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Corrosion tests on spent PWR fuel in
synthetic groundwater

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CORROSION TESTS ON SPENT PWR FUEL IN SYNTHETIC
GROUNDWATER

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

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ABSTRACT

Short fuel/clad segments from a high burnup PWR fuel rod have been exposed to simulated groundwater under both oxidizing and reducing conditions. Two methods of establishing reducing conditions were employed: by using H_2 gas in the presence of Pd catalyst, and by circulating the groundwater over rock-cores from a deep borehole.

The results from the first two contact periods of 82 and 172 days are in good agreement with those obtained previously on a high burnup BWR fuel rod. In particular, it was found that under oxidizing conditions, uranium saturates at about the 1 mg/l level, and plutonium at about the 1 μ g/l level.

Under reducing conditions, these solubilities decreased by about two orders of magnitude.

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1. INTRODUCTION

The joint SKB/STUDSVIK experimental program to study the corrosion of spent fuel in granitic groundwater is now in its sixth year. The experiments, which are performed in Studsvik Energitekniks' Hot Cell Laboratory, have so far been mainly applied to fuel specimens from a high burnup BWR fuel rod (max. pellet fuel burnup 42 MWd/kg U), although some experiments have also been performed on low burnup fuel (ca 0.5 MWd/kg U) to examine the possible influence of alpha radiolysis on UO_2 dissolution rates. The results of these experiments have been published earlier (1, 2, 3, 4).

Concurrently with continued experiments on the BWR fuel, extending the integrated contact times in groundwater, experiments have been in progress since early 1986 on fuel from a PWR fuel rod with about the same burnup. This report presents the first results from these experiments.

2. SPENT FUEL SOURCE MATERIAL

The rod selected for the experimental program was peripheral rod B15 in assembly D07 (Rod manufacturers' number 03688). This assembly had been irradiated for 5 cycles in the Ringhals 2 PWR between 1977 and 1983, up to a calculated assembly burnup of 41.3 MWd/kg U. The last day of irradiation was 28th April 1983. Since the first corrosion experiments commenced on 19th March 1986, the cooling time prior to ground-water contact was about 3 years.

On arrival at the Hot Cell Laboratory, the fuel rod was subjected to a series of non-destructive examinations as part of an extensive characterization program to define the fuel rod and fuel parameters necessary to evaluate the results obtained during the corrosion tests. The results from the first part of the characterization program are now published (5).

Fig 1 shows the axial gamma scan of the rod, using Cs-137 as the monitored nuclide. The curve thus represents the axial burnup distribution, which is shown to be uniform (with minima at spacer positions) over a large part of the rod.

The sampling plan for this phase of the experimental program is also shown in Fig 1. Following completion of the non-destructive part of the rod characterization program, a metre-long rod section was cut out and sampled as shown. The remaining sections of the rod were stored in sealed cans to minimise oxidation during storage, which has previously been suspected to lead to enhanced uranium dissolution (4).

For the corrosion tests described in this report, 14 fuel/clad segments, about 18 mm long, were dry-cut from the test section, and weighed. Two 10 mm long segments were also cut out for burnup and inventory determination.

The uranium content of each fuel/clad segment was established by calculating the contribution of the Zircaloy-4 clad to the segment weight. This was checked by weighing the clad remaining after dissolution of the fuel in the inventory samples.

In the previous experiments on BWR fuel (1, 2, 3, 4), in addition to fuel/clad segments of about the same size as described above, even selected fuel fragments have been exposed to groundwater. The use of fuel fragments has the advantage that only fuel pellet surfaces fractured during reactor operation are available for corrosive attack, while for fuel/clad segments, local surface oxidation during the cutting operation may give enhanced dissolution. However, in this report, experiments on fuel/clad segments of the PWR fuel serve as useful comparisons with the earlier BWR work.

3. EXPERIMENTAL

3.1 General procedure

As in previous experiments, each fuel/clad specimen was suspended in a platinum wire spiral in 200 ml of leachant in a 250 ml Pyrex flask. All tests were performed at 20-25°C, the ambient hot-cell temperature. After completion of each contact period (the results of two such contact periods are reported here) the specimen was transferred to a new flask and exposed to new 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 empty flask, after a rapid rinse with deionized water, was exposed for a few days to 200 ml of 5M HNO₃/0.5M HF to desorb any activity on the vessel walls.

Centrifugate, membrane filter and vessel rinse solution were then analysed for uranium, Sr-90, gamma-emitting fission products, and alpha-emitting nuclides (alpha spectrometry without separation).

All experiments were performed in a synthetic groundwater with the initial composition shown in Table 1.

Table 1. Groundwater composition

| Species | ppm |
|--------------------|-----|
| HCO_3^- | 123 |
| SiO_2 | 12 |
| SO_4^{2-} | 9.6 |
| Cl^- | 70 |
| Ca^{2+} | 18 |
| Mg^{2+} | 4.3 |
| K^+ | 3.9 |
| Na^+ | 65 |

pH: 8.0-8.2, ionic strength: 0.0085

3.2 Oxidizing and reducing conditions

On the basis of thermodynamic data, the solubility of UO_2 is predicted to be several orders of magnitude lower in highly-reduced deep granitic groundwater (E_H range: - 200-300 mV) than under surface (oxidizing) conditions. Such reducing conditions, however, are difficult to establish, maintain and measure in a hot-cell environment. In the BWR fuel test series, a number of experiments were performed where spent fuel specimens were contacted with the synthetic groundwater which had been reduced by means of hydrogen gas in the presence of a Pd catalyst electrodeposited on Pt mesh. Significant decreases in the concentrations of leached species were obtained compared with oxidizing conditions. However, this method for establishing reducing conditions has the disadvantage that the leachant is saturated with hydrogen,

which may depress solubilities compared with the real groundwater case, for example by preventing possible surface oxidation by alpha radiolysis of the solution.

In the PWR fuel experimental series, in addition to experiments performed under oxidizing conditions, and under reducing conditions imposed by means of H_2/Pd as above, experiments were carried out where the fuel was contacted with the synthetic groundwater reduced under more realistic conditions. Fig 2 shows the system used.

In a closed glass system, placed in a flowing nitrogen glove-box, the groundwater was circulated continuously, by means of an internal pump, over rock cores from one of SKB's deep granite test bore-holes. The gradual decrease in E_H was followed by means of Au and Pt electrodes with a Ag/AgCl reference electrode.

As shown in Fig 3, reduction was slow, extending over 2-3 months, before an acceptably low value of E_H was attained. This value, for these first experiments, was arbitrarily decided to be about -100 mV.

It is apparent from the shape of the curves shown in Fig 3, and the levelling out at about E_H -100 mV, that the system had both larger intermittent and smaller continuous leaks. This was found difficult to avoid, however, in a system of this type, with joints and valves to facilitate repair, and to permit groundwater transfer through the cell wall to the leaching vessels.

Transfer of reduced groundwater was effected by means of the in-cell manifold shown in Fig 3.

The manifold, and the leaching vessels with the fuel/clad specimens in place, were evacuated, flushed with pure nitrogen, and re-evacuated. After closing the evacuated leaching vessels, reduced groundwater was drawn into the calibrated volumes (200 ml) above each vessel. By opening the vessel valves, these 200 ml groundwater batches were drawn into the vessels and contacted the fuel.

After groundwater transfer, the vessels were disconnected from the manifold, and placed under water in stainless steel cans in order to prevent or minimise in-leakage of air.

In this stage of the program, where 14 fuel/clad specimens are examined in parallel to allow an assessment to be made of experiment reproducibility, E_H has not been measured in the leaching vessels after transfer. This will be performed later in the program when selected fuel fragments are contacted with groundwater reduced in situ in specially designed and instrumented vessels.

For the present experiments, however, all that can be stated regarding the E_H after transfer, is that it is almost certainly higher than -100 mV.

The situation is similar for the H_2/Pd experiments where no leachant transfer is involved: tests performed out-of-cell without spent fuel, showed that an E_H of about -300 mV could be readily attained and maintained for periods of weeks or months. However, as will be discussed later, it is apparent that 2 of the 4 tests performed failed to maintain this low value over the whole contact period.

The experimental parameters for the experiments so far are summarized in Table 2.

Table 2. Experimental parameters

| 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 |

1st contact: 82 d

2nd contact: 172 d

3.3 Membrane filter tests

As mentioned above in Section 3.1, the experimental and analytical procedures applied after each completed period of contact between fuel and groundwater are directed in principle towards establishing the distribution of each species of interest between a) true solution (centrifugate) b) particulate and colloidal material (membrane filter) and c) material adsorbed on the vessel walls.

In practice, in the case of the results from the BWR fuel experiments, it has been shown (4) that no such clear distinctions can be made. The amounts of materials recovered in the vessel rinse solutions showed no correlation with contact time or other experimental parameters, and their composition strongly indicated that they consisted of small fuel particles. This is hardly surprising since the spent fuel specimens are highly cracked, contain fines from the cutting operation, and are in direct contact with the leachant.

Analytical results on the materials on the membrane filters from the BWR tests showed a somewhat different pattern: compared with their ratios in the spent fuel itself, Cs-134, Cs-137, Sr-90 and Sb-125 gave much higher ratios, and the amounts on the filters could be correlated with the amounts in the centrifugate. For the rare-earth fission products and the actinides, however, the ratios to uranium were about the same as in the spent fuel but showed appreciable scatter because of the very low levels involved.

In order to further examine this problem, 5 leachant solutions from the PWR fuel tests, 2 from the first 82 d contact time, and 3 from the 172 d contact time, were subjected to 3 consecutive centrifugations through new membrane filters. For each test, the final centrifugate and the 3 membrane filters were analyzed according to the normal procedure.

4. RESULTS AND DISCUSSION

At this early stage of the experimental program on the PWR fuel, the available measurement data are somewhat limited and hence only a few items of key interest will be addressed in this report.

4.1 Material distribution

As discussed above in Section 3.3, three fractions are analyzed after each leaching experiment: centrifugate, membrane filter and vessel rinse. An understanding of the nature of these fractions is essential for a correct interpretation of the measurement results.

The problem can be illustrated by means of the measurement data, presented in Tables 3 and 4 respectively, from two experiments, one under oxidizing conditions, and one under reducing conditions (H_2/Pd). Each of these data sets is roughly representative for their respective groups (7.1.1 - 7.6.1 and 7.13.1 - 7.14.1).

The first point to bear in mind is that, with the exception of Cs-137 and Sr-90, the uranium weights and activity levels measured are low and therefore associated with appreciable measurement uncertainty. Contamination of samples in hot-cell or fume-hood can cause problems.

Inspection of the data in the tables, again with the exception of the Cs-137 and Sr-90 results, shows:

- a) that the levels in the centrifugates reflect the expected differences between corrosion in oxidizing and reducing environments

Table 3 EXPT 7.4.1
 Oxidizing conditions
 82 d contact: 200 ml

| | Centrifugate | Membrane | Vessel Rinse |
|----------------|--------------|----------|--------------|
| U (micrograms) | 234 | 30 | 100 |
| Cs-137 (Bq) | 2.9 E8 | 7.2 E6 | 1.3 E6 |
| Sr-90 | 1.2 E7 | 8.0 E5 | 2.8 E5 |
| Ru-106 | ND | 8.1 E3 | 5.0 E4 |
| Sb-125 | 1.1 E5 | 2.6 E3 | ND |
| Ce-144 | ND | 1.3 E4 | 1.5 E5 |
| Eu-154 | 1.8 E4 | 1.3 E4 | 1.5 E4 |
| Pu-239/240 | 1.2 E3 | ND | 5.0 E3 |
| Pu-238/Am-241 | 7.8 E3 | 2.9 E3 | 2.1 E4 |
| Cm-244 | 2.7 E3 | 5.4 E3 | 1.6 E4 |

Table 4 EXPT 7.14.1
 Reducing conditions: H₂/Pd
 82 d contact: 200 ml

| | Centrifugate | Membrane | Vessel Rinse |
|----------------|--------------|----------|--------------|
| U (micrograms) | <0.3 | 9 | 126 |
| Cs-137 (Bq) | 4.2 E8 | 3.5 E7 | 2.5 E5 |
| Sr-90 | 1.1 E6 | 1.9 E5 | 3.9 E5 |
| Ru-106 | ND | ND | 1.0 E5 |
| Sb-125 | ND | ND | ND |
| Ce-144 | ND | 2.6 E3 | 2.5 E5 |
| Eu-154 | ND | ND | 3.1 E4 |
| Pu-239/240 | ND | 1.9 E2 | 7.5 E3 |
| Pu-238/Am-241 | 4.0 E1 | 6.5 E2 | 3.0 E4 |
| Cm-244 | ND | 6.6 E2 | 2.6 E4 |

- b) that the levels measured in the vessel rinse solutions represent a large or even dominant part of the total uranium or activities recovered.
- c) that the levels in both membrane filter and vessel rinse fractions are roughly proportional to the U contents.
- d) that the sums of all three fractions, centrifugate, membrane filters and vessel rinse, for the two experiments are very similar. If such a summation was used as an expression of total loss from the fuel specimen, it could be concluded that congruent dissolution had occurred and that all material removed from the fuel was distributed between leachant and vessel walls.

The observation under c) can be more clearly illustrated if the fraction of total specimen inventory for each species is normalised to the corresponding inventory fraction for uranium. (Table 5) Values close to unity would then suggest a composition equivalent to that of the spent fuel itself.

Table 5. Fractions of inventory normalised to U

| | Vessel Rinse | | Membrane Filter | |
|---------------|--------------|--------|-----------------|--------|
| | 7.4.1 | 7.14.1 | 7.4.1 | 7.14.1 |
| U | 1.0 | 1.0 | 1.0 | 1.0 |
| Cs-137 | 3.0 | 4.7 | 55 | 894 |
| Sr-90 | 0.8 | 0.9 | 7.9 | 6.3 |
| Ru-106 | 0.3 | 0.4 | 0.2 | ND |
| Sb-125 | ND | ND | 0.8 | ND |
| Ce-144 | 0.9 | 1.2 | 0.3 | 0.2 |
| Eu-154 | 0.7 | 1.1 | 2.0 | ND |
| Pu-239/240 | 1.5 | 1.8 | ND | 0.7 |
| Pu-238/Am-241 | 1.0 | 1.2 | 0.5 | 0.4 |
| Cm-244 | 1.0 | 1.3 | 1.1 | 0.5 |

This appears to be the case for the vessel rinse results. The high values for Cs-137 are probably due to incomplete removal of the leachant from the vessel prior to the rinse, while the slightly high values for Pu-239/-240 probably represent a positive bias in its alpha spectrometric determination (low peak on high-energy tail). The cause of the low Ru-106 values is tentatively assigned to the non-dissolution of noble metal particles in the fuel (Mo, Tc, Ru, Rh, Pd).

The hypothesis that the vessel rinse solutions represent dissolved fuel particles is supported by the fact that the amounts of uranium recovered in the 14 rinse solutions from the first 82 day contact period were in the hundreds of microgram range (but with a spread from 40 microgram to 12 milligram) while those from the second 172 day period were one or two orders of magnitude lower. No significant variation in rinse solution composition as a function of experimental conditions (oxidizing or reducing or contact time) could be noted.

Table 6 presents values of the mean of all fractions of inventory normalised to uranium.

Table 6 Vessel rinse solutions: first and second contact period.
Mean values of fractions of inventory normalised to uranium.

| | Mean | Std.Dev. |
|---------------|------|----------|
| U | 1.0 | - |
| Sr-90 | 0.90 | 0.16 |
| Ru-106 | 0.41 | 0.10 |
| Sb-125 | ND | - |
| Ce-144 | 1.07 | 0.22 |
| Eu-154 | 1.26 | 0.38 |
| Pu-239/240 | 1.69 | 0.42 |
| Pu-238/Am-241 | 1.03 | 0.22 |
| Cm-244 | 1.30 | 0.40 |

For the membrane filter results, the values show considerably more scatter, probably due to the very low amounts of material analyzed. For many of the samples, uranium analysis by NAA only gave limit values because of high counting background levels, and this, of course, prevents comparison with spent fuel inventories. The result of the membrane filter tests involving multiple centrifugation gave some confirmation for the main experimental results, but, again, uranium levels were at the detection limit preventing inventory comparison. Thus, it cannot yet be established with reasonable certainty whether the retained material on the membranes is spent fuel particles, colloidal material or a combination of both. Further work is planned, including SEM examination of selected membranes.

4.2 Uranium concentrations: oxidizing conditions

In the main series of experiments on BWR fuel, it was found that the uranium in solution (centrifugate) appeared to saturate in the synthetic groundwater under oxidizing conditions at about 1 mg/l (mean of all results: 950 ppb \pm 435). This is a result of some significance for the safety analysis for a final repository for spent fuel, and one of the aims of the PWR fuel program was to check this finding on another fuel type (and vendor). The results for the PWR fuel specimens are presented in Table 7 and it can be seen at once that they represent a satisfactory confirmation of the previous results. The results are also presented in Fig 4. together with the BWR fuel results.

Table 7. Uranium concentrations: Oxidizing conditions

| Con- tact (d) | Uranium concentration (ppb) | | | | | | Mean | Std. Dev. |
|---------------------|-----------------------------|------|------|------|------|------|------|--------------|
| | 7.1 | 7.2 | 7.3 | 7.4 | 7.5 | 7.6 | | |
| 82 | 845 | 1215 | 1005 | 1170 | 1395 | 1555 | 1198 | 234 |
| 172 | 1050 | 900 | 650 | 800 | 900 | 1000 | 883 | 131 |

4.3 Plutonium concentrations: oxidizing conditions

For the BWR fuel, an initial plutonium solubility of a few ppb was found, which decreased by about an order of magnitude when the contact times were longer than about a year. Hence, it can be noted the plutonium/uranium ratios in the centrifugates under oxidizing conditions were always less than that in the spent fuel itself. The plutonium concentration results for the PWR fuel experiments are presented in Table 8 and plotted together with the BWR fuel results in Fig 5. Again, good agreement is demonstrated.

Table 8. Plutonium concentrations: oxidizing conditions

| | | Plutonium concentration (ppb) | | | | | | | |
|----------|------|-------------------------------|------|------|------|------|------|------|--|
| Con- | 7.1 | 7.2 | 7.3 | 7.4 | 7.5 | 7.3 | Mean | Std | |
| tact (d) | | | | | | | | Dev. | |
| 82 | 1.32 | 1.77 | 2.07 | 1.77 | 1.92 | 2.22 | 1.85 | 0.28 | |
| 172 | 0.69 | 0.59 | 0.56 | 0.38 | 0.56 | 0.43 | 0.54 | 0.10 | |

4.4 Cs-137: oxidizing conditions

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 1.06×10^{-2} . (5). Hence, the Cs-137 release during leaching should approach this value.

All results on Cs-137, including the multiple centrifugation tests (see section 3.3) have indicated that about 3 % of the total Cs-137 in the aqueous phase is retained on the membrane filter at each centrifugation, indicating an adsorption effect. Thus, for Cs-137, the combined fractional releases in centrifugate and membrane filter, are used as a measure of release in the following. (FIAP - Fractional Release in the Aqueous Phase).

In the 6 PWR experiments under oxidizing conditions, the mean FIAP during the first 82 day contact period was 7.7×10^{-3} , with an apparent difference of about 10 % between specimens from the two parts of the fuel column sampled. (See Fig 1.)

In the BWR experiments substantial differences in Cs-137 release behaviour were noted between different parts of the rod (4), 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 5.8×10^{-4} , giving a mean cumulative FIAP value of 8.29×10^{-3} for a cumulative contact time of 254 days.

The individual results are plotted together with the corresponding values for the sequential leach tests on specimens from the two rod parts of the BWR fuel rod in Fig 6. The PWR values are seen to be somewhat lower.

4.5 Sr-90: oxidizing conditions

For Sr-90, all results show that about 7 % of the total Sr-90 in the aqueous phase, under oxidizing conditions, is adsorbed on the membrane filter at each centrifugation. Under reducing conditions a somewhat larger percentage is retained. Thus, as for Cs-137, FIAP values for Sr-90 are used in the following.

The mean FIAP for the first 82 day contact for the six experiments was $4.01 \cdot 10^{-4}$, again with the same apparent difference between specimens as observed for the Cs-137 results.

For the second 172 day contact, the mean FIAP was $1.18 \cdot 10^{-4}$, giving a cumulative 254 day value of $5.19 \cdot 10^{-4}$. The individual results are presented in Fig 7 together with the corresponding BWR results as comparison.

4.6 Actinides: reducing conditions

In this section, the results for uranium, plutonium and curium will be presented together in order to aid comparison.

The centrifugate concentrations for uranium and plutonium for the 8 tests performed under reducing conditions are presented in Tables 9 and 10 respectively, together with the mean values for the tests under oxidizing conditions reported above.

Table 9. Uranium concentrations in centrifugates (ppb)

| CONTACT | MEAN | ROCK CORES/GW | | | | | | H ₂ /Pd/GW | |
|---------|---------|---------------|-----|------|------|------|------|-----------------------|-------|
| | | 7.7 | 7.8 | 7.9. | 7.10 | 7.11 | 7.12 | 7.13 | 7.14 |
| (d) | OXIDIZ. | | | | | | | | |
| 82 | 1198 | 605 | 485 | 450 | 400 | 525 | 840 | < 1.5 | < 1.5 |
| 172 | 883 | 400 | 160 | 50 | 10 | 15 | 1130 | 800 | 500 |

Table 10. Plutonium concentrations in centrifugates (ppb)

| CONTACT | MEAN | ROCK CORES/GW | | | | | | H ₂ /Pd/GW | |
|---------|---------|---------------|-------|-------|-------|-------|-------|-----------------------|-------|
| | | 7.7 | 7.8 | 7.9 | 7.10 | 7.11 | 7.12 | 7.13 | 7.14 |
| (d) | OXIDIZ. | | | | | | | | |
| 82 | 1.85 | 0.21 | 0.070 | 0.008 | 0.011 | 0.005 | 0.77 | 0.005 | 0.009 |
| 172 | 0.54 | 0.44 | 0.013 | 0.010 | 0.065 | 0.007 | 0.006 | 0.014 | 0.010 |

For the 6 experiments using rock-core reduced groundwater, only a minor decrease in uranium concentrations was obtained during the first contact period, while the second contact gave much lower values. Experiments 7.7 and 7.12, however, the two flasks located at the ends of the manifold during filling, showed the highest values in both cases, suggesting leakage.

In contrast, low plutonium concentrations were obtained during both contact periods, again with the exception of experiments 7.7 and 7.12.

This non-correlation between uranium and plutonium concentrations is shown particularly clearly in the results from the experiments in H₂/Pd reduced groundwater, where in the first contact period, the uranium concentrations were below the detection limit (1.5 ppb), while, probably due to leakage, relatively high values were obtained in the second. In spite of this, plutonium concentrations in all 4 experiments were at the same level.

It was noted above in section 4.3, that the Pu/U ratios in the centrifugates from the experiments under oxidizing conditions were less than the ratio in the fuel. (With some reservations, since the ratio is not constant over the fuel radius, and selective corrosive attack in the central part of the fuel pellets could give the same effect. There is, however, no evidence for such selective attack).

Now, from the results from the experiments when U dissolution or solubility is repressed under reducing conditions, it is seen that the Pu/U ratio decreases abruptly with small changes in U concentration. To illustrate this, the fractional

releases (centrifugates) for Pu for the complete PWR experimental series are plotted against the corresponding values for U in Fig. 8.

Fig 9 presents the correlation for uranium and curium release fractions. (Note that no results are plotted for the first H₂/Pd experiments - uranium release fraction < 3 10E-8 - since Cm-244 was not detected. The detection limit, however, should correspond to a fractional release for curium of the order of 10E-9).

Although the results show not-unexpected scatter, the two figures show reasonably good correlation. For both Pu and Cm, it can be seen that at an E_H (unmeasured) corresponding to a U release fraction of 10E-5 (in these experiments, this is equivalent to a U molarity of about 2 10E-6M), the fractional release has already decreased to a value of about 10E-8. (Pu 2 10E-11M: Cm 1.2 10E-13M).

The experimental data indicates no further change within the range of E_H values (unmeasured) in this experiment series. Only at the lowest value of E_H (-300 mV?) is congruence displayed between the three species at a release fraction of about 10E-8.

4.7 Cs-137: reducing conditions

As stated in section 4.4, a mean Cs-137 fractional release (FIAP) of 7.7 10E-3 was obtained for the first contact period of the experiments under oxidizing conditions. The corresponding values for the experiments using groundwater reduced by rock-cores and H₂/Pd were higher: 8.7 10E-3 and 1.15 10E-2 respectively. This is probably due to differences in experimental procedure during initial contact between fuel and groundwater. In

the case of the rock-core reduced water, the fuel/clad gap was evacuated, facilitating ground-water ingress, while in the H₂/Pd experiments, hydrogen was bubbled through the water for a prolonged period with the fuel specimen in place.

Even in the second contact period, the Cs-137 FIAP values were about the same for all experiments, indicating that at this stage of leaching, cesium release is essentially independent of UO₂ matrix attack.

4.8 Sr-90: reducing conditions

In these experiments, under both oxidizing and reducing conditions, the fractional release of Sr-90 was always larger than the corresponding value for uranium. This was also observed in the experiments on BWR fuel (4) and can be attributed to attack and preferential dissolution of strontium-rich segregations in the fuel.

The data available so far from the PWR fuel experiments, however, also confirms the finding in the BWR series, that the Sr-90 release fraction decreases under reducing conditions, even though the effect is relatively small.

Relative to the release under oxidizing conditions at the same point of time, it corresponds to a decrease of about an order of magnitude at the lowest values of E_H used (H₂/Pd/GW).

5. CONCLUSIONS

The experiments on the PWR fuel/clad segments are still in progress, and later data may modify or contradict the detailed observations presented above.

However, the data so far available confirm the findings in the earlier BWR fuel experiments. In particular, it was found that under oxidizing conditions uranium solubility levelled out at about the same value, 1 mg/l, as was observed with the BWR fuel. Plutonium solubilities were also virtually identical. The release behaviours of Cs-137 and Sr-90 were similar to the BWR series, but were somewhat lower.

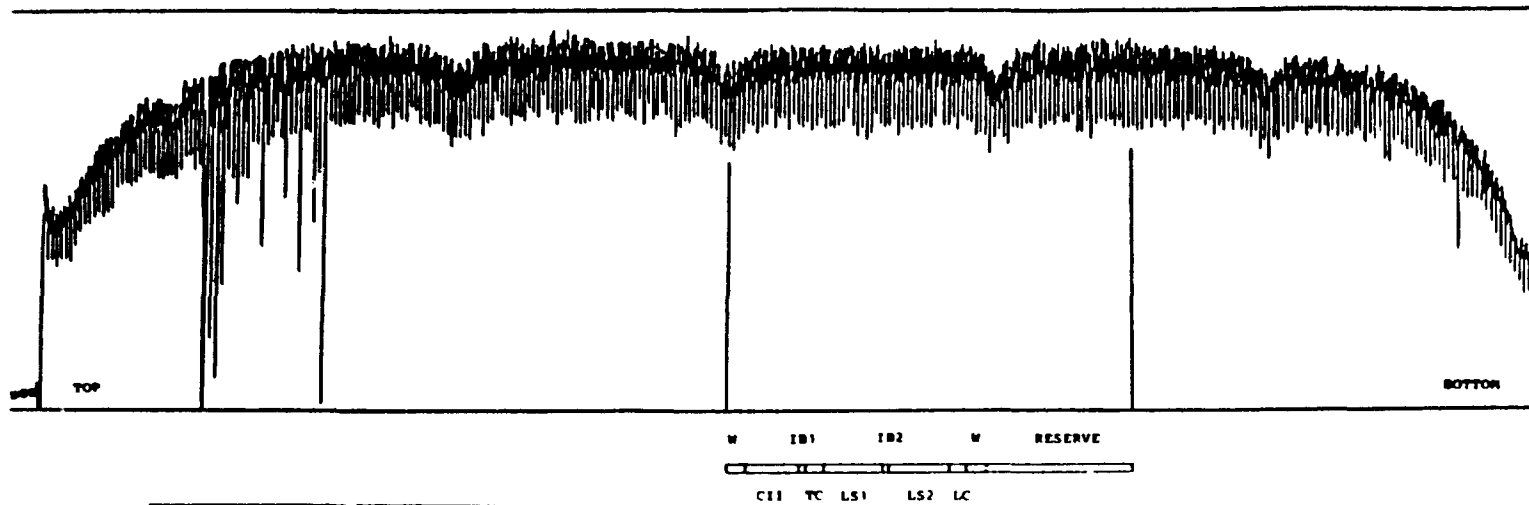
Simulated groundwater reduced under realistic conditions, by circulating over rock cores from a deep bore-hole, was shown to be effective in reducing the solubilities of uranium, plutonium and curium.

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| SPECIMEN | INVESTIGATION |
|----------|--|
| IB1 | INVENTORY DETERMINATION |
| IB2 | " |
| TC | CERAMOGRAPHY: TRANSVERSE SECTION MICRO GAMMASCAN, AUTORADIOGRAPHY |
| LC | CERAMOGRAPHY: LONGITUDINAL SECTION MICRO GAMMASCAN, AUTORADIOGRAPHY |
| C11 | INSPECTION OF CLAD INNERWALL |
| LS1 | LEACH TESTS |
| LS2 | " |
| W | WASTE |

| LS1 | | LS2 | |
|----------|-----------------------|----------|-----------------------|
| SPECIMEN | WT. FUEL AND CLAD (g) | SPECIMEN | WT. FUEL AND CLAD (g) |
| 7.1 | 14.9069 | 7.2 | 14.7221 |
| 7.3 | 14.4891 | 7.4 | 14.8794 |
| 7.5 | 14.5245 | 7.6 | 14.5715 |
| 7.7 | 14.4721 | 7.8 | 14.4752 |
| 7.9 | 14.7204 | 7.10 | 14.6158 |
| 7.11 | 14.7354 | 7.12 | 14.6063 |
| 7.13 | 13.8901 | 7.14 | 14.0633 |

Fig 1. Axial gamma scan of fuel rod and sampling plan.

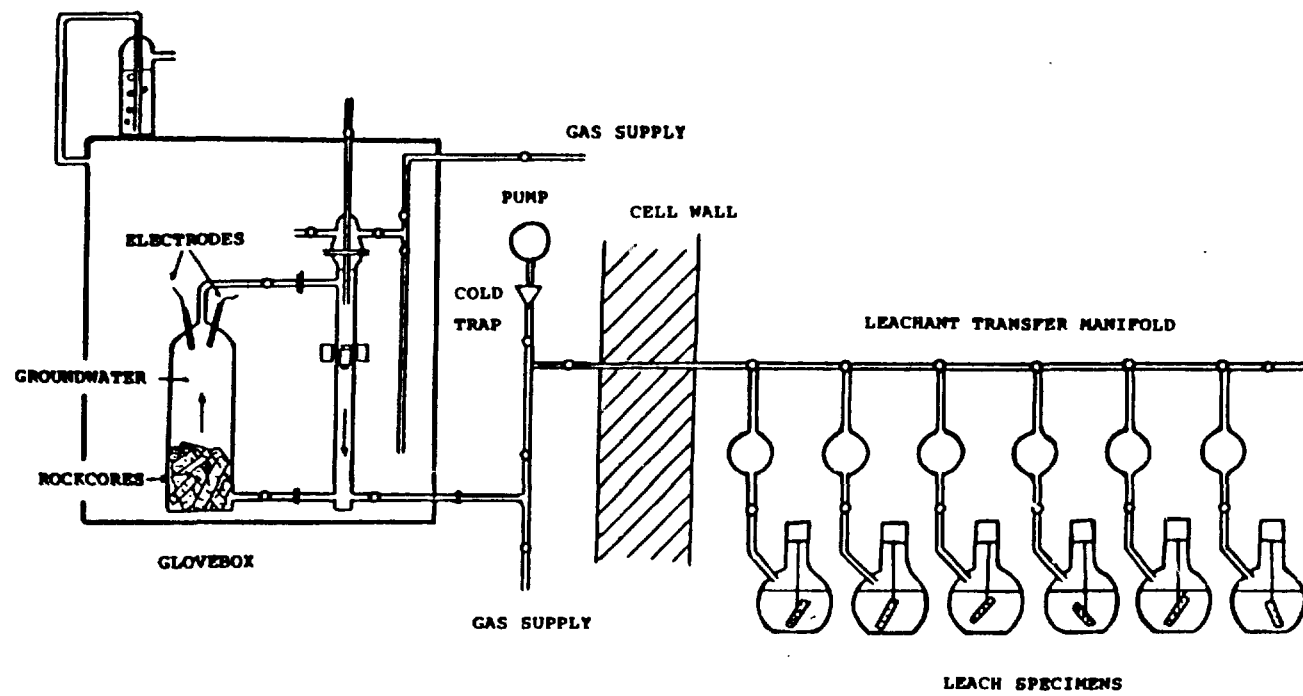


Fig 2. Apparatus for reduction and transfer of groundwater.

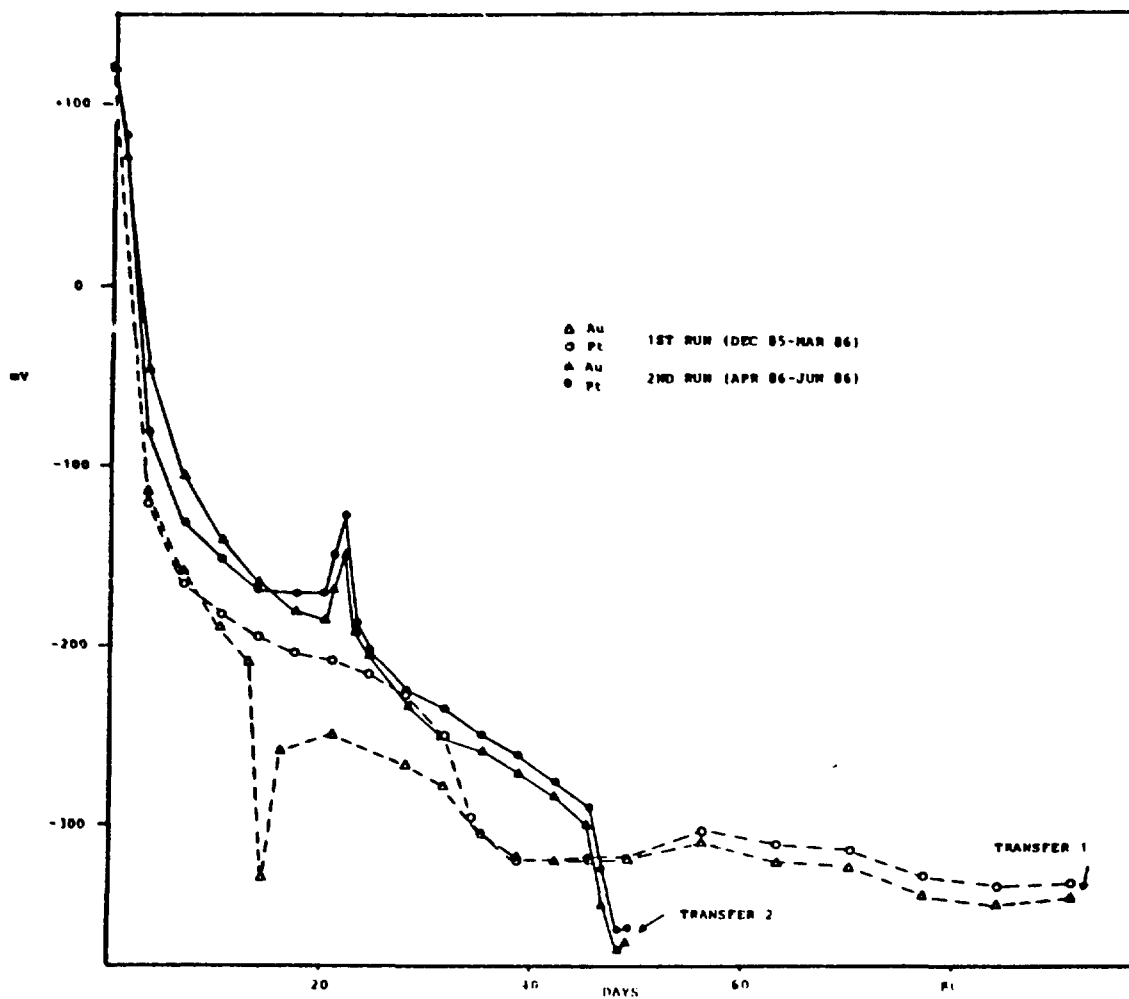
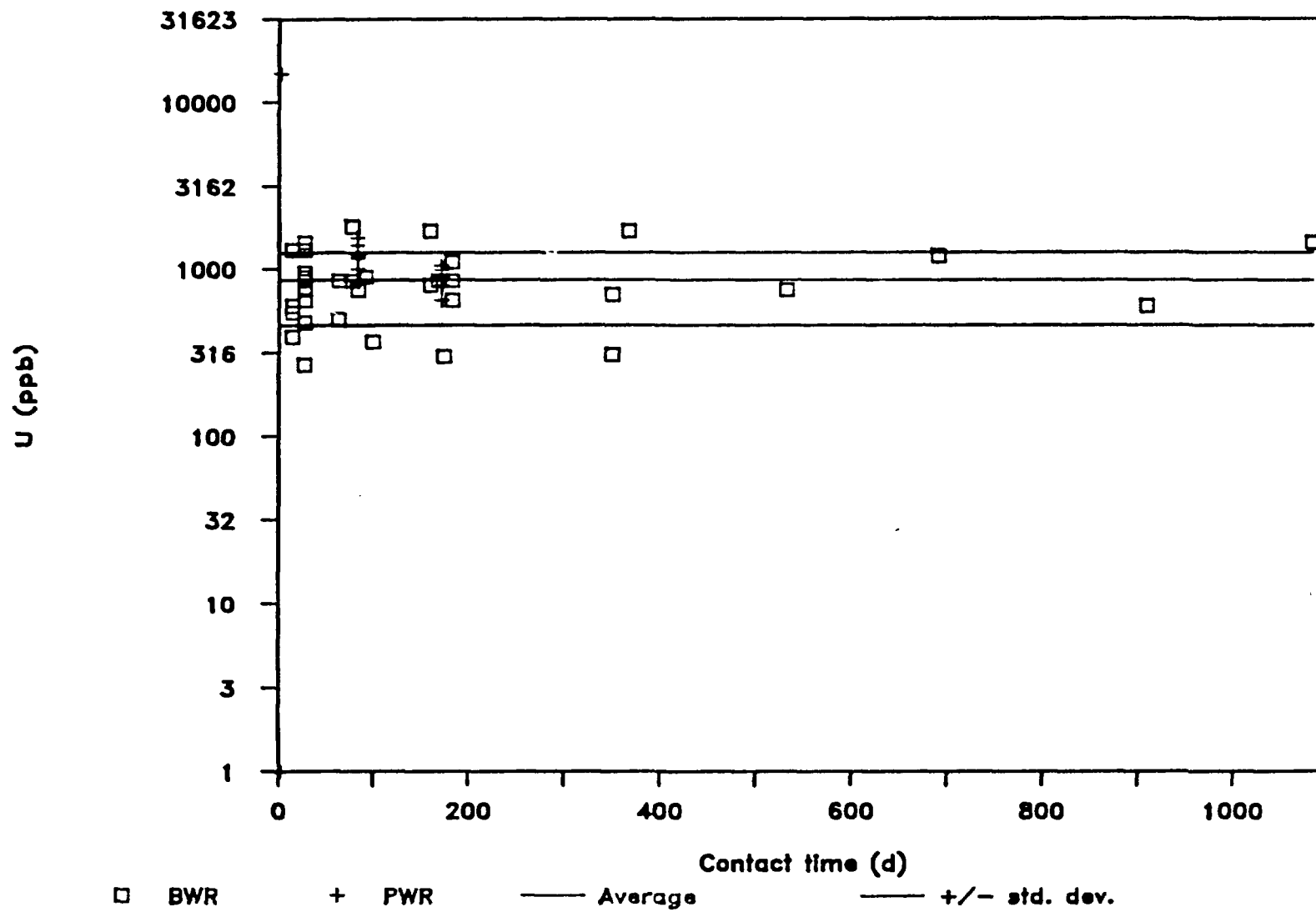


Fig 3. Reduction of groundwater using rock-cores.
(Ag/AgCl reference electrode).

Uranium concentrations



Plutonium Concentrations

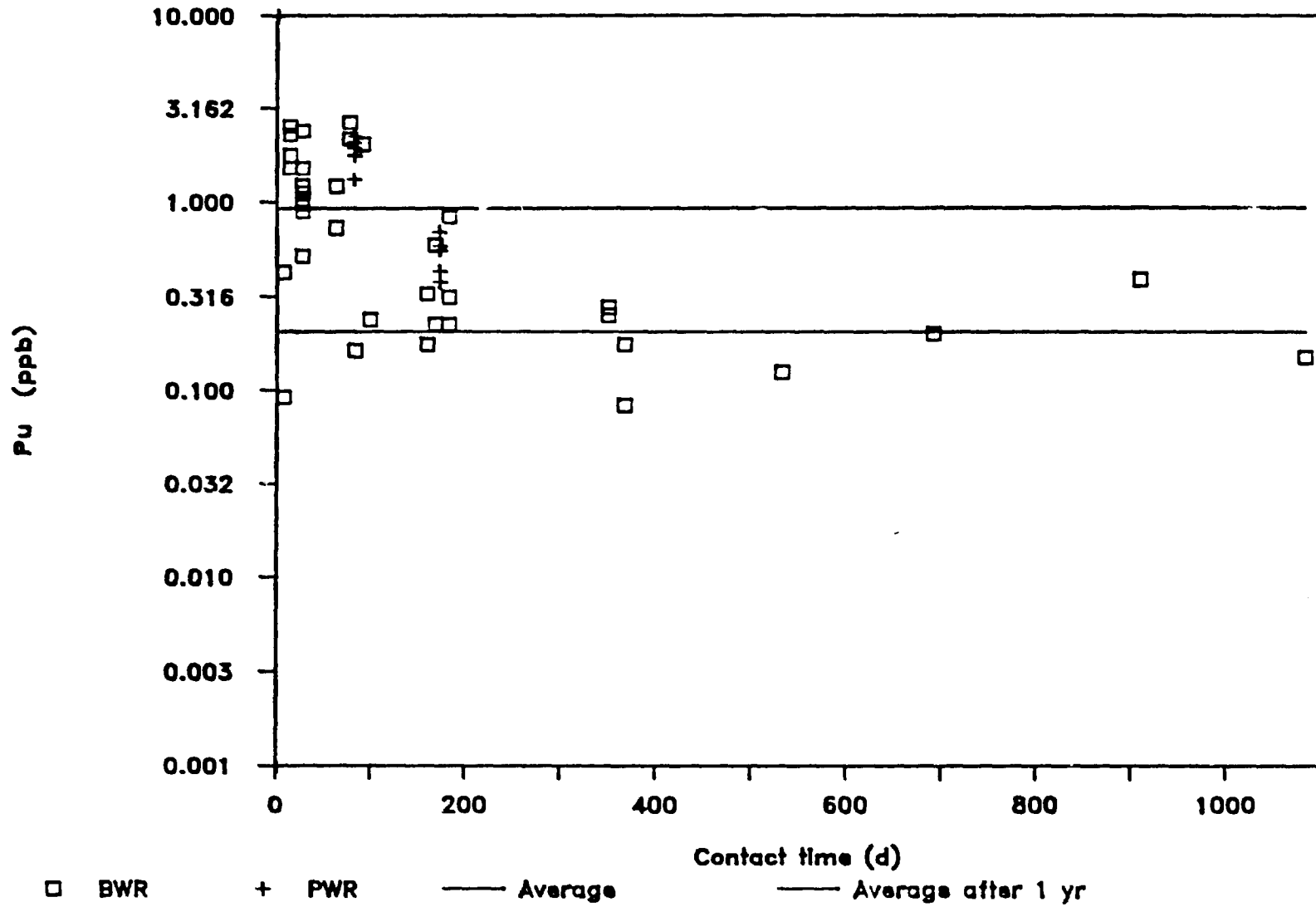


Fig 5

Cesium, corrected FIAP

sequential tests

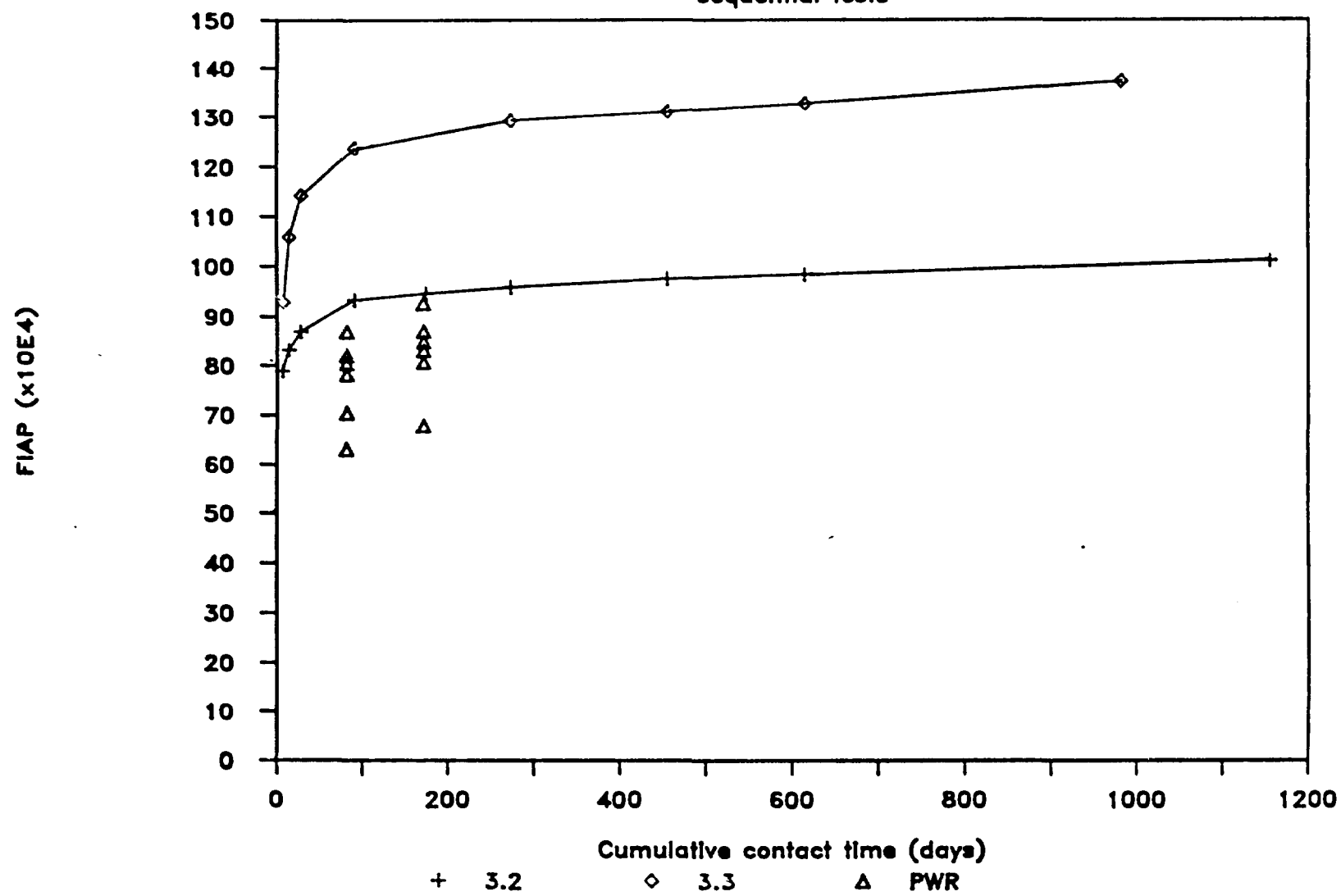
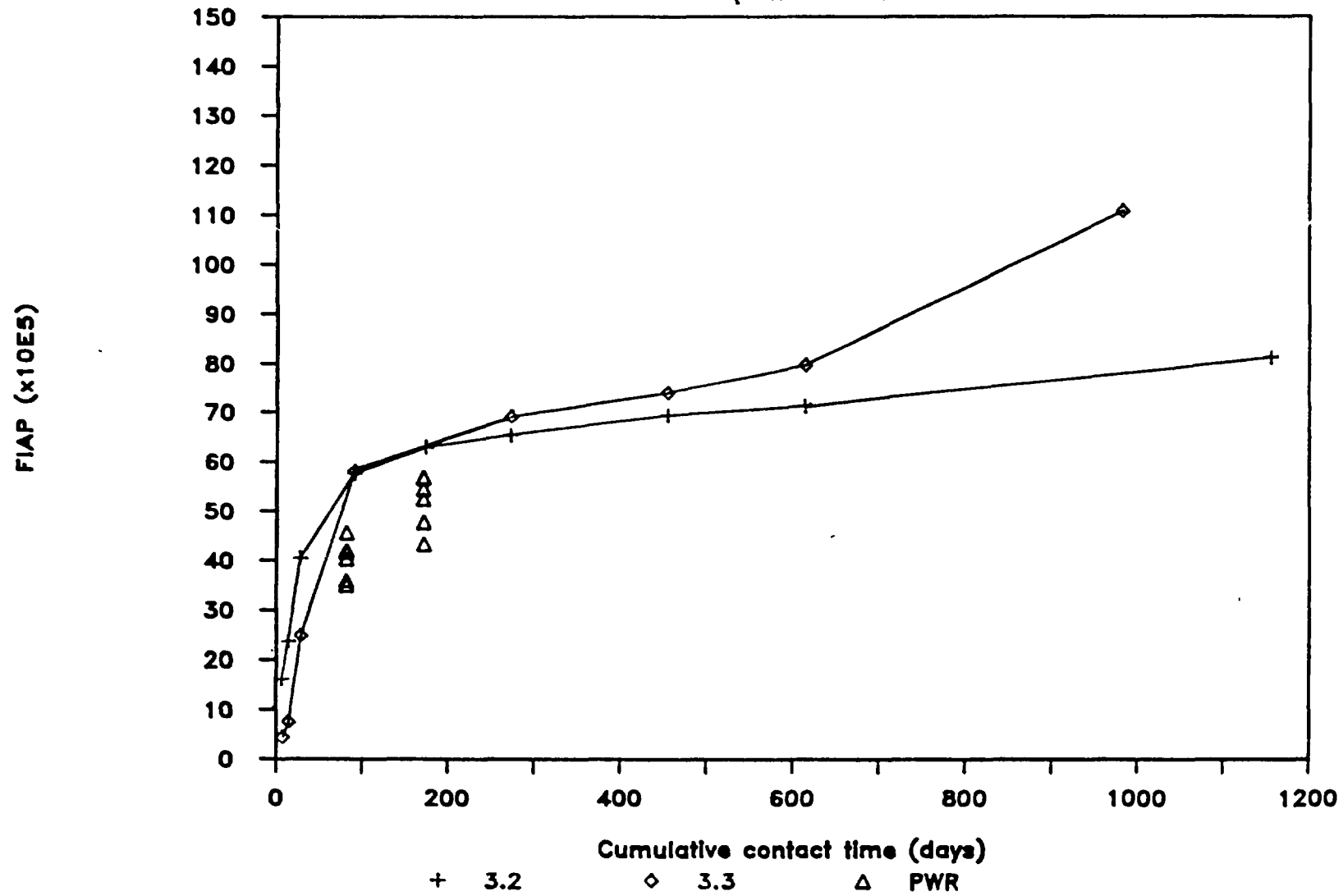


Fig 6

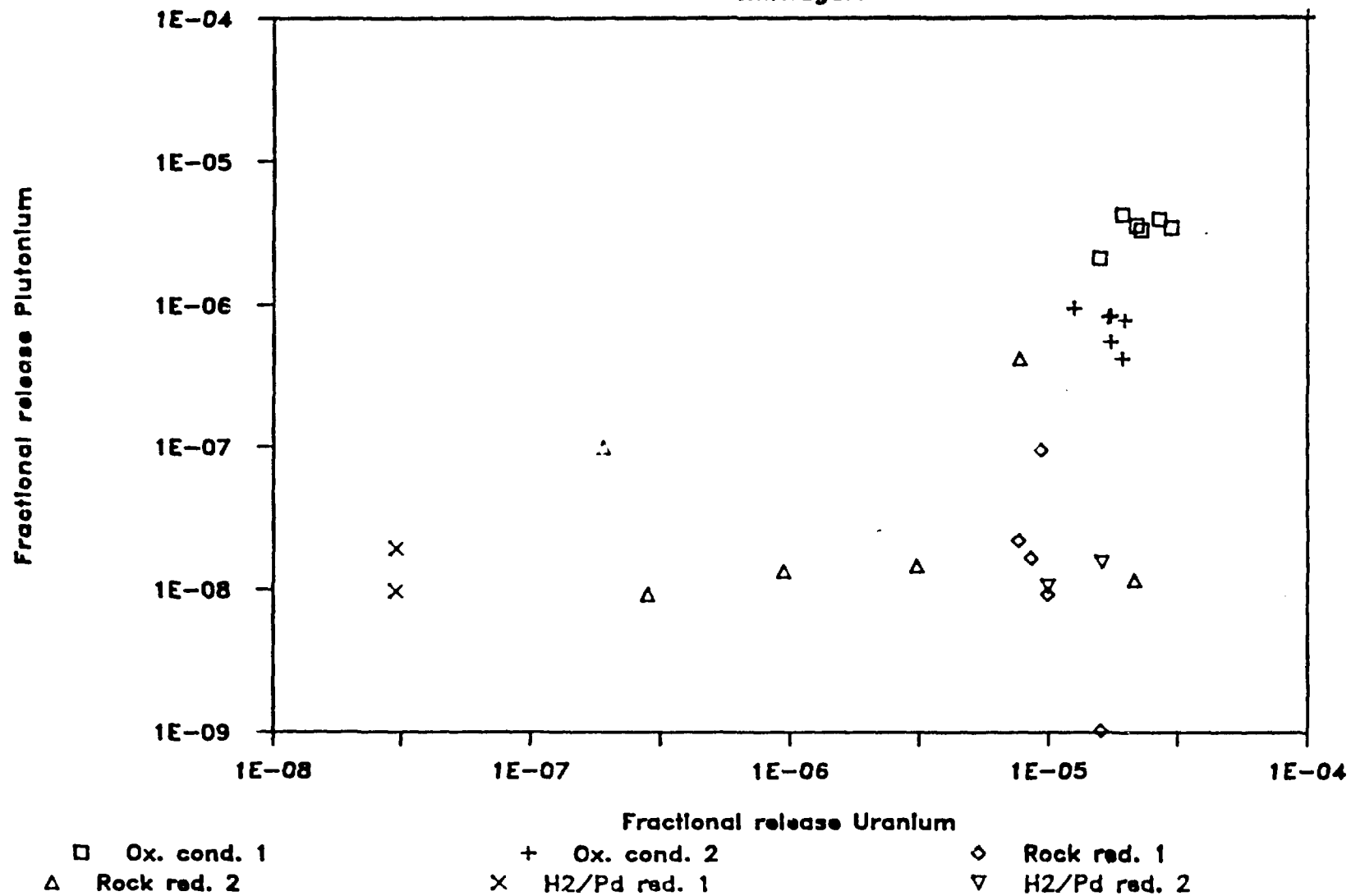
Strontium, corrected FIAP

sequential tests



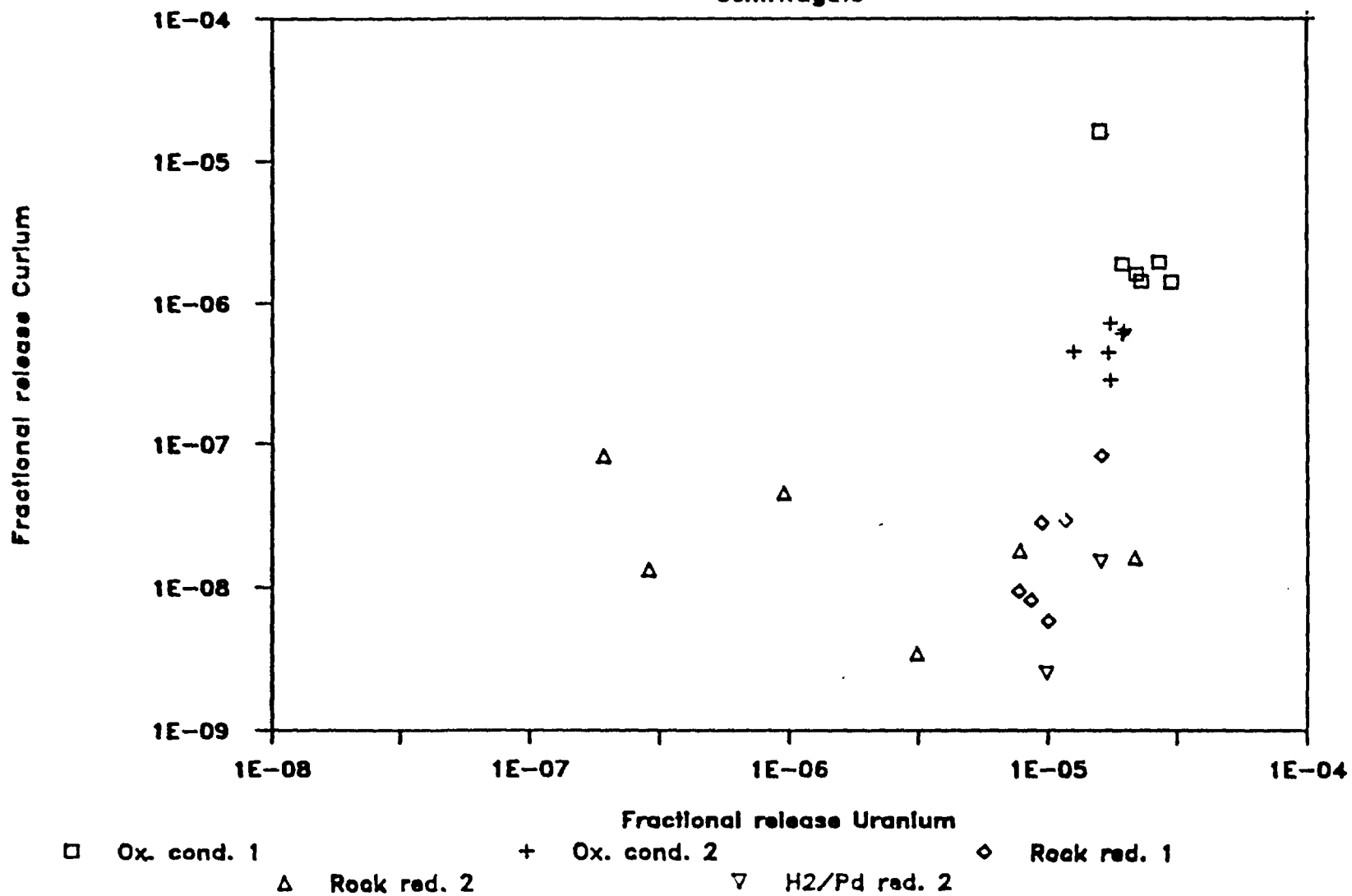
Correlation Fractional Release U/Pu

Centrifugate



Correlation Fractional Release U/Cm

Centrifugate



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TR 87-01

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Seje Carlsten, Olle Olsson, Stefan Sehlstedt,
Leif Stenberg
Swedish Geological Co, Uppsala/Luleå
February 1987

TR 87-02

Fuel rod D07/B15 from Ringhals 2 PWR: Source material for corrosion/leach tests in groundwater Fuel rod/pellet characterization: program part one

Roy Forsyth, Editor
Studsvik Energiteknik AB, Nyköping
March 1987

TR 87-03

Calculations on HYDROCOIN level 1 using the GWHRT flow model

Case 1 Transient flow of water from a borehole penetrating a confined aquifer

Case 3 Saturated-unsaturated flow through a layered sequence of sedimentary rocks

Case 4 Transient thermal convection in a saturated medium

Roger Thunvik, Royal Institute of Technology, Stockholm
March 1987

TR 87-04

Calculations on HYDROCOIN level 2, case 1 using the GWHRT flow model Thermal convection and conduction around a field heat transfer experiment

Roger Thunvik
Royal Institute of Technology, Stockholm
March 1987

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Lynn W Gelhar
Massachusetts Institute of Technology
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Y W Tsang, C F Tsang, I Neretnieks
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December 1986

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GP March, KJ Taylor, SM Sharland, PW Tasker
Harwell Laboratory, Oxfordshire
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Swedish Geological Co, Lund
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Lennart Börgesson
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Ove Stephansson
University of Luleå
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Kåre Tjus* and Peter Wikberg**
*Institute for Surface Chemistry, Stockholm
**Royal Institute of Technology, Inorganic
Chemistry Stockholm
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Trine Dahl-Jensen
Jonas Lindgren
University of Uppsala, Department of Geophysics
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Jan-Erik Andersson
Per Andersson
Seje Carlsten
Lars Falk
Ole Olsson
Allan Strähle
Swedish Geological Co, Uppsala
1987-06-30

TR 87-15
Geochemical interpretation of groundwaters from Finnsjön, Sweden

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August 23, 1987