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**TECHNICAL  
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**85-16****The corrosion of spent  $\text{UO}_2$  fuel  
in synthetic groundwater**

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THE CORROSION OF SPENT UO<sub>2</sub> FUEL IN SYNTHETIC GROUNDWATER

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THE CORROSION OF SPENT UO<sub>2</sub> FUEL IN SYNTHETIC GROUNDWATER

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## ABSTRACT

Leaching of high burnup BWR fuel for up to 3 years showed that both U and Pu attain saturation rapidly at pH 8.1, giving values of 1-2 mg/l and 1  $\mu$ g/l respectively. The leaching rate for Sr-90 decreased from about 10<sup>-5</sup>/d to 10<sup>-7</sup>/d but was always higher than the rates for U, Pu, Cm, Ce, Eu and Ru. Congruent dissolution was only attained at pH values of about 4.

When reducing conditions were imposed on the pH 8.1 groundwater by means of H<sub>2</sub>/Ar in the presence of a Pd catalyst, significantly lower leach rates were attained.

The hypothesis that alpha radiolytic decomposition of water is a driving force for UO<sub>2</sub> corrosion even under reducing conditions has been examined in leaching tests on low burnup (low alpha dose-rate) fuel. No significant effect of alpha radiolysis under the experimental conditions was detected. Thermodynamically the calculated uranium solubilities in the pH range 4-8.2 generally agreed, well with the measured ones, although assumptions made for certain parameters in the calculations limit the validity of the results.

## INTRODUCTION

Common to all proposed methods for the safe, permanent disposal of spent reactor fuel is the concept of multiple barriers to radionuclide release to the environment. One of these barriers is the limited solubility in groundwater of the UO<sub>2</sub> fuel itself, and over the past few years a number of investigations have been published /1-6/ which have been directed to the study of the dissolution mechanism and dissolution rates of fuel of various burnups and heat ratings under a range of experimental conditions.

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The experiments described here have been performed using spent BWR fuel with a burnup (42 MWd/kgU) higher than the current average for discharged fuel, but of the same order as that projected for the near future.

In addition to these experiments, a series of experiments using low burnup fuel ( $\sim 0.5$  MWd/kgU) was also performed in order to study the possible influences of  $\alpha$ -radiolysis on the dissolution of  $UO_2$  in groundwater.

For both high and low burnup fuel, experiments were also performed where reducing conditions were imposed during one contact period after leaching under oxidizing conditions.

## HIGH BURNUP FUEL: SEQUENTIAL AND STATIC LEACH TESTS

### Experimental

All specimens used in these experiments consisted of 20 mm long segments of fuel and clad cut out from a well-characterized BWR fuel rod irradiated to a burnup (rod maximum) of 42 MWd/kg U.

Each fuel specimen, containing about 16 g  $UO_2$ , was suspended in a spiral of platinum wire in 200 ml of the leachant in a 250 ml Pyrex flask. All leach tests were performed at 20-25°C, the ambient temperature of the hot cell.

On completion of the planned contact period, the specimen was removed from the flask and transferred to a new flask with new leachant in the case of sequential leaching, or discarded in the case of the static tests (or exposed to low pH leachant).

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 (Aminco Corp, USA) with apertures of 1.5-2 nm). The material retained on these membranes has been defined arbitrarily here as "colloidal". Both centrifugate and membrane were subjected to radiometric and radiochemical analysis. The empty flask, after a rapid rinse with deionized water, was exposed for a few days to 200 ml of 5M  $HNO_3$ /0.5M HF to desorb any activity on the vessel walls. This rinse solution was also analyzed.

The experiments discussed in this section, three series each with a fuel/clad specimen exposed to sequential leaching and two series of static tests - each with 8 fuel/clad specimens, were all performed under so-called oxidizing conditions. Other test parameters are given in TABLE 1.

TABLE 1  
Summary of leach test conditions

Series	Leachant	Procedure	Contact period (days)
3.1	DIW	SEQU	7,7,14,63,91,83,182,159,218,174
3.2	GW	SEQU	"-
3.3	"	SEQU	7,7,14,63,91,182,182,159,218,174
3.4	"	STAT	14d Preleach. 14:77:168:350:532:909
3.5	"	STAT	" " 14:77:168:350:691:1083

The leachant used for Series 3.1 was deionized water while a synthetic groundwater whose composition is shown in Table II was used for the other tests. The deionized water, which was also used in preparation of the groundwater, was de-aerated by bubbling with nitrogen prior to use. However, as mentioned above, each leachant was in contact with about 50 ml of air during leaching.

TABLE II  
Composition of the synthetic groundwater

Species	HCO <sub>3</sub> <sup>-</sup>	SiO <sub>2</sub>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>
ppm	123	12	9.6	70	18	4.3	3.9	65

pH: 8.0 - 8.2 Ionic strength: 0.0085.

#### Analysis

All samples were analysed for a) uranium (neutron activation) b) Sr-90 c)  $\gamma$ -emitting fission products d)  $\alpha$ -emitting nuclides ( $\alpha$ -spectrometry).

In some samples, the cesium activities were so intense that an ion exchange separation procedure was required prior to analysis of the other constituents.

Radionuclides retained on the membrane filters were removed by treatment with warm 6M HCl for 5-6 hours. This solution was then subjected to the normal analysis scheme.

### Adsorption on the vessel walls

It had been anticipated that adsorption effects would be significant in these solutions with very low concentrations of highly-charged species. It had also been expected that small fuel fragments could be lost from the suspended fuel specimens and later be dissolved during the desorption treatment. The analytical results for the rinse solutions were therefore evaluated very carefully.

Small quantities of uranium were detected in all the rinse solutions but in a few cases quantities of 100-300 ug were found, of the same order of magnitude as those found in the other fractions, i e, the centrifugate and the membrane filter. No correlation with any parameter of the leaching experiments was observed.

It was found, however, that the ratios of the amounts of Sr-90, Ce-144, Eu-154 and the actinides also found in the rinse solutions to the amounts of detected uranium, agreed reasonably well with the ratios in the spent fuel, suggesting that dissolution of small particles lost from the fuel was the major contribution to activity in the rinse solutions, and that no significant absorption effects could be observed.

### Reporting units

Because of the difficulty in defining the surface area of highly-cracked spent UO<sub>2</sub> fuel, the experimental results are expressed as fractions of the initial inventories of each radionuclide. Also, since what is actually measured - the amount of the nuclide in the leaching flask at the conclusion of the contact period - is the resultant of such processes as selective leaching, dissolution, colloid formation, and precipitation and adsorption, the neutral term Fraction of Inventory in Aqueous Phase (FIAP) is used here. The term Apparent Leach Rate (ALR), in units of FIAP/day, is used as the corresponding definition of rate.

Since no significant quantities of radionuclides could be unequivocally detected in the flask rinse solutions (see preceding section), each FIAP value reported here is the sum of the corresponding fractions in the centrifugate and retained on the membrane filter.

### Results and discussion

As was shown in TABLE I, data for contact times ranging from 7 to 1083 days have been accumulated. Since the behaviour of the radionuclides are very different between themselves, they will in the following be treated individually.

## Uranium

The concentrations of uranium in the groundwater leachant centrifugates at pH 8.1 in the experimental Series 3.2 - 3.5 are shown in Figure 1. The results show appreciable scatter but concentrations can be seen to level out rapidly and attain saturation at a level of 1-2 mg/l. The concentration levels in deionized water - Series 3.1 - were around or below the detection limit of about 50  $\mu\text{g/l}$ . Although the experiments were not primarily designed to determine solubility limits, the rapidity with which the final concentrations was reached as well as the lack of a long term evolution of the uranium concentrations in solution lead to a tentative description of the uranium leaching in terms of thermodynamical equilibria. This will be discussed further elsewhere in this paper.

## Plutonium

The concentrations of plutonium in the groundwater presented in Figure 2 also show the rapid attainment of saturation at the level of a few parts per billion but here, the results show a decreasing trend after about 100 days of contact.

## Cesium and strontium

The migration of fission product cesium in operating  $\text{UO}_2$  reactor fuel from the warmer central regions to the neighbourhood of the fuel/clad gap is well-established, and results for Cs-134 and Cs-137 in this program confirm previous work.

Cumulative FIAP values for Cs-137 in groundwater of pH 8.0-8.2 in both sequential leaching and static tests as a function of contact time are shown in Figure 3. The similarity in results between the two test methods demonstrates the absence so far of saturation effects.

It can be seen that about 1% of the initial Cs-137 inventory is leached out rapidly, most during the first 10 days, and in good agreement with the reported value of 0.7% for the release of fission gases from the whole fuel column. The results for the 3.1 series in deionized water, which are not plotted in Figure 3, lie towards the middle of the range.

After the initial phase, corresponding to dissolution of cesium compounds, probably cesium uranates in the neighbourhood of the fuel/clad gap, and characterized by ALR values of over  $10^{-3}$  FIAP/d, the dissolution rate decreased substantially for longer contact periods, as can be seen in Figure 4.

Figure 3 also presents the cumulative FIAP results for Sr-90 for the experimental series using groundwater (pH 8.0-8.2). Even here the ALR values (Figure 5) show a steady decrease as a function of contact time (a slope of +1 would indicate

a constant dissolution rate), approaching a value of about  $10^{-7}$  FIAP/d at the end of the period. The agreement between the sequential leaching and static test results suggest the absence so far of saturation effects.

The results presented in Figure 3 also show a clear difference in the early leaching behaviour of Sr-90 of fuel from different zones of the rod, since the specimens for Series 3.2 and 3.5 were taken from the upper middle of the fuel rod, and for Series 3.3 and 3.4 from the lower middle. The burnup and Sr-90 inventories of the fuel in these zones were very similar: only their irradiation histories differed, reflecting control rod movements.

For both nuclides, after the first 2 weeks, the apparent leach rates were nearly inversely proportional to the contact time over the next 3 years. The values of Cs-137 were always higher than the corresponding values for Sr-90 by a factor of 3-5, suggesting perhaps grain boundary attack. This effect has also been observed by Vandergraaf and Johnson /4,5/.

It is also of interest to note that the leaching behaviour of Cs-137 and Sr-90 in deionized water was very similar to that in the groundwater, although the measured uranium solubility in DIW was found to be very low (about 50 ppb).

#### Other fission products

All specimens have also been analysed for such fission products as Ru-106, Sb-125, Ce-144 and Eu-154 during the course of this program, but analytical detection limits have prevented collection of a complete set of results. However the results obtained indicate values of ALR for Cm-244, Ce-144 and Eu-154 were apparently two orders of magnitude lower than those for Sr-90, but since these nuclides were usually only measurable on the membrane filters, and contamination with small fuel particles can be suspected, it is possible that their real ALR values are an order of magnitude lower.

#### Actinides

The actinides Cm and Am were also analyzed for and ALR values generally two orders of magnitude lower than those for Sr-90 were found. However, even the actinides were strongly retained on the membrane filters and contamination with small fuel particles cannot be excluded, resulting in too high ALR values as mentioned above.

#### HIGH BURNUP FUEL: LOW pH TESTS

In order to explain the marked differences in the leaching behaviour of the various nuclides reported above, two main hypotheses can be advanced:

- 1) that in the groundwater used here (pH 8.1, 123 ppm  $\text{HCO}_3^-$ ), uranium saturation is attained rapidly (1-2 mg/l). Other actinides and lanthanides are released congruently to the solution but are precipitated and/or adsorbed on available surfaces. Cs and Sr are preferentially leached from the fuel: cesium partly as an instant release fraction comparable in size to the release of fission gases from the fuel during reactor operation, and then, as for strontium, from enriched inclusions or zones in the fuel matrix, perhaps from grain boundaries.
- 2) that Cs is leached as in the first hypothesis above, but the leaching rate for Sr represents the dissolution rate of the fuel matrix, and although dissolution occurs congruently, the amounts in solution of the actinides and lanthanides are determined by solubility limitations.

The second hypothesis implies that after long exposures to groundwater, as in the static tests in Series 3.4 and 3.5, significant quantities of U, Pu and lanthanides would have entered and then left the solution by precipitation or adsorption, or been retained on the fuel surfaces as alteration products.

Analysis of the more than 100 flask rinse solutions examined has indicated that this material does not appear to have deposited on the flask walls, since their contents correspond to the dissolution of small fragments of fuel which have been lost during handling.

#### Experimental

As a practical check on the second hypothesis, the 6 fuel/clad specimens from the 3.4 and 3.5 series with the longest contact times in the pH 8.1 groundwater (350-1083 days) were subsequently contacted for 20 days with 200 ml of new groundwater which had pH values adjusted to lower values by means of HCl.

It was expected, of course, that the dissolution of the matrix would increase at low pH, but if the redeposited material or alteration products were also soluble, then the ratios of actinides and lanthanides to strontium in the leachants would be enhanced compared with those in the fuel itself.

#### Results

Since the apparent leaching rate for Sr-90 decreases with increasing contact time as shown in Figure 5, the results are expressed (in Table III) as rounded ratios to the Sr-90 values.

TABLE III  
Normalised apparent leaching rates in low pH tests.

pH	2.0	3.2	3.4	4.0	4.1	5.5
Initial contact (d)	532	1083	909	350	691	350
Sr-90: ALR ( $\times 10^6$ )	25.8	14.0	16.4	9.6	10.7	10.3
Sr-90	100	100	100	100	100	100
U	100	80	120	90	40	4
Pu	80	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

Although the results for Cm appear to show some enhancement, this is thought to be a combination of experimental error and variation in local Cm inventories, and 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 surface.

However, the results do show that congruent dissolution is attained at pH 4 and below, although significant fractions of several leached species were retained on the membrane filters. Another interesting feature is that at low pH, the Sr-90 dissolution rate exceeded the Cs-137 rate, indicating, perhaps, different attack sites on the fuel surface than those at high pH. In addition to these findings, the measured U concentrations at different pH also supported the interpretation of U release as controlled by thermodynamical equilibria, as discussed later in this paper.

#### HIGH BURNUP FUEL: REPLENISHMENT EXPERIMENT

The experimental finding that uranium saturation at 1-2 mg/l was attained rapidly in the groundwater is, of course, of significance for safety analysis, and it was decided to check the finding in a further experiment series.

#### Experimental

The 6 experiments were all performed under the same oxidizing conditions used in the main program, i.e., there was 50 ml of air in contact with the 200 ml of the synthetic groundwater leachant (pH 8.1). Polypropylene flasks were also compared with Pyrex flasks. The fuel fragments were

suspended in the leachant on Pt trays. Details of the experiments are given in Table IV.

TABLE IV  
Replenishment experiment: Summary of test conditions

Experiment	Flask	Fuel Specimen	Wt UO <sub>2</sub> (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

After initial filling, the flasks were allowed to stand for 27 days in the hot-cell at ambient temperature, following which 40 ml of the leachants were removed (and subjected to the same procedures as previously) and immediately replaced by 40 ml of fresh groundwater. This was repeated four times after different contact periods. On the basis of the previous results, all solutions should have shown uranium saturation at the 1-2 mg/l level.

### Results

The measured uranium concentrations in the centrifugate samples from the various replenishment tests are presented in TABLE V.

TABLE V  
Uranium concentrations (ppb) as a function of total contact time.

Contact time (d)	27	47	91	117	145	211
3.13	4 950	11 500	10 000	9 000	8 000	2 450
3.14	650	1 300	1 900	1 600	1 450	340
3.15	800	1 100	1 600	1 450	1 700	875
3.16	4 150	6 000	7 500	5 500	3 900	2 400
3.17	600	950	900	1 250	1 000	700
3.18	900	2 050	1 750	1 900	1 050	850

The results for the fuel fragment experiments show fairly good agreement with the previously established saturation concentration but the high (4-5 mg/l) initial U concen-

trations found for the fuel/clad segment experiments, increasing over the first few months and then decreasing approximately at the same rate as dilution, were unexpected.

Figure 6 presents the FIAP values for Cs, Sr, U and Pu for the experimental series. Note that the abscissa represents the number of replenishment stages, although the time for each contact period is also given.

To simplify the figure, the results have been averaged for the 3 groups shown in the legend, and the dashed line represents the slope of successive 20% dilutions.

The Cs curves display, as expected, the initial release fraction of about 1% of inventory during the first 27 day contact period. The concentrations then almost follow the 20% successive-dilution curve, but show some further Cs leaching, particularly for the fuel/clad segments. FIAP values for fuel/clad segments and fuel fragments are very similar suggesting that only a minor part of the cesium released from the fuel during reactor operation was deposited on the inner surface of the clad.

The Sr results also show good agreement with the earlier results from the program. During the initial contact periods, the ALR values were higher for fuel fragments than for fuel/clad segments, probably reflecting easier access of the leachant to the fuel surface, but calculation of the cumulative leach fractions at 211 days showed all specimens to have released about the same fraction ( $8 \cdot 10^{-4}$ ) of inventory. (The derived values for ALR for the two fuel/clad segments are plotted in Figure 5).

As mentioned above, the U results are somewhat surprising. For fuel fragment leaching, the leach fractions agree well with previous work, being an order of magnitude lower than those for Sr-90. and the measured uranium concentrations were in the range 1-2 mg/l. Leaching of the 2 fuel/clad segments, however, showed increasing dissolution of U over the first 91 days, attaining U concentrations of the order of 10 mg/l, which then decreased roughly following the 20% successive dilution curve. This suggests the same effect of supersaturation and precipitation observed by Johnson /5/. A tentative explanation for the initial high concentrations is that the cut fuel surfaces of the two segment specimens had experienced some oxidation during the two years of air storage prior to leaching.

The Pu results also show a somewhat high initial concentration, but appear to attain saturation after about 91 days at a level of a few ug/l.

## HIGH BURNUP FUEL: DISSOLUTION UNDER REDUCING CONDITIONS

All the experiments reported above were performed under oxidizing conditions. In the deep repository projected in the KBS program, however, extremely reducing conditions - unfavourable to oxidative dissolution of the  $UO_2$  matrix - are expected to obtain. Such reducing conditions are difficult to establish and maintain in a laboratory, and in particular a hot-cell, environment.

Norris /7/ has reported experiments at Los Alamos where hydrogen gas in the presence of a palladium catalyst was used to impose reducing conditions on the fuel/leachant system. Six experiments have been performed in this program where the fuel/clad specimens were first subjected to two pre-leaches in groundwater under oxidizing conditions followed by a 28 or 56 day exposure under reducing conditions using the Los Alamos method. Although the leaching flasks were sealed immediately after a final in situ reduction process, the possibility of the entry through minor leaks of the hot-cell air atmosphere during the subsequent 4 or 8 weeks could, of course, not be excluded. After re-opening the flasks, the same experimental and analytical procedures were applied as for the previous experiments. Table V presents the apparent leach rate values for the most significant nuclides for both the reduction stages and the immediately preceding 27 day pre-leach under oxidizing conditions.

TABLE VI

Comparison of apparent leach rate values under oxidizing and reducing conditions.

ALR (FIAP/d x $10^6$ )						
Experiment	3.6.1	3.6.2	3.6.3	3.7.1	3.7.2	3.7.3
Contact time (d)						
(Reducing)	28	28	56	28	56	56
Sr-90						
Pre-leach	3.0	2.7	2.7	2.2	2.4	2.0
Red. conditions	0.13	0.10	4.9	0.73	0.11	0.09
U						
Pre-leach	0.53	0.47	0.62	0.49	0.80	0.54
Red. conditions	0.03	0.04	0.08	0.09	0.08	0.08
Pu						
Pre-leach	0.11	0.09	0.08	0.09	0.08	0.06
Red. conditions	0.05	0.07	0.01	0.003	0.005	0.001

Although these experiments must be regarded as preliminary method trials, it is evident that significantly lower apparent leach rate values were achieved under reducing conditions.

It should be noted that for uranium, the ALR values for preleading under oxidizing conditions correspond to centrifugate concentrations of about 800 ppb or less, i.e., the solutions had attained saturation, while the values for reducing conditions represent results at the analytical detection limit and are probably too high.

## THERMODYNAMICAL MODELLING

### Background

As was discussed previously, the uranium concentrations in the groundwater leach solutions rapidly approached an apparent saturation at about 1-2 ppm ( $4-8 \cdot 10^{-6}$  mol/l) and stayed constant for contact times up to three years. Further more, acid rinses of the leach vessels as well as exposure of sample and cladding to low pH solutions gave no support to the assumption of large scale adsorption of uranium or actinides on the vessel wall and/or the fuel/clad surfaces.

Indeed, when the measured uranium concentrations are plotted against pH, the resulting diagram is strikingly similar to a solubility versus pH plot, as can be seen in Figure 7. This observation further supported the assumption that the uranium release is solubility controlled and an attempt was made to model the experimental results using available thermodynamical data and the SOLGASWATER code/8/. For comparison, attempts were also made to model the measured plutonium.

### Method

#### Assumptions

For the calculation, three different leach solutions have been considered, depending on the condition of the leach experiments, ie deionized water, synthetic groundwater, and synthetic groundwater with low pH, adjusted by adding the appropriate acid.

The initial  $UO_2(s)$  solid phase was assumed to be partly oxidized at the surface to some higher oxide phase. On spent fuel specimens, the oxidation state has not been determined, but  $U_3O_8(s)$  was chosen as a reasonable hypothesis.

No direct assessment of the oxidation state of the leach solutions was possible during the experiments. Based on the experimental conditions, they were therefore assumed to be in equilibrium with oxygen in air and the pE of the solutions was calculated under this hypothesis.

### The thermodynamic data base, uranium

The set of thermodynamic data used in the calculations is given in Table 1 in the Appendix. The constants regarding the solid phases mainly come from the critical compilations by Langmuir /9/ and Lemire and Tremaine /10/. The value used for the solubility constant is the one determined by Bruno et al /11/ for the solubility of  $UO_2(s)$  fuel pellets in 3.0M  $NaClO_4$  and extrapolated to zero ionic strength. The stability constants for  $U(VI)$ ,  $U(IV)/F^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$  have been taken from Sillén and Martell's /12/ and Högfeltdt's /13/ compilations and extrapolated to zero ionic strength. All extrapolations have been made using the SIT approach /14/. The constants for the uranium-carbonate system are mostly from Grenthe et al /15-18/. The data regarding uranium hydrolysis have mainly been taken from Baes and Mesmer /19/, although for  $U(OH)_5^-$ , the stability constant reported by Ryan and Rai /20/ has been chosen as it is believed to be a better alternative than previously proposed values.

### The thermodynamic data base, plutonium

The set of thermodynamic data used in the calculations is given in Table 2 in the Appendix. Most of the constants in the plutonium modelling come from the compilation by Lemire and Tremaine /10/. The plutonium hydrolysis constants have been taken from Baes and Mesmer /19/. Due to the lack of data, some of the  $Pu(IV)$  and  $Pu(VI)$  carbonate constants were assumed to be similar to those for  $U(VI)$  and  $U(VI)$ . The  $Pu(VI)$  nitrate stability constants were taken from Högfeltdt's compilation /13/. The solid phases were all taken from Lemire and Tremaine /10/. except in the case of  $PuO_2(s)$ , where the crystalline phase has been substituted with  $PuO_2 \cdot xH_2O$  (amorphous) according to Rai /21/. When extrapolations to zero ionic strength were needed, the SIT approach /14/ was used.

## Results

### Uranium

The results of the calculations are summarized in Table VII and also indicated in Figure 6.

The predicted solubilities in the acidic range show a good agreement with the experimentally measured concentrations at pH values higher than 4. The complex responsible for the solubility in the acidic range is mainly  $UO_2Cl^+$  when HCl was used for acidification, although the contributions of  $UO_2CO_3$  and  $UO_2Si(OH)_3^+$  are relevant. As the pH increases, the relative concentration of the carbonate complex (relative to the fluoride complex) gets larger, as would be expected.

In the case of the experiments carried out in deionized water, the predicted solubilities are 2-3 orders of

magnitude lower than the experimental ones. (The main contributors to the uranium solubility are naturally the hydrolysis complexes). However, the experimentally determined uranium concentrations are near or at the analytical detection limits and are often reported as "less than" values. Consequently, the reported uranium concentrations in deionized water are more to be seen as maximum limits than actually determined concentrations.

The modelling of the experiments carried out in synthetic groundwater at pH 8.1 is also in satisfactory agreement with the experimental measurements. Nevertheless, in this range the calculations are very sensitive to variations in both pE and "critical constants". The error stemming from the uncertainty in the definition of the oxidation state of the solutions accounts for a variation of approximately half a logarithmic unit in the calculated uranium solubilities. However, the most critical factor is the choice of solubility constant for  $UO_2(OH)_2(s)$ . This solid phase determines the uranium solubility in this pH range. Variations within the error limits reported in the literature ( $\pm 0.5$  in  $\log K_{SO}$ ) give rise to the uncertainty indicated in Table VII and Figure 6.

TABLE VII  
Uranium solubilities. Results of the calculations.

pH	pE	calc U TOT (mol/l)	exp U TOT (mol/l)
4.0	9.5	$1.5 \cdot 10^{-4}$	$5.3 \cdot 10^{-5}$
5.0	8.5	$2.7 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$
6.0	7.4	$7.7 \cdot 10^{-7}$	
		$4.5 \cdot 10^{-9}$ (DI)	
7.0	6.4	$3.6 \cdot 10^{-10}$ (DI)	$2 \cdot 10^{-7*}$ (DI)
8.1	5.3	$8.4 \cdot 10^{-6}$ $\begin{matrix} +1.2 \cdot 10^{-5} \\ -5 \cdot 10^{-6} \end{matrix}$	$4-8 \cdot 10^{-6}$

\* Near or at detection limit,  
(DI) Calculations, deionized water

## Lanthanides

For the lanthanides, exemplified by europium in the modelling, the agreement was not satisfactory between the calculated and measured concentrations in the acidic range. For pH 4.0 and 5.0 the measured concentration were considerably lower than the calculated solubilities. At pH 8.1 the measured concentrations were at or most often below the detection limit and no meaningful comparisons could be made. There may be several reasons for this disagreement, such as errors in the used thermodynamical data or in assigning proper solid phases. However, an alternative explanation can be deduced from the experimental observation that at low pH, the spent fuel matrix dissolves congruently and the release of these nuclides is therefore most likely controlled by the dissolution of the fuel matrix and the uranium solubility, rather than the solubility of the nuclide itself.

## Plutonium

The leach behaviour of plutonium for spent fuel is even more anomalous than that of uranium. As for uranium, an apparent solubility limit is rapidly reached, but as is evident from Figure 2, the equilibrium concentration appears to decrease with time.

Using available literature data, the modelling generally gave plutonium solubilities much lower than the measured values. However, the data base is very uncertain for many species and this could well account for the observed discrepancies. The most critical datum seems to be the solubility of the precipitating hydrolyzed plutonium oxide. It is reasonable to assume that initially the precipitating phase will be amorphous. Indeed, if the solubility for amorphous  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$  (amorphous) given by Rai /20/ was used, the fit between the calculated and measured concentrations improved considerably and gave quite satisfactory agreement as can be seen in Table VIII. The species responsible for the plutonium solubility are in the acidic range (pH 3-4)  $\text{Pu}^{3+}$  and  $\text{PuSO}_4^+$ . In the pH range 5-8.1,  $\text{Pu}(\text{OH})_4$  is the main responsible species. However, very little is known about Pu(IV) carbonate species, which might play an important role in this pH range.

TABLE VIII  
Plutonium solubilities. Results of calculations\*

pH	pE	calc	exp
		Pu TOT (mol/l)	Pu TOT (mol/l)
3.0	10.5	$7.9 \cdot 10^{-7}$	$6.4 \cdot 10^{-7**}$
3.5	10.0	$2.5 \cdot 10^{-9****}$ $2.5 \cdot 10^{-10}$	$3.5 \cdot 10^{-7}$
5.0		$1.7 \cdot 10^{-11}$	$7.5 \cdot 10^{-9***}$
8.1		$1.0 \cdot 10^{-11****}$	$4.9 \cdot 10^{-9}$

\* Solubilities calculated using  $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})/20/$ . When  $\text{PuO}_2(\text{cryst})$  was used, the solubilities were generally three orders of magnitude lower.

\*\* Interpolated value.

\*\*\* At pH 5, two numbers were below detection limit and have been neglected in calculating the average Pu-concentration.

\*\*\*\* Calculated assuming No  $\text{F}^-$ .

The long term decrease in Pu concentration in solution could then be explained by a slow crystallization of the  $\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ . It is known that the crystalline material has a lower solubility. The timescale for this type of aging is comparable to the experimental time scale (several years /22/.

#### LOW BURNUP FUEL. ALPHA RADIOLYS EXPERIMENT

The corrosion of spent fuel in deep groundwater, which is highly reducing, is expected to occur several orders of magnitude more slowly than under the oxidizing conditions employed in most leaching experiments. It has been postulated, however, that local oxidizing conditions, caused by alpha radiolytic decomposition of water, may be created in a thin aqueous film adjacent to the fuel surface, and that a continuous dissolution of the fuel matrix may nevertheless occur in this way.

In experiments where leaching of the high burnup BWR fuel was performed in the synthetic groundwater on which reducing conditions had been imposed by means of  $\text{H}_2/\text{Ar}$  bubbled over a

Pd catalyst suspended in the leaching vessel, the leaching rates were shown to be reduced by about a factor of 20 compared with oxidizing conditions. It is possible, of course, that these lower leaching rates represent fuel dissolution by the alpha radiolysis effect, and postulated conditions for this have been discussed in the context of calculations of the radiolysis induced by radiations from spent fuel /23/.

In the following section, results are presented from leaching tests on fuel irradiated to a low burnup, such that the actinide content, and hence the alpha particle dose to the leachant, was much lower than in the fuel considered previously in this paper.

### Experimental

A short fuel rod was irradiated for one reactor cycle (17 days) in the Studsvik R2 test reactor at a linear power of about 22 kW/m up to a burnup of about 0,5 MWd/kg U. After a few weeks cooling the fission product radioactive inventories were similar in size if not in isotope to those in the high burnup fuel, while the inventory of alpha emitters was much less. TABLE IX compares the inventories of the two fuels at their respective reference dates prior to leaching.

TABLE IX

Nuclide	Bq/gU	
	High burnup	Low burnup
Sr-89	-	4.06 E 09
Sr-90	2.46 E 09	-
Zr-95	-	3.84 E 09
Ru-103	-	2.79 E 09
Ru-106	1.31 E 09	-
Cs-137	4.43 E 09	5.13 E 07
Ba-140	-	2.11 E 09
Ce-141	-	5.12 E 09
Ce-144	2.02 E 09	1.53 E 09
Nd-147	-	6.48 E 08
Eu-154	2.14 E 08	-
Pu-239/240	3.38 E 07	5.33 E 05
Pu-238/Am-241	1.52 E 08	-
Cm-242	6.76 E 07	-
Cm-244	1.52 E 08	-

14 segments of fuel/clad (20 mm long) were cut out from the rod and exposed to the synthetic groundwater (pH 8.1) for 3 weeks under oxidizing conditions as a pre-leach to remove

the cesium instant release fraction and to dissolve up any uranium oxidized by the cutting procedure. The leachants were analyzed by the standard procedure. The fuel specimens were then transferred to 14 new leaching flasks where 6 of them, in pairs, were leached again under oxidizing conditions for periods of 2, 4 and 8 weeks. The remaining 8 specimens were leached, under the reducing conditions described above, for the same periods.

## RESULTS

The results are summarized in TABLES VII and VIII

TABLE X  
Uranium concentrations in centrifugates (ppb)

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

\* Pre-leach

TABLE XI  
Comparison of ALR values under oxidizing and reducing conditions

		ALR (FIAP/d) ( $\times 10^6$ )			
Contact time (d)	22	15	28	55	
Oxidizing conditions					
U	5.1	3.9	3.7	2.5	
Cs-137	23.6	6.8	4.9	3.9	
Sr-89	5.2	5.6	4.1	2.6	
I-131	4.1	4.1	4.1	2.6	
Ba-140	3.9	4.4	2.7	1.4	
Pu	1.0	1.0	1.0	1.0	
Reducing conditions					
U		0.04	0.03	0.04	
Cs-137		1.6	0.8	0.7	
Sr-89		0.36	0.24	0.21	
I-131		1.7	ND	ND	
Ba-140		0.53	0.39	0.22	
Pu		0.05	0.02	0.07	

Inspection of the results leads to the following conclusions:

- a) The measured U concentrations under oxidizing conditions were much higher than expected and even after 55 days had probably not attained saturation.
- b) Cs, Sr, I and Ba appeared to dissolve congruently with the UO<sub>2</sub> matrix, while Pu and the lanthanides (not reported here) showed lower values of leach rate.
- c) Although there are some differences between nuclides, and depending on whether the values for centrifugate concentration or FIAP are used, the decreases in leaching rates for leaching under reducing conditions were of the same order as those obtained with the high burnup fuel.

It seems unlikely that the presence (or absence) of alpha radiolytical effects can be advanced as the cause of these observations. The explanation is probably to be found in differences in microstructure and stoichiometry between the high burnup and low burnup fuel types.

#### CONCLUSIONS

- 1 The results from the Swedish program on sequential and static leaching of high burnup BWR fuel extended to 3 year contact times is in general in agreement with the earlier results from the program and with those of other workers.
- 2 Calculated uranium solubilities agree well with the measured ones for synthetic groundwater over the pH range 4-8.5. However, the limited validity of the calculation must be recognized.
- 3 Although with the high burnup fuel, uranium saturation in the groundwater (pH 8.1) appears to be attained at a level of 1-2 mg/l, there is some evidence that this level can be raised if the fuel is air-stored for prolonged periods prior to leaching.
- 4 For high burnup fuel, congruent dissolution was attained at pH values lower than 4.
- 5 Experiments designed to test the hypotheses that the Sr-90 leach rate represents the dissolution of the fuel matrix, and that the concentrations of the actinides and lanthanides are much lower due to solubility limitations gave indecisive results. SEM and EPMA examination of fuel before and after leaching will probably be needed to give pertinent data.

- 6 No evidence that alpha radiolytic decomposition of leachant is a significant factor for fuel leaching was obtained in a comparison of leaching rates under oxidizing and reducing conditions of two fuel types which gave alpha doses to be leachant differing by a factor of about 1000.
- 7 Differences in leaching behaviour between these two fuel types may be due to differences in fuel morphology and stoichiometry.

#### ACKNOWLEDGEMENTS

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Uranium  
concentration  
(ppb)

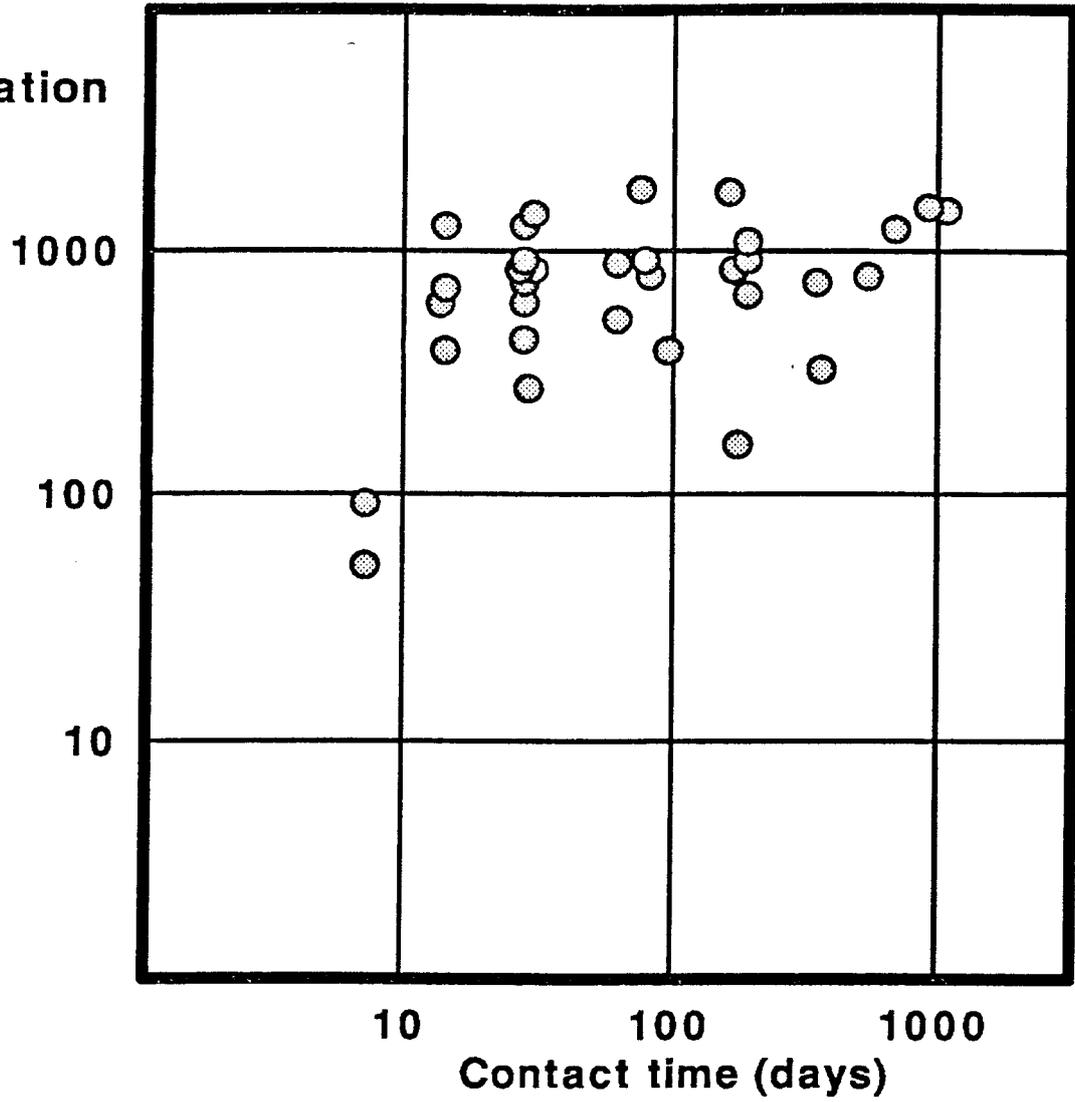


Figure 1 Measured concentrations of uranium in leach solution centrifugates as a function of time

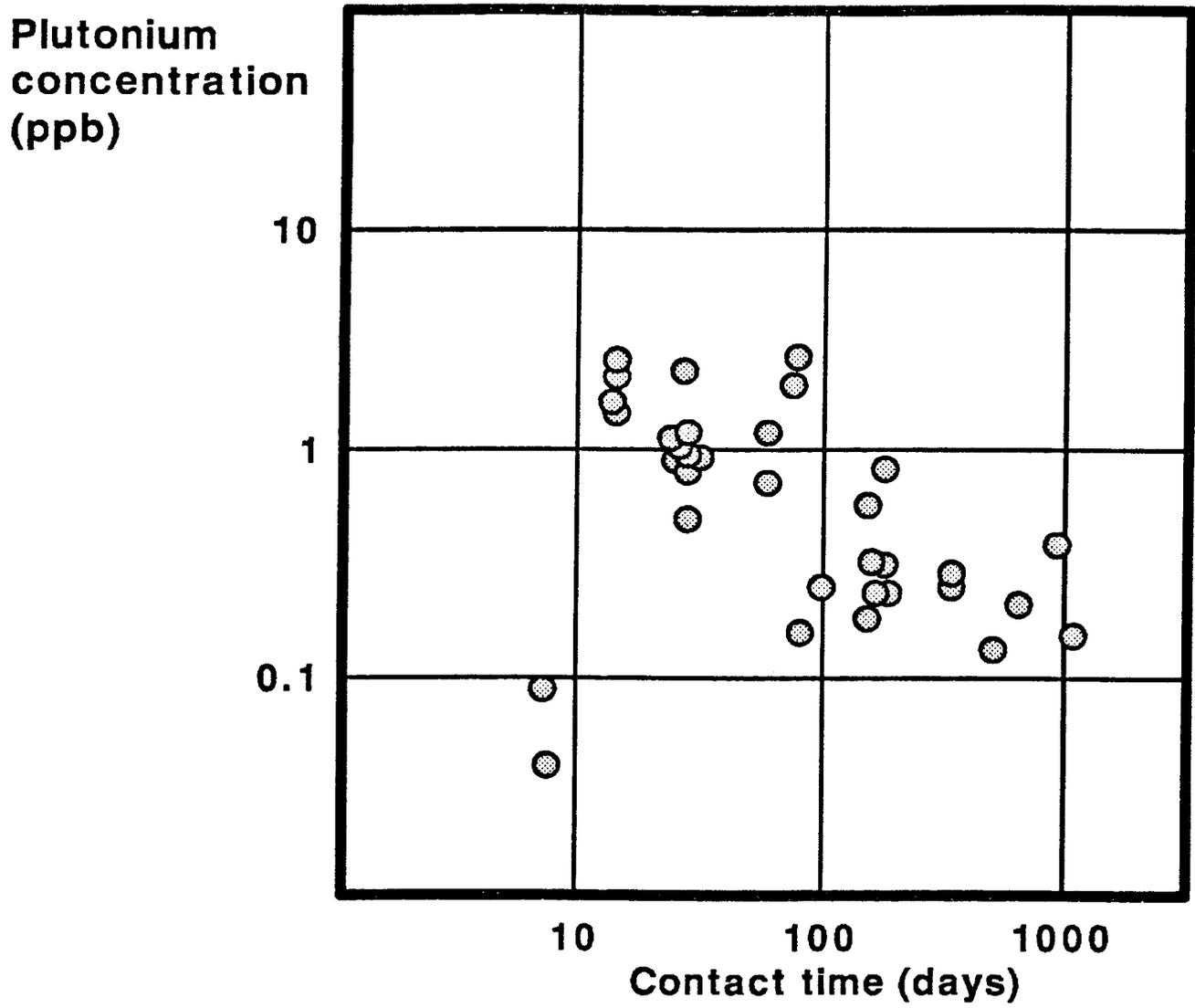


Figure 2 Measured concentrations of plutonium in leach solution centrifugates as a function of time

Cumulative  
FIAP ( $\times 10^6$ )

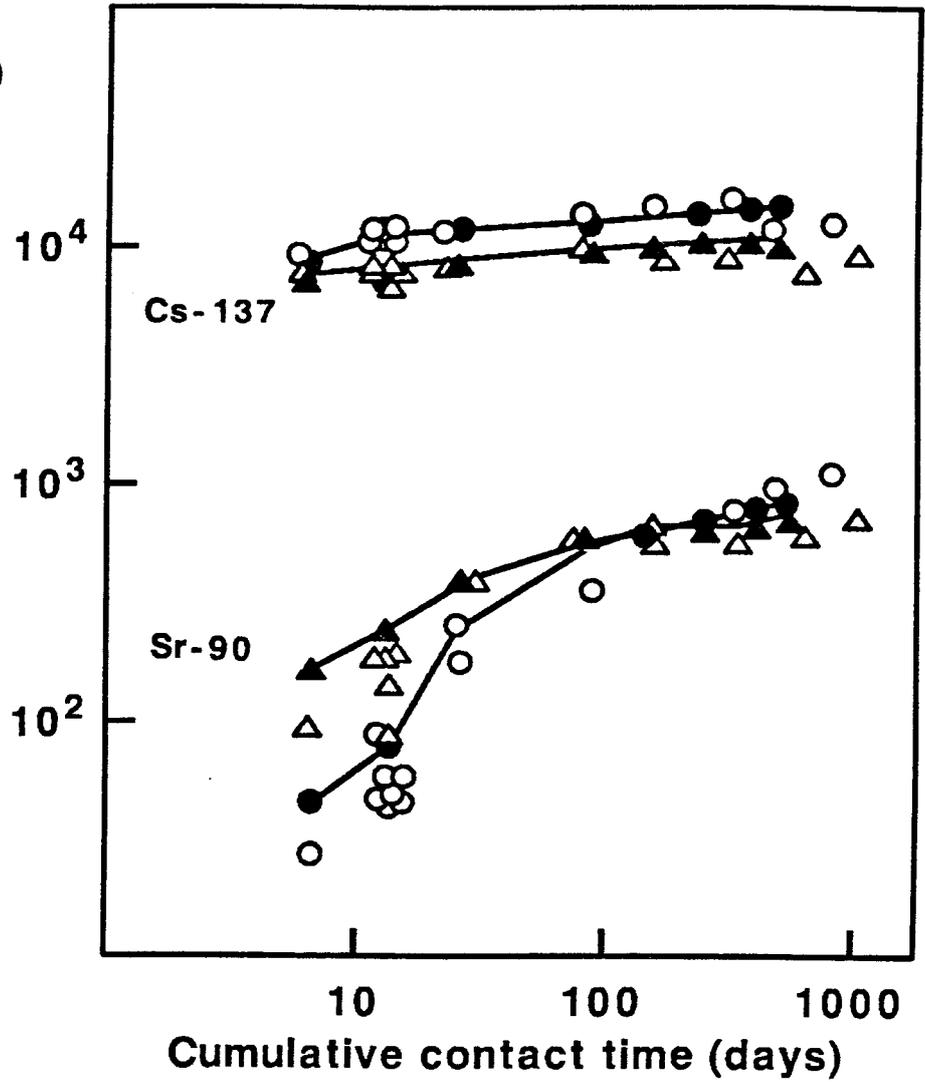


Figure 3 Comparison of results from sequential and static leaching in groundwater (p. H 8.0-8.2)

- ▲ 3.2 - series
- △ 3.5 - "
- 3.3 - "
- 3.4 - "

Apparent  
leach rate  
(FIAP / d)

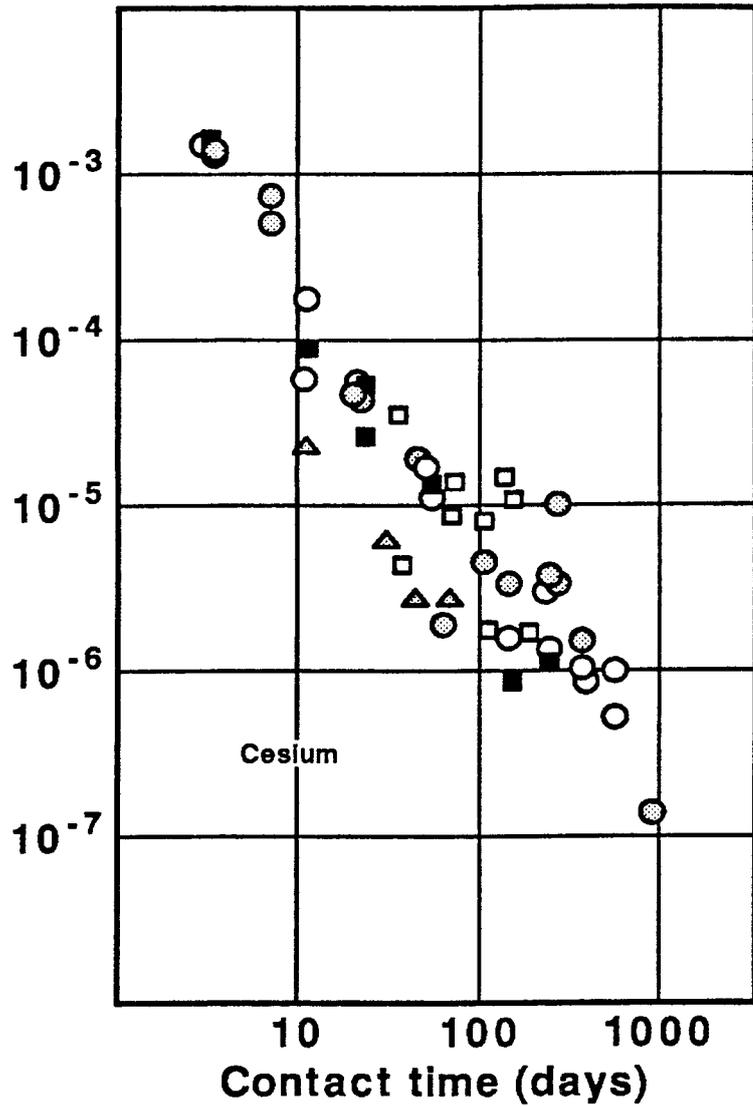


Figure 4 Values of Apparent Leach Rate for Cs-137 as a function of contact time (chronological midpoint of contact period)

<b>High burnup fuel:</b>	
○	Sequential leach
■	Sequential leach (DIW)
●	Static leach
□	Replenishment expt.
<b>Low burnup fuel:</b>	
△	Static leach

Apparent  
leach rate  
(FIAP / d)

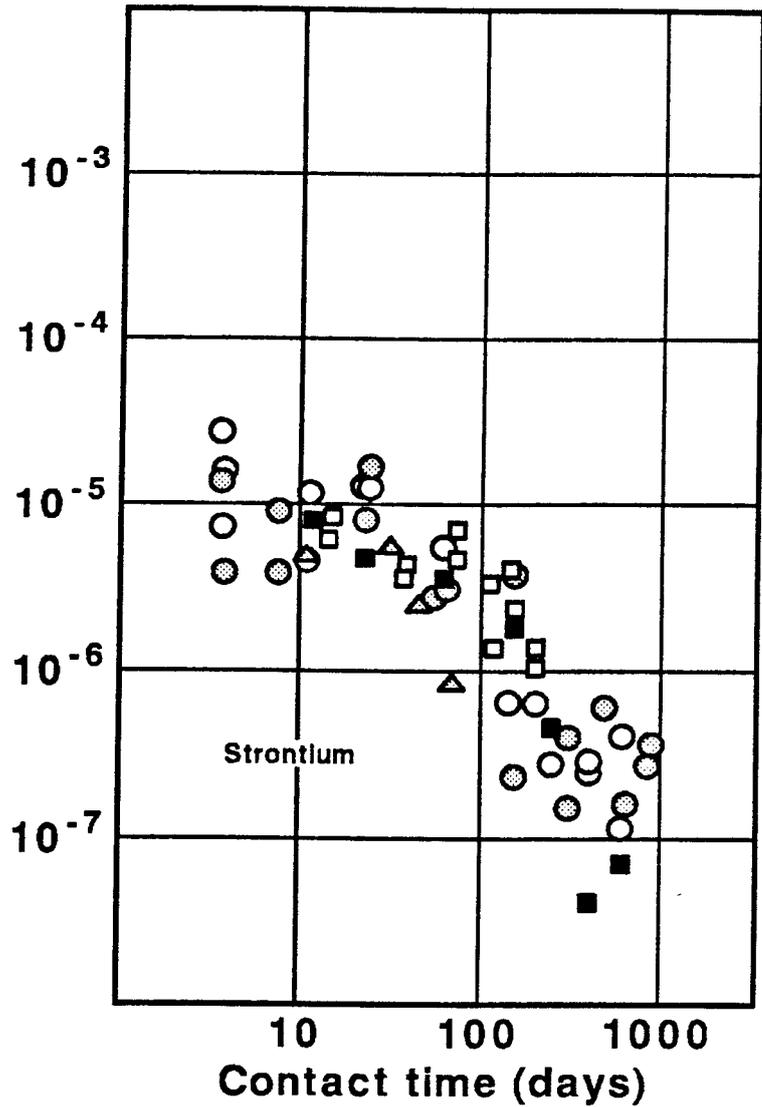


Figure 5 Values of Apparent Leach Rate for Sr-90 as a function of contact time (chronological midpoint of contact period)

High burnup fuel:

- Sequential leach
- Sequential leach (DIW)
- Static leach
- Replenishment expt.

Low burnup fuel:

- △ Static leach

Fraction of inventory in aqueous phase

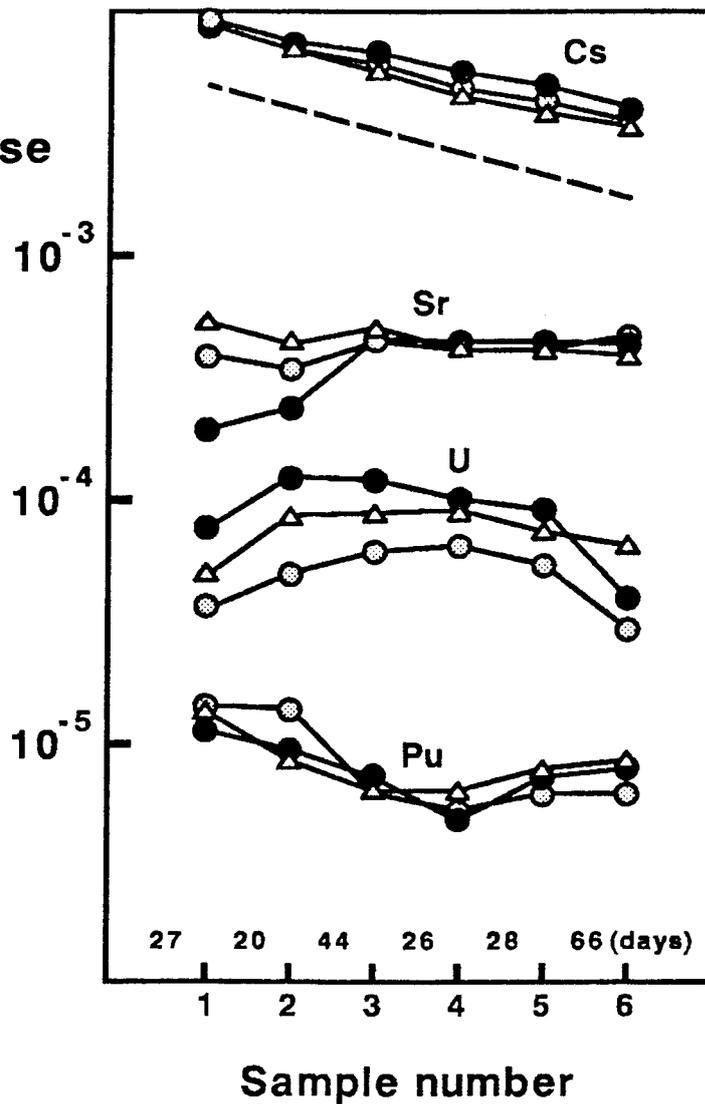


Figure 6 Replenishment experiments: Variation of leach fraction with successive replenishment

- Fuel segments
- ⊙ Fuel fragments >4 mm
- △ Fuel fragments 2-4 mm

Uranium  
concentration  
(ppm)

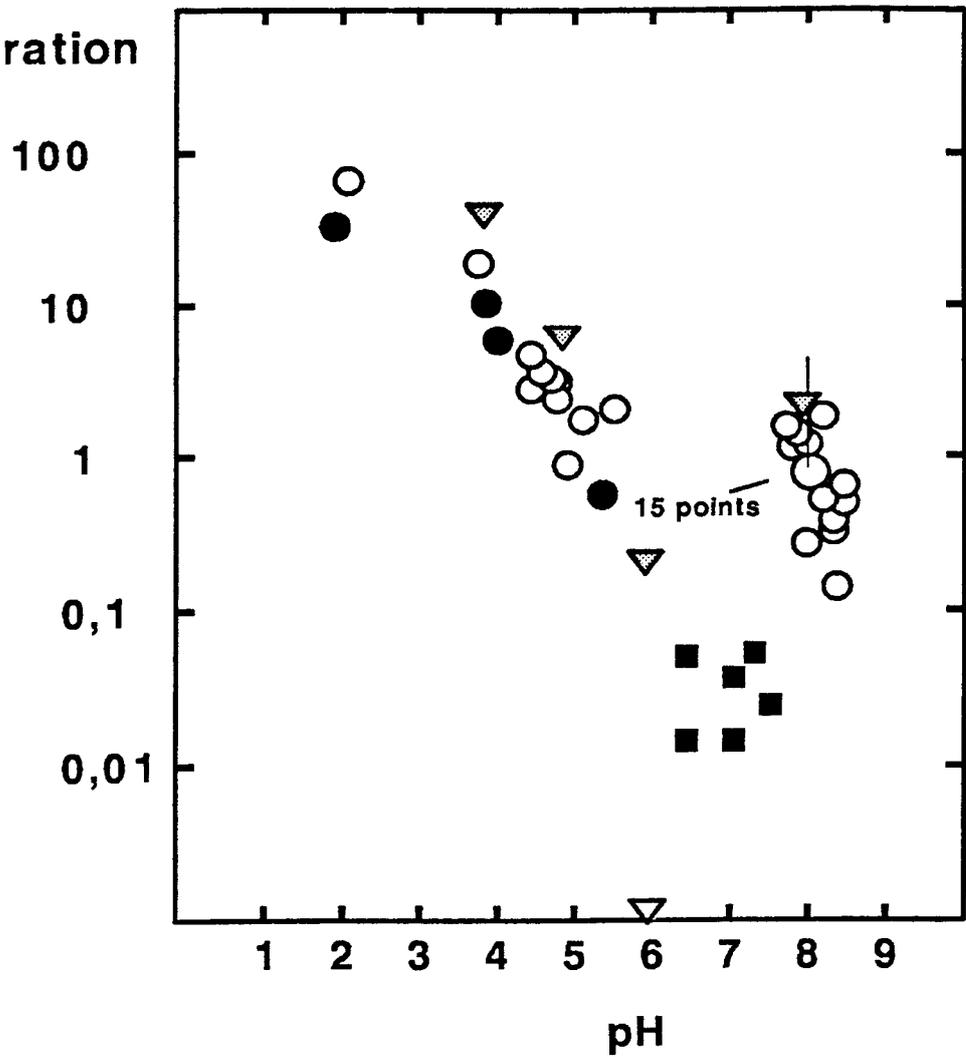


Figure 7 Measured concentrations of uranium at different pH.

- In the acidic range, 91 days exposure. At pH 8.2 14 days to 3 years
- 20 days exposure
- Exposure in DI-water
- ▼ Calculated solubilities for synthetic groundwater
- ▽ Calculated solubility for DI-water

APPENDIX

10, 38, 7, 1

e-  
H+  
CO3 2-  
F-  
HPO4 -  
Cl-  
SO4 2-  
NO3 -  
H4SiO4  
U3O8(s)

TABLE 1. Thermodynamic data base for the uranium-synthetic groundwater system. The input consists of a list of the components chosen and then the species present followed by the stability constants plus the related stoichiometric coefficients. The solid phases are given after the soluble complexes.

OH-	-14.000	0.00	-1.00	0.00	0.00	0.00	0.00
O2(g)	-84.486	-4.00	-4.00	0.00	0.00	0.00	0.00
HCO3 -	10.200	0.00	1.00	1.00	0.00	0.00	0.00
H2CO3	16.500	0.00	2.00	1.00	0.00	0.00	0.00
H2PO4 -	6.700	0.00	1.00	0.00	0.00	1.00	0.00
PO4 3-	-12.400	0.00	-1.00	0.00	0.00	1.00	0.00
H5O4 -	1.980	0.00	1.00	0.00	0.00	0.00	0.00
H2SO4	-9.300	1.00	0.00	0.00	0.00	0.00	0.00
H3SiO4 -	-9.460	0.00	-1.00	0.00	0.00	0.00	0.00
U4+	11.433	1.33	5.33	0.00	0.00	0.00	0.00
UOH 3+	10.533	1.33	4.33	0.00	0.00	0.00	0.00
U(OH)5 -	-10.967	0.00	0.00	0.00	0.00	0.00	0.00
U(CO3)5 6-	51.033	1.33	5.33	5.00	0.00	0.00	0.00
UMPO4 2+	23.533	1.33	5.33	0.00	0.00	1.00	0.00
U(HPO4)2	33.533	1.33	5.33	0.00	0.00	2.00	0.00
U(HPO4)3 2-	43.533	1.33	5.33	0.00	0.00	3.00	0.00
U(HPO4)4 4-	50.533	1.33	5.33	0.00	0.00	4.00	0.00
UC1 3+	14.533	1.33	5.33	0.00	0.00	0.00	1.00
USO4 2+	17.533	1.33	5.33	0.00	0.00	0.00	0.00
U(SO4)2	21.533	1.33	5.33	0.00	0.00	4.00	0.00
UF 3+	20.533	1.33	5.33	0.00	1.00	0.00	0.00
UF2 2+	25.533	1.33	5.33	0.00	2.00	0.00	0.00
UO2OH +	-3.367	-0.67	0.33	0.00	0.00	0.00	0.00

(UO2)2(OH)2	-0.433	-1.33	0.67	0.00	0.00	0.00	0.00
(UO2)3(OH)5	-12.710	-2.00	-1.00	0.00	0.00	0.00	0.00
UO2CO3	11.933	0.00	0.00	0.00	1.00	0.00	0.00
UO2(CO3)2 2-	19.033	-0.67	1.33	2.00	0.00	0.00	0.00
UO2(CO3)3 4-	23.833	0.00	0.00	0.00	0.33	0.00	0.00
(UO2)3(CO3)6	60.800	-0.67	1.33	3.00	0.00	0.00	0.00
UO2(CO3)3 5-	19.863	0.00	0.00	0.00	0.33	0.00	0.00
UO2F +	7.533	0.33	1.33	3.00	0.00	0.00	0.00
UO2HPO4	12.633	-0.67	1.33	0.00	1.00	0.00	0.00
UO2Cl +	4.433	0.00	0.00	0.00	0.33	0.00	1.00
UO2SO4	5.733	-0.67	1.33	0.00	0.00	0.00	0.00
UO2(SO4)2 2-	7.533	1.00	0.00	0.00	0.33	0.00	0.00
UO2NO3 +	3.253	-0.67	1.33	0.00	0.00	0.00	0.00
UO2SiO(OH) +	1.153	0.00	1.00	0.00	0.33	0.00	0.00
UO2 2+	2.000	-0.67	0.33	0.00	0.00	0.00	0.00
UF4(s)	35.833	0.00	0.00	0.00	0.33	0.00	0.00
U(HPO4)2(s)	38.633	1.33	5.33	0.00	0.00	2.00	0.00
UO2(OH)2(s)	-1.400	0.00	0.00	0.00	0.33	0.00	0.00
UO2CO3(s)	17.133	-0.67	-0.67	0.00	0.00	0.00	0.00
UO2HPO4(s)	25.833	0.00	0.00	0.00	0.33	0.00	0.00
(UO2)3(PO4)2	32.200	-0.67	1.33	1.00	0.00	0.00	0.00
UO2(s)	14.033	0.00	0.00	0.00	0.33	0.00	0.00

9, 44, 8, 1

e-  
H+  
CO3 2-  
F-  
Cl-  
HPO4 2-  
SO4 2-  
NO3 -  
PuO2(s)

TABLE 2. Thermodynamic data base for the plutonium-synthetic groundwater system. The input has the same meaning as in Table 1.

OH -	-14.000	0.00	-1.00	0.00	0.00	0.00	0.00
HCO3 -	10.200	0.00	1.00	1.00	0.00	0.00	0.00
H2CO3	16.500	0.00	0.00	0.00	0.00	0.00	0.00
O2(g)	-84.486	-4.00	-4.00	0.00	0.00	0.00	0.00
Pu 4+	-0.900	0.00	4.00	0.00	0.00	0.00	0.00
PuOH 3+	-1.300	0.00	0.00	1.00	0.00	0.00	0.00
Pu(OH)4	-11.000	0.00	0.00	0.00	0.00	0.00	0.00
Pu(CO3)5 6-	38.000	0.00	4.00	5.00	0.00	0.00	0.00
PuCl 3+	0.100	0.00	4.00	0.00	0.00	1.00	0.00
PuF 3+	7.200	0.00	4.00	0.00	1.00	0.00	0.00
PuSO4 2+	5.200	0.00	4.00	0.00	0.00	0.00	0.00
Pu(SO4)2 +	2.200	1.00	0.00	1.00	0.00	0.00	0.00
PuHPO4 2+	11.200	2.00	0.00	1.00	0.00	0.00	1.00
Pu(HPO4)2 -	23.200	0.00	4.00	0.00	0.00	0.00	2.00
Pu(HPO4)3 4-	32.200	0.00	0.00	1.00	0.00	0.00	3.00
Pu(HPO4)4 6-	42.200	0.00	4.00	0.00	0.00	0.00	4.00
PuNO3 3+	0.800	0.00	0.00	1.00	0.00	0.00	0.00
Pu(NO3)2 +	1.900	0.00	1.00	1.00	0.00	0.00	0.00
PuO2 +	-19.800	0.00	4.00	0.00	0.00	0.00	0.00
PuO2(OH)	-29.500	-1.00	0.00	1.00	0.00	0.00	0.00
PuO2(CO3)3 5-	-6.900	-1.00	-1.00	0.00	0.00	0.00	0.00
PuO2 2+	-36.000	0.00	0.00	1.00	0.00	0.00	0.00
PuO2(OH) +	-41.600	-2.00	0.00	0.00	0.00	0.00	0.00
(PuO2)2(OH)2	-80.400	0.00	-1.00	0.00	0.00	0.00	0.00
		0.00	0.00	2.00	0.00	0.00	0.00

(PuO2)3(OH)5	-129.650	-6.00	-5.00	0.00	0.00	0.00	0.00
PuO2CO3	-27.400	0.00	0.00	3.00	0.00	0.00	0.00
PuO2(CO3)3	-12.200	-2.00	0.00	1.00	0.00	0.00	0.00
PuO2F +	-30.400	0.00	0.00	1.00	0.00	0.00	0.00
PuO2F2	-25.000	-2.00	0.00	0.00	1.00	0.00	0.00
PuO2F3 -	-20.100	0.00	0.00	0.00	2.00	0.00	0.00
PuO2F4 2-	-17.200	-2.00	0.00	0.00	3.00	0.00	0.00
PuO2H2PO4	-25.000	0.00	0.00	1.00	4.00	0.00	0.00
PuO2SO4	-27.300	-2.00	1.00	0.00	0.00	0.00	0.00
PuO2Cl +	-36.300	0.00	0.00	0.00	0.00	1.00	0.00
Pu 3+	16.300	0.00	0.00	1.00	0.00	0.00	0.00
PuOH 2+	8.300	1.00	4.00	0.00	0.00	0.00	0.00
Pu(OH)3	-10.700	0.00	0.00	1.00	0.00	0.00	0.00
PuHCO3 2+	14.500	1.00	1.00	0.00	0.00	0.00	0.00
PuCO3 +	9.900	0.00	5.00	1.00	0.00	0.00	0.00
Pu(CO3)2 -	27.300	1.00	0.00	1.00	0.00	0.00	0.00
Pu(CO3)3 3-	28.600	0.00	4.00	2.00	0.00	0.00	0.00
Pu(CO3)4 5-	30.800	1.00	0.00	1.00	0.00	0.00	0.00
PuH2PO4 2+	25.900	0.00	4.00	3.00	0.00	0.00	0.00
PuSO4 +	19.700	1.00	0.00	1.00	0.00	0.00	0.00
PuO2OH(s)	-25.200	1.00	5.00	0.00	0.00	0.00	0.00
PuO2CO3(s)	-22.900	-1.00	0.00	0.00	0.00	0.00	0.00
Pu(OH)3(s)	-6.700	0.00	-1.00	0.00	0.00	0.00	0.00
Pu2(CO3)3(s)	31.120	0.00	0.00	1.00	0.00	0.00	0.00
PuF4(s)	12.200	2.00	8.00	3.00	0.00	0.00	0.00
PuO2HPO4(s)	-23.000	0.00	0.00	2.00	4.00	0.00	0.00
Pu(HPO4)2(s)	27.200	0.00	4.00	0.00	0.00	0.00	1.00
PuF3(s)	26.200	0.00	0.00	1.00	0.00	0.00	2.00
		1.00	4.00	0.00	3.00	0.00	0.00
		0.00	0.00	1.00	0.00	0.00	0.00

# List of Technical Reports

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TR 121

**KBS Technical Reports 1 – 120.**

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TR 79-28

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TR 82-28

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TR 85-02

**The Taavinunnanen gabbro massif.**

**A compilation of results from geological, geophysical and hydrogeological investigations.**

Bengt Gentszsch

Eva-Lena Tullborg

Swedish Geological Company

Uppsala, January 1985

TR 85-03

**Porosities and diffusivities of some non-sorbing species in crystalline rocks.**

Kristina Skagius

Ivars Neretnieks

The Royal Institute of Technology

Department of Chemical Engineering

Stockholm, 1985-02-07

TR 85-04

**The chemical coherence of natural spent fuel at the Oklo nuclear reactors.**

David B. Curtis

New Mexico, USA, March 1985

TR 85-05

**Diffusivity measurements and electrical resistivity measurements in rock samples under mechanical stress.**

Kristina Skagius

Ivars Neretnieks

The Royal Institute of Technology

Department of Chemical Engineering

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TR 85-06

**Mechanical properties of granitic rocks from Gideå, Sweden**

Christer Ljunggren

Ove Stephansson

Ove Alm

Hossein Hakami

Ulf Mattila

Div of Rock Mechanics

University of Luleå

Luleå, Sweden, October 1985

TR 85-07

**Complex forming properties of natural occurring fulvic acids  
Part 1. Complexes with cadmium, copper and calcium**

Jacob A. Marinsky,

A. Mathuthu,

M. Bicking and

J. Ephraim

State University of New York at Buffalo

Buffalo, New York 14214,

July 1985

TR 85-08

**In situ one-year burial experiments with simulated nuclear waste glasses**

Larry L Hench, Derek Spilman and T Buonaquisti

College of Engineering, Univ. of Florida, Gainesville, USA

Alexander Lodding

Chalmers Univ. of Technology, Gothenburg, Sweden

Lars Werme

SKB, Stockholm, Sweden

TR 85-09

**Concentration and distribution of natural radionuclides at Klipperåsen and Bjulebo, Sweden**

Björn Sundblad, Ove Landström, Rune Axelsson  
Studsvik Energiteknik AB, Nyköping, Sweden

TR 85-10

**Chemical interactions between the bentonite and the natural solutions from the granite near a repository for spent nuclear fuel**

Bertrand Fritz and Marie Kam

Université Louis Pasteur de Strasbourg, Institut de Géologie, France

July 1985

TR 85-11

**Hydrochemical investigations in crystalline bedrock in relation to existing hydraulic conditions: Experience from the SKB test-sites in Sweden**

John Smellie, Nils-Åke Larsson

Swedish Geological Company, Uppsala, Sweden

Peter Wikberg

Royal Institute of Technology, Stockholm Sweden

Leif Carlsson

Swedish Geological Company, Göteborg, Sweden

November 1985

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**Hydrogeological investigations and tracer tests in a well-defined rock mass in the Stripa mine**

Peter Andersson

Carl-Erik Klockars

Swedish Geological Company

Division of Engineering Geology

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TR 85-13

**Analysis of hydrodynamic dispersion in discrete fracture networks using the method of moments**

Anders Rasmuson

Dep of Chemical Engineering, Royal Inst of Technology Stockholm

June 20, 1985

TR 85-14

**Radionuclide migration in strongly fissured zones—The sensitivity to some assumptions and parameters**

Anders Rasmuson, Ivars Neretnieks

Dep of Chemical Engineering, Royal Inst of Technology Stockholm

August 7, 1985

TR 85-15

**Diffusion measurements of cesium and strontium in biotite gneiss**

Kristina Skagius, Ivars Neretnieks

Dep of Chemical Engineering, Royal Inst of Technology Stockholm

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