongruent release is observed. For uranium, the data (Figure 3) suggest solubility control of the solution concentrations and the lower, in the long-term constant (Figure 4) plutonium concentrations are also most probably controlled by the solubility of a precipitated solid phase, such as amorphous $\text{Pu}(\text{OH})_4$ [8,15].

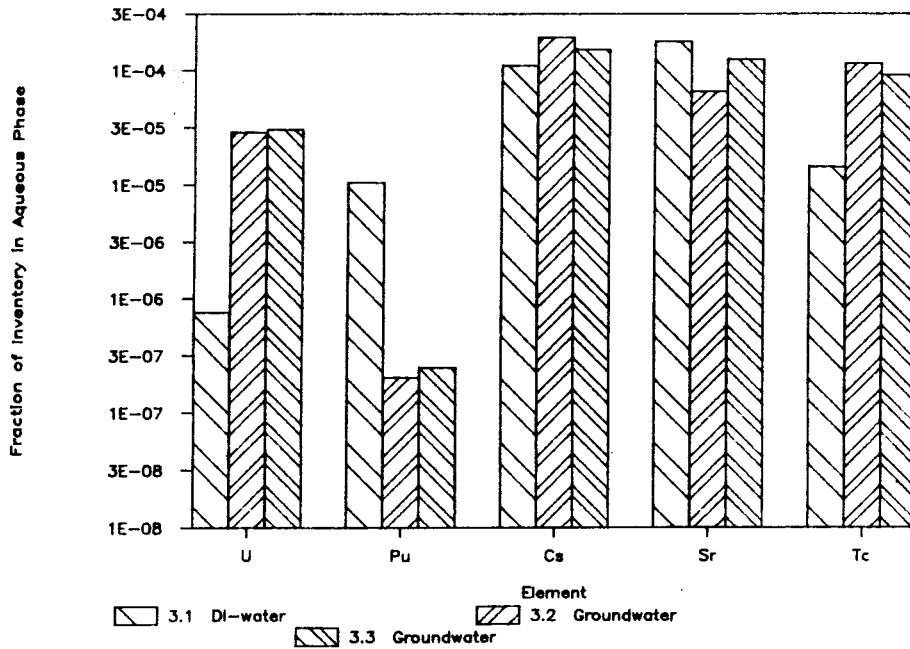


Figure 8. High burnup BWR fuel, comparison between fractional releases of uranium, plutonium and fission products during the 13th (238 days) contact period in sequential leaching. Cumulated contact time at the end of the 13th contact period: 6 years. 3.1 refers to leaching in deionized water; 3.2 and 3.3 to leaching in groundwater. The 3.1 and 3.2 are cut from one section of the fuel rod; the 3.3 specimens are cut from a different section.

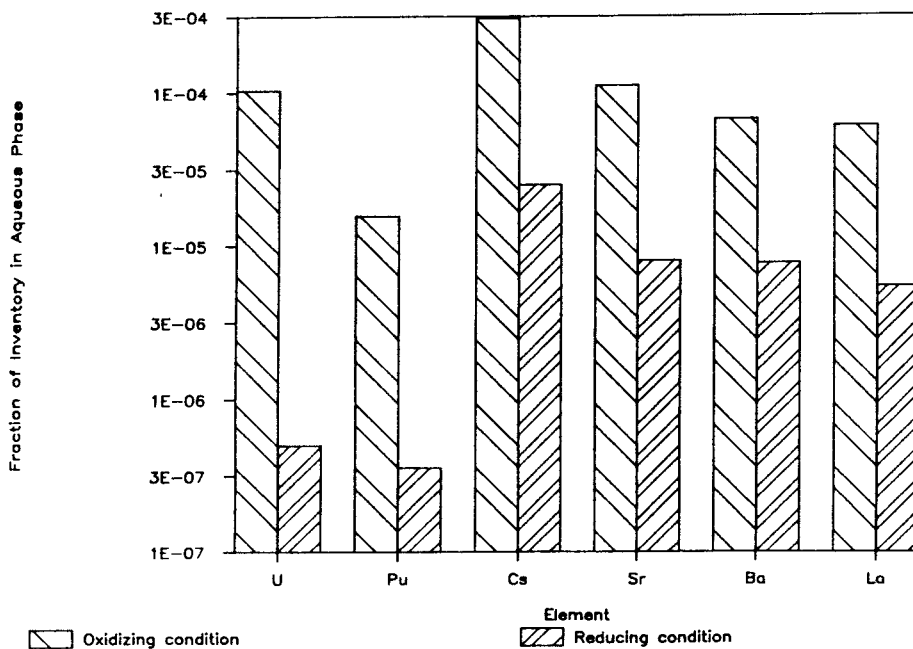


Figure 9. Low burnup BWR fuel, comparison between fractional releases of uranium, plutonium and fission products under oxidizing and reducing conditions. Contact time: 22 - 56 days.

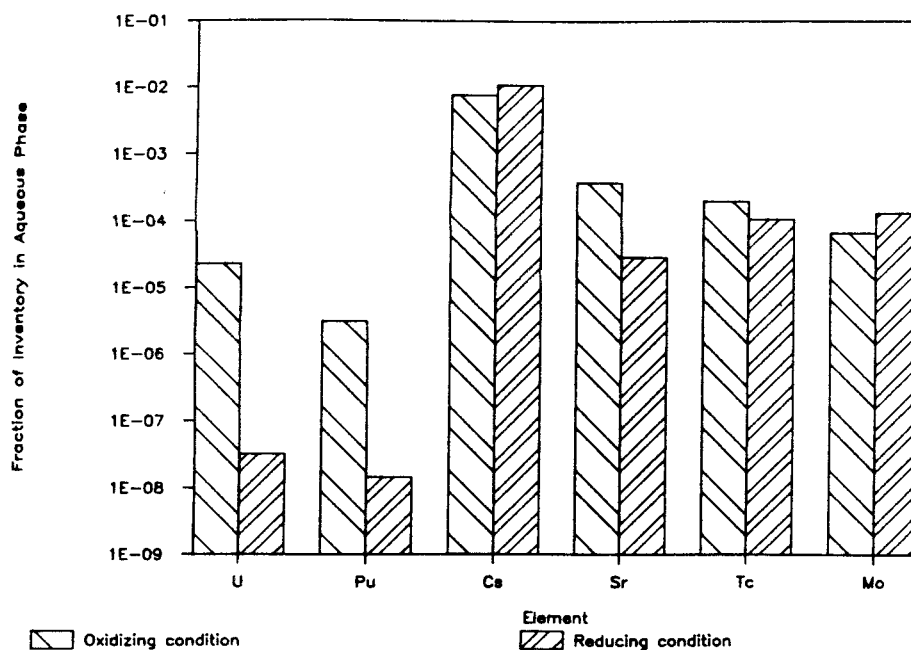


Figure 10. PWR fuel, comparison between fractional releases of uranium, plutonium and fission products under oxidizing and reducing conditions. Contact time: 82 days.

In deionized water (Figure 3), the uranium concentrations are considerably lower than in groundwater. This is to be expected, since no relatively soluble carbonate complexes can be formed in deionized water. However, as is evident from Figure 8, although the uranium release is lowered considerably there is no lowering of the plutonium releases. In fact the concentrations in solution are even slightly increased (Figure 4). Compared to the groundwater case, there is a reverse incongruent release of plutonium in deionized water. The reasons for this difference in plutonium behaviour in groundwater and deionized water remain to be resolved.

Under reducing conditions, all fuel types have near congruent release of plutonium, as is shown for PWR fuel and low burnup BWR fuel in Figures 8 and 9. Under reducing conditions, UO_2 is stable and limits the uranium concentrations in solution. However, according to reference 18, plutonium is expected to be redox insensitive under the test conditions. Thus, under reducing conditions the leachants must be under-saturated with respect to plutonium. The plutonium release is controlled by the fuel matrix

dissolution and as the matrix dissolution is greatly retarded when the leachant is saturated with uranium, no measurable increase in plutonium concentrations are detected.

However, recent experiments seem to contradict this [13]. In these experiments it was attempted to obtain reducing conditions by circulating groundwater over crushed rock until a low E_H was obtained and thereafter transfer the reduced groundwater to the leach vessels in the hot cell. No monitoring of the redox potential was performed during leaching, but the observed uranium concentrations in solution indicated that actual reducing conditions were not achieved. The plutonium concentrations, on the other hand, were lowered considerably. The reason for this is not yet established, but sorption of plutonium (IV) onto active mineral particulates (possibly released from the crushed rock) is very strong and could be responsible for lowering the solution concentrations.

In the deionized water case, an equally low uranium concentration was not reflected in a lower plutonium concentration. Thus, in oxidizing deionized water, saturating the leachant with uranium does not stop the oxidation of the UO_2 -matrix to higher uranium oxides. During this alteration of the solid phase, or formation of a new solid phase, plutonium appears to be released to the leachant. Indeed, Stroes-Gascoyne et al. have identified precipitated schoepite ($UO_3 \cdot H_2O$), or a related hydrate on the surface of leached spent fuel [17]. Also at Studsvik, a yellow precipitate has been found on specimens leached for extended periods in deionized water. However, it has not yet been possible to identify this precipitate.

Strontium

For the low burnup BWR fuel, where no fission product segregation is expected, strontium and other fission products are released practically congruent with uranium under oxidizing conditions (Figure 9). Under reducing conditions an incongruent release can be seen, indicating that a small fraction of the studied fission

products may be segregated and can be released independent of the uranium dissolution.

For high burnup BWR fuel, there is an apparent incongruent release of strontium even after an integrated contact times of nearly six years (13th contact shown in Figure 8). Two explanations for this observation can be put forth. (1) Strontium is known to be a fission product mainly dissolved in the fuel matrix [14]. Thus, the incongruent strontium release is an indication of ongoing fuel matrix alterations after the leachant has been saturated with uranium, i.e., strontium is released to the leachant similarly to the release of plutonium in the case of leaching in deionized water. (2) The dominating fraction of the strontium detected in the experiments is preferentially leached segregated material (from fuel cracks, fissures and grain boundaries).

The first hypothesis seems to be refuted by the fact that in low burnup fuel, where very little segregation is expected, the release of strontium is in fact congruent.

The second hypothesis is supported by the fact that the factors such as fuel irradiation history as well as size and type of specimens used appears to have a larger influence on the strontium leaching than the saturation state of uranium in solution.

An alternative hypothesis for the strontium has recently been put forth, where an attempt is made to interpret the strontium release as controlled by oxygen diffusion into the fuel matrix [19].

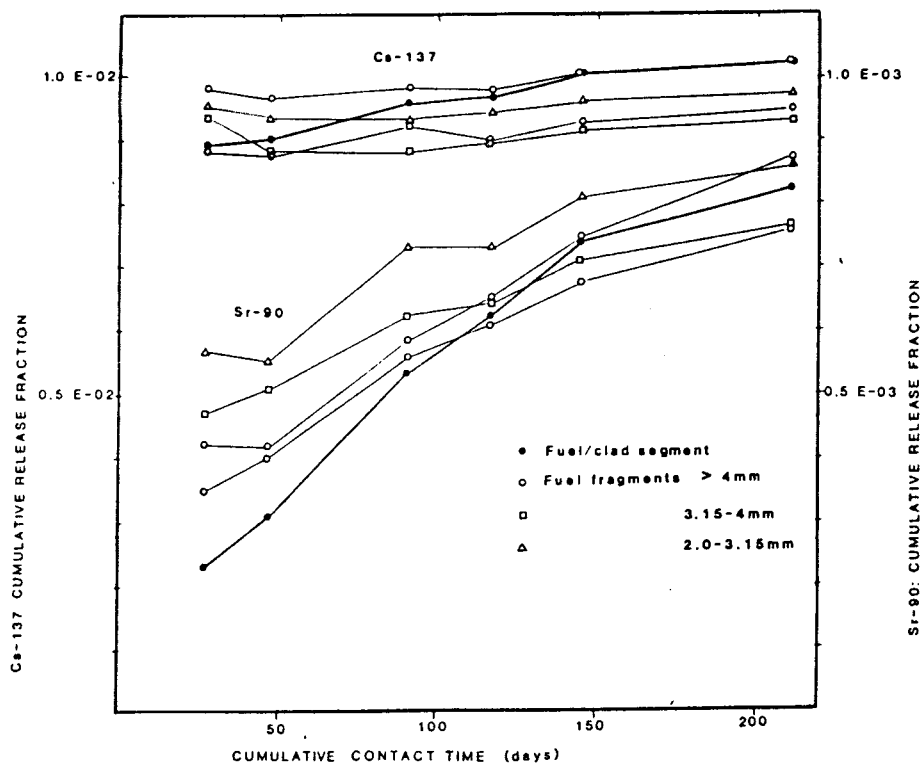
In Figure 6, it can be seen that the release of strontium from BWR fuel depend only on the cumulated contact time. Sequential tests and static tests give the same cumulated releases after the same cumulated contact time, even though for a sequential test the leachant was changed several times during the leaching and thus saturated with uranium several times. Also, there is no difference between the strontium leaching in deionized water and groundwater, reflecting the vast differences in uranium behaviour in the leachants. However, as was mentioned before, two sets of

data points can be distinguished in Figure 6, particularly at longer cumulated contact times. This difference is related to the position within the fuel rod from where the specimens were cut. These different regions within the same fuel rod have slightly different irradiation histories, depending on control rod movements etc. A similar difference can also be seen in the cesium release curves in Figure 5.

In an experiment where fuel segments and fuel fragments of various sizes were used [8], a correlation between fragment size and strontium release was observed (Figure 11). The fuel/clad segments, where leachant penetration to crack, fissures and grain boundaries is expected to be less effective than in smaller fragments, showed an initially lower release of strontium. This difference disappears at longer contact times. For these particular specimens, the fuel/clad segments had been stored in air for nearly a year and the exposed fuel surfaces had been oxidized. As a result of this, the uranium release from the segment specimens was about a factor ten higher than from the fragments [8].

Based on these observations, the most probable explanation for the strontium leach data appears to be that the leached strontium is segregated material from fuel crack, fissure or grain boundaries. The fact that imposing reducing conditions on the system reduces the strontium releases (see e.g. Figure 10) could be then be a result of reduced grain boundary dissolution in the absence of grain boundary oxidation. However, scanning Auger studies of transgranular/intergranular fracture surfaces in high gas release (18 %) PWR fuel show no indications of any strontium enrichments at grain boundaries [20].

Thus, the reasons for the observed strontium behaviour remain to be resolved.



Figur 11. High burnup BWR fuel, comparison between cumulated fractional releases of strontium and cesium for fuel/clad segment specimens and fragment specimens of different fragment sizes.

Other fission products

Only for Sb-125 has a complete set of data been acquired as is shown in Figure 7. Antimony is one of the fission products known to form metallic precipitates in the fuel [14]. However, it is unlikely that the leached antimony fraction in the tests stem from oxidation and dissolution of such precipitates. Nevertheless, the Sb-125 releases correlate neither with the uranium dissolution, nor with the strontium releases, indicating that antimony is most probably released from more or less isolated inclusions in the fuel.

During the past year, technetium and molybdenum analyses have also been included in the programme. These fission form metallic

precipitates in the fuel. However, the present data indicate that an appreciable fraction of the technetium and molybdenum are accessible to leaching. After long contact times, the data for technetium and molybdenum appear to be similar to other fission products (Figure 8). Without a more complete set of data, showing the evolution of technetium and molybdenum in solution, no definite conclusion can be drawn from the BWR fuel data. The early data from the PWR fuel (Figure 10) show releases in the range of what is found for strontium. However, unlike what is found for strontium, the preliminary data indicate that there is no influence of reducing conditions on the technetium and molybdenum releases. In this respect these elements behave more like cesium. A preliminary interpretation for this observation is that technetium and molybdenum are segregated in fuel, but are less dependent than strontium on grain boundary oxidation for their release.

CONCLUSIONS

- (1) The present results from the on-going Swedish programme on leaching of spent UO_2 fuel are in agreement with earlier results from the programme and also with those of other laboratories.
- (2) Leach vessel rinse solutions always show compositions congruent with the composition of the fuel. In by far the most cases, this is also found for the fractions retained on the 1.8 nm filters. The results so far indicate that these release fractions are composed of small fuel fragments, probably released mechanically from the fuel and give therefore no information on the release mechanisms.
- (3) For high burnup BWR and PWR fuel, uranium saturation in the groundwater appears to be attained at a level of 1 mg/l. However, there is some evidence that this level can be raised by factors such as fuel oxidation prior to leaching, fuel morphology and fuel stoichiometry. However, solid phases or mechanisms controlling the uranium concentration have not been identified.

- (4) In deionized water, uranium saturation appears to be attained at a level about a factor of 1000 lower than in groundwater. This is not reflected in a correspondingly lower plutonium release, indicating that fuel oxidation/alteration continues after the leachant has been saturated with uranium.
- (5) Under reducing conditions, the absence of fuel oxidation and the very low uranium solubility leads to a stronger tendency towards congruent releases, controlled by the solubility of the fuel matrix.
- (6) The fission products Cs, Sb, Tc and Mo appear to be selectively leached, most probably from inclusions or from fuel cracks, fissures and grain boundaries.

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