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Editor
Lars Werme
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PROCEEDINGS OF THE THIRD SPENT FUEL WORKSHOP

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A list of other reports published in this series during 1983 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28) is available through SKBF/KBS.

CONTENT

PREFACE

The multinational spent fuel workshops have been held annually since 1981. The purpose of these meetings has been to create an informal forum for discussions on experimental techniques for studying the corrosion/dissolution of spent fuel in aqueous media as well as the interpretation of such experiments.

The first and second workshops were held in Studsvik, Sweden, on the initiative of SKBF/KBS. The third workshop, held in Boston, Mass., was organized by Battelle PNL. In the workshops, the contributing organizations have been Battelle PNL, AECL/Whiteshell and SKBF/KBS and its consultants, mainly Studsvik. At the third workshop also a representative from CEA was present as an observer.

Up to now, no workshop proceedings have been issued. However, the spent fuel workshops apparently fill a need as an international forum for discussing questions concerning spent fuel behaviour in nuclear waste repositories. It has therefore been decided to issue proceedings from the meetings to give continously the updated position of the research in this field.

In addition to establishing the position of the spent fuel studies, the workshop has also assumed the objective of recommending topics for further studies in this field.

Stockholm March 9, 1984

Lars Werme
SKBF/KBS

THE CORROSION OF SPENT UO_2-FUEL IN SYNTHETIC GROUNDWATER

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ABSTRACT

Segments of fuel and clad have been leached in deionized water and in groundwater. The leachants were centrifuged through membrane filters. Both centrifugate and the filters were analysed for U, Sr-90, α- and γ-emitters. The results are discussed in terms of preferential leaching, solubility limitations and adsorption effects. For U an apparent saturation at about 800 ppb was observed. Pu also appeared to attain saturation at a few ppb. For Sr the leach rate was $3 \cdot 10^{-7}$/d after ca 400 days. Attempts to impose reducing conditions showed decreased leach rates.

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_2 fuel itself, and over the past few years a number of investigations have been published (1-4) 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.

The experiments described here, as part of the current KBS program on spent fuel corrosion, have been performed using spent BWR fuel with a burnup (∿41 MWd/kgU) higher than the current average for discharged fuel, but of the same order as that projected for the near future.

EXPERIMENTAL

Fuel

Following the same procedure used in a previous program (1), 20 mm long segments of fuel and clad were cut from fuel rod A6 of fuel assembly 418 from the initial loading of the Oskarshamn I BWR. This rod had been well-characterized in an earlier PIE program, giving values of 42 MWd/kgU for the maximum burnup, and 0.7% for the fission gas release during operation. The radionuclide inventories for each specimen were calculated using the BEGAFIP code (5).

The specimens were cut from different zones along the rod, but with about the same burnup, and in the leaching experiments, duplicate tests were always performed using fuel from different zones.

Leachants

One sequential leaching test was performed in deionized water (pH 7.0), while all other tests employed the so-called KBS groundwater (pH 8.0-8.2) whose composition is shown in Table I. The deionized water, which was also used in preparation of the groundwater, was de-aerated by bubbling with nitrogen prior to use. A new groundwater batch was prepared for each new leaching period.

TABLE I
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.

Program

Most of the experiments reported here were performed under oxidizing conditions in order to provide benchmarking data and to permit comparison with other published results. Some experiments, however, were performed where an attempt was made to impose reducing conditions (which are expected to obtain in the deep repository projected in the KBS program) on the leachant by bubbling with H_2/Ar gas in the presence of a palladium catalyst.

As shown in the table below, five experimental series have been performed under oxidizing conditions, three (Series 3.1-3.3) where the fuel/clad specimen was exposed to sequential leaching with new batches of deionized water or groundwater in a modified IAEA test, and two (Series 3.4 and 3.5) where individual fuel/clad specimens were contacted statically with groundwater for different periods of time. Series 3.4 and 3.5 each consist of 8 fuel specimens.

Two experimental series (3.6 and 3.7), with reducing conditions imposed during the last contact period, each consisting of three individual fuel specimens, have been performed. Here, two pre-leaches under oxidizing conditions for 91 and 27 days respectively were carried out on each specimen in order to remove the appreciable cesium activities which rapidly leach out from the fuel/clad gap and which complicate subsequent analysis, and to avoid the initial high leach rates possibly caused by local oxidation of the fuel surface during cutting. Following these pre-leaches, the specimens were contacted with fresh groundwater which had been treated with H_2/Ar gas in the presence of palladium catalyst, subjected to a further reduction treatment in the leaching flask, and then sealed for 28 or 56 days.

TABLE II
Summary of leach test conditions

Series	Leachant	Conditions
3.1	Deionized water	Oxidizing: Sequential leaching
3.2	Groundwater	" : " "
3.3	"	" : " "
3.4	"	" : Static leaching
3.5	"	" : " "
3.6	"	Oxidizing/reducing: Two pre-leaches
3.7	"	Final reducing conditions

Procedure

All leach tests were performed in 250 ml Pyrex flasks, the fuel specimens, which contained about 16 g UO_2, being suspended almost vertically in a platinum wire spiral in 200 ml of the leachant. All tests were carried out at the ambient temperature of the hot cell, in the range 20-25 °C.

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 the sequential leaching tests, or discarded in the case of the static tests.

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 filter (denoted Samples A and C respectively) were subjected to analysis. Finally 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 adsorbed on the vessel walls. This rinse solution (Sample B) was also analysed.

Analysis

All samples were analysed for a) uranium (neutron activation) b) Sr-90 c) γ emitting fission products d) α emitting nuclides (α 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.

RESULTS AND DISCUSSION

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 µg 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_2 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.

Exposure at low pH

A contamination incident, still not satisfactorily explained, occurred during the program which perturbed the pattern of results but which, in retrospect, was fortunate for their evaluation. On removal of the leachants from the 91-182 day contact periods of the 3.1-3.3 series, and from the initial 91 day preleaches of the 3.6-3.7 series, it was found that the pH had apparently decreased to about 5 in seven of the leachants, and as low as 2.3 in the groundwater from the 3.2 series. Even the deionized water sample (Series 3.1) showed a low pH of 3.9. Not unexpectedly, the ALR values for all radionuclides in these leachants were markedly higher than those measured for the preceding contact periods at normal pH values.

Formation of nitric acid by radiolysis was first suspected but thought unlikely in view of the fact that the leachants from the static tests removed at the same time showed no pH decrease in spite of larger radiation doses. All the low pH leachants belonged to the same deionized water/groundwater batch and analysis of the three leachants with the lowest pH values indicated that they had been contaminated with traces of the 5M HNO_3/0.5M HF desorption solution.

Subsequent leachant samples have shown no significant pH decrease and the ALR values for the contact periods immediately after the low pH exposure returned to the levels obtained previously, indicating the absence of memory effects. However, an interesting feature of the low pH exposure results was that the substantial differences in ALR values for the various nuclides observed earlier at high pH, and which could be caused by either preferential dissolution or by saturation/readsorption constraints, almost disappeared, indicating congruent dissolution and the retention of most species in solution.

If adsorption of dissolved species at the fuel/clad surfaces was a major contributor to the differences in ALR values, this could be tested by a low pH exposure following a long exposure at high pH.

Higher ALR values for the actinides than for Sr-90, which is not expected to be significantly adsorbed, would then suggest desorption of previously adsorbed species. To effect such a test, the fuel/clad specimens from the subsequent static tests were immediately afterwards subjected to 20 day exposures at various low pH values. The results from these experiments will be discussed below.

Dissolution under oxidizing conditions

Cesium. The migration of fission product cesium in operating 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 1. 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 1, 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 and at the end of the contact period ALR values in the range $4 \cdot 10^{-7} - 10^{-6}$ were obtained.

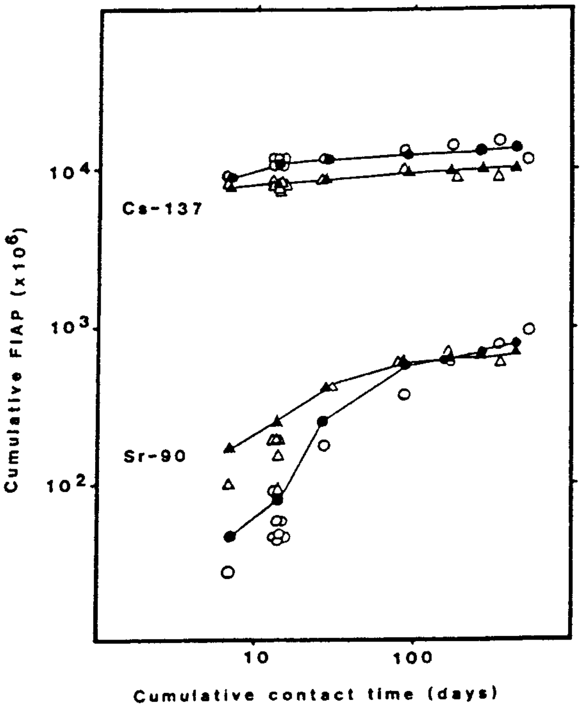


Fig. 1. Comparison of results from sequential and static leaching in groundwater (pH 8.2-8.2)

▲ 3.2-series
△ 3.5 "
● 3.3 "
○ 3.4 "

Open symbols: static tests.

Strontium. Figure 1 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 show a steady decrease as a function of contact time (a slope of +1 would indicate a constant dissolution rate), approaching a value of $2 \cdot 10^{-7}$ FIAP/d after 450 days. The agreement between the sequential leaching and static test results suggest the absence so far of saturation effects.

The results 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, but according to calculations, at no time did the linear heat rating reach as high as even 30 kW/m.

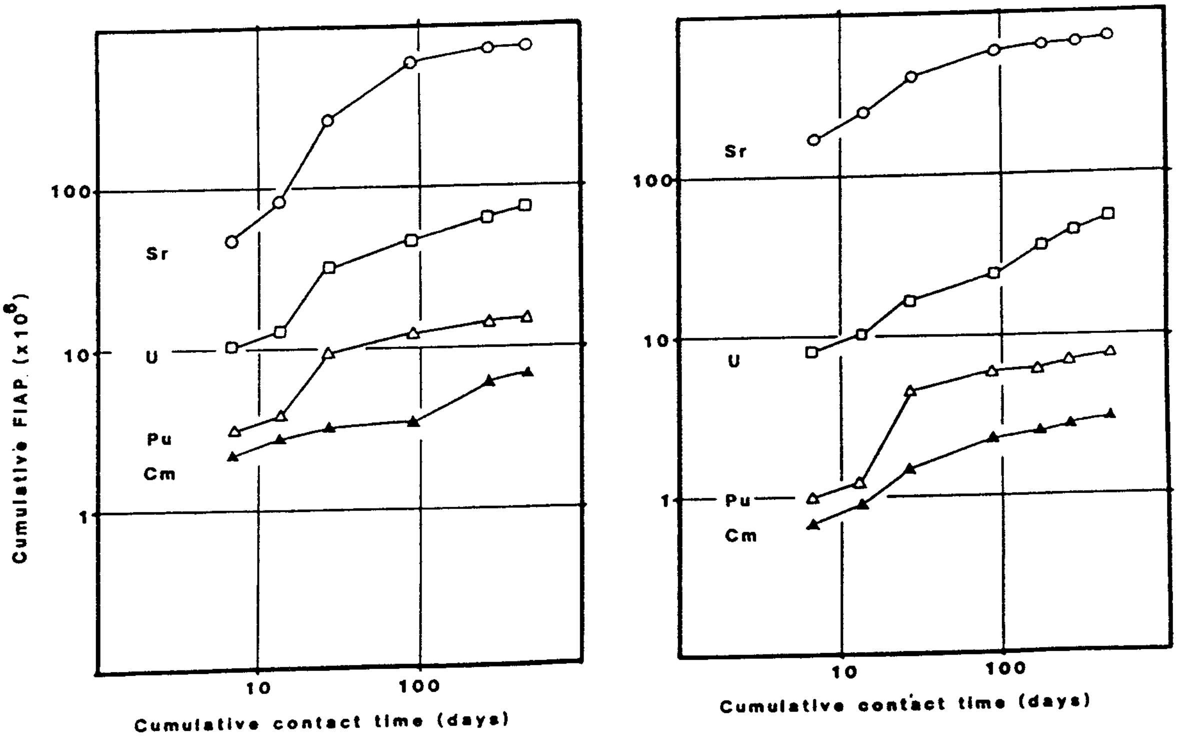
The cumulative FIAP results for the deionized water Series 3.1 (the fuel specimen was taken from adjacent to 3.2) were initially somewhat lower than those for Series 3.2, but attained the same value after 6 months. It is also noteworthy that although the total release of Sr-90 was similar in both groundwater and deionized water after this period, its fate after entering solution was different: as can be seen from Table III, the Sr-90 in the deionized water leachants was predominantly in the colloidal form.

TABLE III
Average values of colloidal fraction (% FIAP retained on membrane filter).

Leachant	pH	Cs	Sr	U	Pu	Cm
Deionized water	7.0	15	65	<50	25	95
Groundwater	8.0-8.2	5	12	23	30	90

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. Because of this, and lack of space, these results will not be presented here. The results, however, are not in contradiction to any conclusions drawn from data on other radionuclides.

Uranium, Plutonium, Curium. These radionuclides are best considered together since there are interesting similarities and differences between them. Figure 2 presents their cumulative FIAP values as a function of contact time for the sequential groundwater leaching Series 3.2 and 3.3 which were near-duplicate specimens (see above).



a) 3.2 series b) 3.3 series

Fig. 2. Sequential leaching results for ground water (pH 8-0-8.2)

The uranium curves should be considered as maximum values since the analytical results were sometimes quoted as detection limits: these values have been treated conservatively at their limit values.

The plutonium curves represent Pu-239/-240 together, while the curium curves are the average of the Cm-242 and Cm-244 values. The Sr-90 curves are also shown in the figure.

Inspection of Figure 2 shows that the results for uranium lie about one order of magnitude, and for plutonium and curium about two orders of magnitude, lower than the corresponding Sr-90 results, but for all species the ALR values fall sharply over the contact period for which analytical results are available.

Values for the initial contact period, when the freshly-cut UO_2 surfaces were first exposed to the groundwater, were for uranium, plutonium and curium about $1.3 \cdot 10^{-6}$, $3 \cdot 10^{-7}$ and $2 \cdot 10^{-7}$ FIAP/d respectively, and for the latest contact period about $7 \cdot 10^{-8}$, $3 \cdot 10^{-9}$ and $3 \cdot 10^{-9}$ FIAP/d. These last results are in good agreement with the values reported by Johnson (4) on Candu fuel leached in KBS groundwater for contact times between 400-600 days.

The results for leaching in deionized water (3.1 series) were quantitatively similar, but were significantly lower for uranium and somewhat higher for plutonium and curium than those for groundwater discussed above.

Possible reasons for the large differences in apparent leaching behaviour between the various radionuclides, in both deionized water and groundwater, include preferential dissolution, solubility limitations, and adsorption processes either directly from solution or after the formation of colloids or pseudocolloids.

Preferential dissolution

For the cesium nuclides, there is some evidence for preferential leaching even after the rapid initial leaching of cesium compounds from the fuel/clad gap: both Vandergraaf and Johnson (3, 4) observed that Cs-137 leaching rates were higher than other species even after 1000 days of contact time, and in the present work, the ALR values for Cs-137 were higher by a factor of 3-4 than those for Sr-90 after about 400 days.

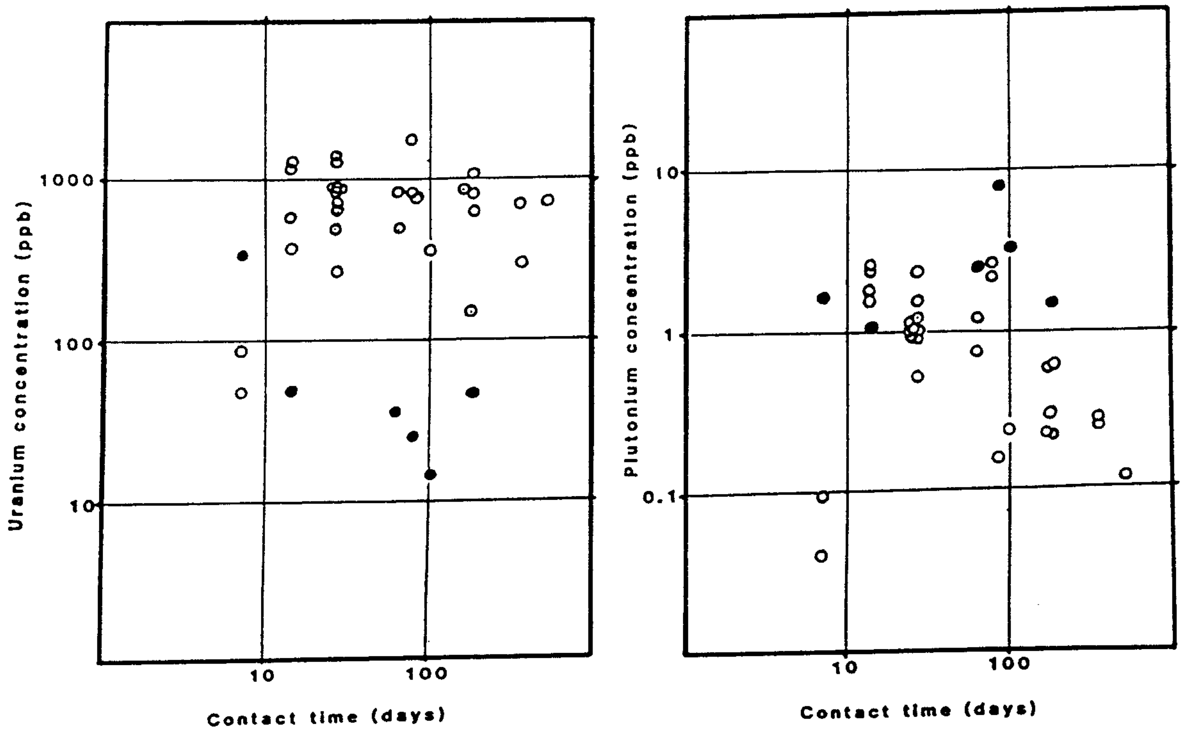
For Sr-90 the evidence for preferential leaching is less substantial: as mentioned above, differences in the ALR values over the first 100 days of leaching for fuel specimens from different parts of the rod were observed (Figure 1), suggesting some correlation with fuel properties. Even after about 400 days of contact the ALR values for Sr-90 were higher than those for uranium by a factor of 3-4, but it is very uncertain to what extent this represents preferential leaching of Sr-90, rather than other restrictions on the amounts of uranium and the actinides entering and retained in the leachants.

In experiments with simulated fission products, Koizumi et al (6) have reported the formation of both $(Ba,Sr)ZrO_3$ and $(Ba,Sr)UO_3$ at 1500 °C, and phases containing both barium and strontium have been found at a radial position corresponding to this temperature in UO_2 irradiated to a heat rating of about 70 kW/m (7). Data on such inclusions, which could be preferentially leached, in commercial LWR fuel is, however, very limited. Hopefully more information will become available from the fuel characterization task of the KBS program, where emphasis will be placed on segregation, and on possible grain-boundary enrichment.

Solubility limitations

The data so far presented has been in the form of FIAP values which, in the absence of significant adsorption on the vessel walls, have represented the sums of the amounts of each radionuclide in the centrifugate and on the membrane filter. Thus, comparison can be made with the results of the Canadian workers (3, 4) who, after removing the fuel specimens from the leaching vessels, acidified the leachants immediately. Subsequent analysis then gave the sum of all fractions.

Inspection of the results for the centrifugates in the KBS program, however, reveals another picture. Figures 3a and 3b show the concentrations of uranium and plutonium respectively as a function of the contact time for all centrifugates with the exception of those arising from the first contact of the fuel specimens with the leachants.



a) Uranium

b) Plutonium

Fig. 3. Concentrations found in leach solution centrifugates (Open symbols: groundwater pH 8.0-8.2. Filled symbols: deionized water pH 7.)

For uranium it can be seen that saturation of the groundwater occurs after about 10 days at a level of about 800 ppb which is in good agreement with the value calculated by Johnson (4), based on data published by Paquette and Lemire (8). The results for the deionized water centrifugates, with the exception of a high result after 7 days of contact time, are much lower than those for groundwater but indicate saturation at a level of 20-30 ppb. Strong complexing of the uranium by the carbonate present in the groundwater is the probable reason for these differences in solubility.

The plutonium concentrations in the groundwater centrifugates presented in Figure 3b 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 time suggesting instability and the formation of colloids and/or adsorption effects.

No comparable results for the curium nuclides can be presented here since they were found to be almost completely retained on the membrane filter.

Adsorption effects

The average values for the percentages of several leached nuclides retained on the membrane filter - and defined as the colloidal fraction - for deionized water and groundwater of pH 8.0-8.2 were presented in Table III. (It should be noted that values of up to 5% probably represent the small amount of liquid retained in the pores of the filter.) The most marked difference between the two leachants was the behaviour of Sr-90 which gave high retention values for deionized water samples. For uranium and plutonium the individual values showed appreciable scatter, but no clear correlation of colloid fraction with contact time was observed.

If, then, the concentrations of uranium in the centrifugates, and the colloidal fractions are independent of contact time, the question again arises whether the higher ALR values for Cs-137 and Sr-90 after long contact times represent preferential leaching of these nuclides, or adsorption of dissolved or colloidal uranium on the fuel/clad surfaces. This situation also applies to plutonium and curium.

To test the latter hypothesis, 3 of the fuel specimens from static leach tests were subsequently exposed to a new 20 days contact period with groundwater adjusted to lower than normal pH. If adsorption effects had been significant during the long static leaching test, and if the adsorption process is reversible, ALR values for the adsorbed species higher than those for Sr-90 could be expected during the low pH exposure. The ALR values for these experiments, together with values for experiments with groundwater at pH 8.0-8.2 and comparable leaching periods are presented in Table IV.

TABLE IV
The effect of pH on apparent leach rate.

Specimen	Leach Period(d)	pH	ALR (FIAP/d x 10^6)			
			Sr-90	U	Pu	Cm
3.3.6	182-364	8.0-8.2	0.61	0.10	0.009	0.014
3.2.6	266-364	"	0.25	0.07	0.006	0.0014
3.2.7	364-546	"	0.22	0.05	0.002	0.0014
3.3.7	364-546	"	0.27	0.08	0.004	0.004
3.5.6.5	365-384	5.0	10.3	0.45	3.9	5.4
3.4.6.3	365-384	3.0	9.6	8.2	9.1	16
3.4.7.2	547-566	2.0	25	25	21	76

The first observation made on inspection of Table IV is the striking increase in ALR of all the radionuclides as a function of decreasing pH, at least over a 20 day contact time before new equilibrium conditions have been established. For Sr-90, the ALR value at pH 2 was about 300 times larger than the value at pH 8, and for uranium and the actinides the increases are even larger.

It can also be seen that at pH 5, the values for plutonium and curium are lower by a factor of about 2, and for uranium by a factor of about 20 than that for Sr-90. Only at pH 3 and below are the same values of ALR for all radionuclides attained, with no apparent solubility or adsorption constraints. For curium, moreover, there is some indication of a desorption effect. There is, however, no support from these results for the hypothesis of large-scale adsorption of uranium or plutonium on the fuel/clad surface. Further experiments of this type will be performed later in the program using fuel specimens subjected to even longer static leach tests at pH 8.0-8-2.

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 (9) 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 V
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 correspond to centrifugate concentrations of about 800 ppb, 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.

CONCLUSIONS

The results presented for sequential and static leaching of high burnup UO_2 fuel in KBS groundwater and in deionized water under oxidizing conditions lead to the following conclusions:

1. The same rapid initial leaching of cesium activities as that reported in previous work occurred. This initial leaching, which probably represents the dissolution of cesium compounds in the neighbourhood of the fuel/clad gap, is of the same magnitude as the release of fission gases from the fuel during operation.

2. Fission product Sr-90 showed initial leach rates within the range $3 \cdot 10^{-6}$ - $2 \cdot 10^{-7}$/d, somewhat different rates being obtained from fuel sampled from different parts of the fuel rod. After 400-500 days of contact, the leach rate had decreased to about $3 \cdot 10^{-7}$/d. In deionized water, about half of the Sr-90 present in the aqueous phase was retained on membrane filters, indicating the presence of a colloid or pseudocolloid.

3. For uranium, the results indicated that saturation of the leachants was rapidly attained, at a level of about 800 ppb in groundwater at pH 8.0-8.2, and about 20-30 ppb in deionized water at pH 7.0. A colloidal fraction was also present in each leachant. Thus, the apparent leach rates for uranium after the initial phase mainly reflect the length of contact time.

4. Plutonium also appears to attain saturation in both groundwater and deionized water at a level of a few ppb, although there is evidence of instability in groundwater at contact times longer than 100 days leading to lower solubility. Colloidal fractions corresponding to about 50% of the amounts in solution were also found.

5. Curium, which was always present predominantly in the colloidal form, had about the same values of apparent leach rate as plutonium.

6. Experiments performed at low pH after long contact times at pH 8.0-8.2, showed the expected increases in leach rates for all nuclides, but no evidence was obtained for the possible desorption of uranium and plutonium which may have been precipitated or adsorbed on the fuel/clad surfaces due to the solubility constraints mentioned above.

Attempts to impose reducing conditions on the fuel/ groundwater system by means of H_2/Ar gas in the presence of a palladium catalyst showed some success, and apparent leach rates for Sr-90, uranium and the actinides were obtained which were an order of magnitute lower than those found under oxidizing conditions.

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LEACHING AND RADIOLYSIS STUDIES ON UO_2 FUEL[*]

by

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ABSTRACT

Results of several studies of the leaching and dissolution of UO_2 fuel are reviewed. The relationship between stable-xenon release, by puncture of used fuel elements, and ^{137}Cs and ^{129}I release, during leaching tests of used fuels, has been investigated. In general, the fractional release of stable xenon exceeds that of ^{137}Cs by a factor of two to ten. Our leaching data for ^{129}I are insufficient to adequately characterize the release relative to that of xenon.

In the presence of gamma radiation, the dissolution of unirradiated UO_2 in groundwater at 100°C is accelerated, whereas, in mixtures of clay and groundwater, it is inhibited, probably due to the release from the clay of reducing agents such as Fe^{2+}.

An electrochemical study of the oxidative dissolution of UO_2 in the presence of alpha radiation is described. The positive shift in potential of a UO_2 electrode when an alpha source is adjacent to it is ascribed to the presence of H_2O_2 produced by the alpha-radiolysis of water.

1. INTRODUCTION

This report describes a major portion of the experimental studies on UO_2 fuel leaching and dissolution performed at WNRE over the past two years. While some of the work is complete, other parts are in the preliminary stages. This paper, therefore, can be considered as a report of recent progress, and focuses on two major areas: fission product leaching and the effects of radiolysis on UO_2 dissolution. Each section is self-contained and includes an outline of future research plans.

2. THE RELATIONSHIP BETWEEN GAP INVENTORIES OF ^{137}Cs, ^{129}I AND STABLE XENON IN USED CANDU FUEL

2.1. Introduction

Fission products in used CANDU fuel can be found at three different locations:

i. in interconnected void space (i.e., the fuel-sheath gap, cracks in the fuel pellets and inter-pellet gaps).

ii. at UO_2 grain boundaries.

iii. within grains, i.e., the UO_2 matrix.

The UO_2 matrix contains by far the largest part (>90%) of the actinide and fission product inventory. For this reason, most leaching studies have considered the dissolution of the UO_2 matrix as the principal mechanism for release of long-lived radionuclides. However, a number of fission products, in particular isotopes of cesium and iodine, appear to be leached preferentially in the early stages of the leaching process, when UO_2-matrix dissolution is not yet the most important contributor to their release. Some of these isotopes have very long half-lives (e.g. ^{135}Cs, ^{129}I), and their preferential release therefore has significant implications for the safety assessment of used-fuel disposal. This report describes studies directed at characterizing the preferential leaching process.

2.2. Migration of Fission Products in CANDU Fuel During Irradiation

Cs and I isotopes migrate during irradiation towards 'cold' regions in the fuel and are deposited in pores, cracks and at the fuel-sheath interface (Grisham et al., 1979), likely in the form of CsI (Mitchell et al., 1981). However, the fission yield for cesium is an order of magnitude higher than for iodine, and a large part of this cesium may be deposited in the fuel-sheath gap as a soluble cesium-uranate compound (Potter, 1979). Fission gases such as krypton and xenon are also trapped in pores and in the interconnected void space within the fuel elements.

2.3. Estimation of Fission-Product Gap Inventories in Used CANDU Fuel

Gap inventories of stable fission gases in used CANDU fuel are largely determined by the linear power rating of the fuel (Notley and Hastings, 1980). The computer program ELESIM (Notley, 1979) calculates the release of fission gas to the gap, using the power history of the fuel. It is difficult to obtain reasonably accurate estimates for the gap inventories of Cs and I isotopes in used CANDU fuel. Sweep gas experiments during actual irradiation have failed to yield an accurate estimate of quantities, despite the volatile character of Cs and I (Hastings et al., 1982).

One method for predicting the releases of ^{137}Cs, ^{135}Cs and ^{129}I from used fuel after disposal is to relate their leachable fractions to stable xenon releases at the end of irradiation. Xenon releases from a fuel element can be both measured in puncture tests and calculated with ELESIM. This can be done for a variety of fuel bundles with different power histories. These data can then be correlated with xenon releases calculated using ELESIM for various fuel bundle irradiation histories. An average leachable fraction of ^{137}Cs, ^{135}Cs and ^{129}I for the fuel can then be obtained for safety assessment calculations.

2.4. Relationships Between ^{137}Cs, ^{129}I and Stable Xenon in the Gap

Recently, it was reported that, for a number of fuels of widely different power histories, a near one-to-one correlation exists between gap inventories of stable xenon (obtained by puncturing followed by gas chromatography) and the amount of ^{137}Cs released during leach tests of days to weeks duration (Johnson et al., 1983)

The present study provides additional data on the leaching of ^{137}Cs, and attempts to establish the relationship between instantaneously released ^{129}I and stable xenon in the gap.

2.4.1. Experiments

To provide additional ^{137}Cs data, leach tests were performed, with replenishing of leach solutions (distilled water), at 25°C, using 2-cm long segments of used CANDU fuel. Johnson et al. (1983) give details of the leaching procedure. A summary of results obtained in this study and by Johnson et al. (1983) is given in Table 1. Fig. 1 shows the relationship between stable xenon in the gap (both measured and calculated) and the percentage of ^{137}Cs released during leaching.

To investigate the relationship for ^{129}I, several 2-cm long segments of outer elements of Pickering bundles A13894W and A07993 (average power ratings of 42 kW/m and 39 kW/m, respectively) were leached at 25°C in distilled water for five days. Samples taken periodically were analyzed for ^{137}Cs by gamma-spectrometry and for ^{129}I by neutron activation analysis, after chemical separation (Burns et al., 1982). Figs. 2 and 3 illustrate the release curves for ^{137}Cs and ^{129}I. Fractional release results for ^{129}I are summarized in Table 2, while Fig. 4 shows the relationship between stable xenon in the gap and rapidly released ^{129}I.

2.4.2. Discussion and Conclusions

The slope of the (solid) regression line in Fig. 1, relating measured xenon release to released ^{137}Cs, is 0.70, which is 17% lower than that found by Johnson et al. (1983). This differs from the near one-to-one correlation suggested by Johnson et al. (1983). The slope of the (dotted) regression line in Fig. 1, relating calculated (ELESIM) xenon release to released ^{137}Cs is 0.58, 15% lower than reported by Johnson et al. (1983). Inspection of Fig. 1 suggests that calculated xenon release is always lower than measured xenon release. Apparently, ELESIM underestimates the release of stable xenon to the gap for these particular fuel elements.

Figs. 2 and 3 illustrate the extremely rapid initial release of both ^{137}Cs and ^{129}I. After two days, the curves are almost flat, suggesting that most of the gap inventory has leached out.

The slope of the regression line relating measured xenon gas release and ^{129}I release in Fig. 4 is 0.73, almost identical to the value found for ^{137}Cs from Fig. 1. However, for ^{129}I only three data points were obtained, and more data are needed before this relationship is firmly established. It should be pointed out that ^{129}I leach tests were performed on duplicate samples from the same fuel element, and results did not agree well, as illustrated by the ranges given in Table 2. This is probably due to local concentration variations in the fuel elements. Averaging of values obtained for duplicate fuel samples (as was done for Figs. 1 and 4) improves the correlation with measured xenon release. Note also that ^{137}Cs and ^{129}I fractional release results show very similar trends for each fuel segment. A regression line with a slope of 0.8 results from correlating the ^{137}Cs and ^{129}I data obtained for Pickering bundles A13894W and A07993W and Bruce bundle F21271C. This means that, for ^{129}I, the leachable fraction is 80% of the ^{137}Cs leachable fraction. However, this number also needs more confirmation, before it can be used with confidence in the safety assessment of used fuel disposal.

3. EFFECTS OF RADIOLYSIS ON THE DISSOLUTION OF UO_2 FUEL

3.1. Introduction

Any study of the dissolution of used UO_2 fuel inevitably involves consideration of the effects of both gamma- and alpha-radiolysis of water on the oxidation of UO_2 and the release of contained actinides and fission products. It may be argued that the effects of gamma-radiolysis of water on UO_2 dissolution are of little significance with regard to disposal, since gamma fields will have decreased to insignificant levels prior to container failure. Nevertheless, gamma radiolysis may have a significant impact on the dissolution kinetics in laboratory studies of used-fuel dissolution. In addition, since there are many similarities between alpha- and gamma-radiolysis in their effects on solution chemistry, these studies may provide valuable information for the assessment of the impact of alpha-radiolysis on UO_2 fuel dissolution.

Alpha-radiolysis is more likely to be an important factor in the assessment of the long-term durability of fuel after disposal, since alpha-fluxes remain high enough to be of potential significance for more than 10^5 years. Calculations (Christensen and Bjergbakke, 1982; Johnson, 1982) have suggested that alpha-radiolysis of water could have a profound effect on the oxidation of fuel and on the redox chemistry of the disposal vault. The studies reported here clearly illustrate that radiolysis effects are significant and must be taken into account in any assessment of used fuel disposal.

3.2. Gamma Radiolysis Effects

These studies were conceived to investigate the effects of gamma-radiation at low dose rates (<10 Gy/h) on the dissolution of UO_2. The data obtained are of particular relevance to studies of used-fuel dissolution, because dose rates of approximately 10 Gy/h occur in such studies. It is experimentally difficult to obtain evidence regarding the importance of radiation effects in used-fuel dissolution studies, because it is impossible to perform such studies in the absence of radiation. For this reason, and because surface analytical techniques such as X-ray photoelectron spectroscopy (XPS), which have proven valuable in studying UO_2 dissolution (Sunder et al., 1981), cannot be applied to used fuel, these studies were performed using pure UO_2.

3.2.1. Experimental

Thirty-two samples of UO_2 were cut from sintered fuel pellets of bulk composition $UO_{2.00-2.01}$ and 97% theoretical density. Average grain size was approximately 10 µm. The samples, approximately 3 mm thick, were polished on one side using 1 µm diamond paste, with a final polish using colloidal silica. The polished surfaces of two samples were analyzed by XPS to determine the degree of surface oxidation. Samples were weighed and placed in vitreous silica tubes approximately 10 cm long. Either eight mL of WN-1 synthetic groundwater (see Table 3 for composition), or a WN-1 groundwater-clay mixture (0.2 g clay/mL), or 10^{-2} mol/L $NaHCO_3$ were added to the tubes. The clay compositions used are shown in Table 4. All solutions were air-saturated. The tubes were then sealed under vacuum.

Control samples, which were not exposed to gamma radiation, were kept in a laboratory oven at 100°C for 455 days. The sample tubes that were to be irradiated were placed in a stainless-steel pressure vessel. This vessel was placed within a larger vessel that also contained 18 used-fuel elements each in a metal sleeve. The gamma dose rate inside the pressure vessel was estimated to be 4.1 Gy/h, based on a number of measurements of the radiation field. The entire apparatus was contained within a large concrete canister with an internal heater that maintained the temperature at 100°C. The sample tubes were removed from the vessels after 485 days and brought to the laboratory for analysis.

The UO_2 samples for XPS were transferred from the silica tubes in a glove bag containing N_2 to prevent oxidation. Samples that had visible alteration products on the surface were scraped for analysis of the products by X-ray diffraction (XRD). All samples were examined by scanning electron microscopy (SEM) and, where appropriate, analysed by energy dispersive X-ray analysis (EDX) to obtain information on the extent of dissolution.

3.2.2. Results

The degree of oxidation of the various UO_2 samples is shown in Table 5. The surface oxide compositions were calculated from the U(VI)/U(IV) ratio measured by XPS (Sunder et al., 1981) and are indicative of the degree of oxidation of the first few atomic layers of the surface. With the exception of one pair of samples, agreement between duplicates was excellent. Scanning electron micrographs of some of the samples are shown in Fig. 5. Silica-rich films were observed on many of the samples (identification by XRD), arising from dissolution of the vials, followed by precipitation of quartz upon cooling of the samples. In the case of samples irradiated in the absence of clays, an unidentified precipitate containing Ca, U, Na, Si and Cl formed. Grain-boundary etching occurred in some of the samples, in particular those exposed to bicarbonate solution and gamma radiation.

Weight loss data provided little useful information. Poor agreement between duplicates was observed, with weight gains occurring in some cases. This was presumably the result of a combination of quartz precipitation, alteration product formation, and oxide dissolution occurring simultaneously.

From the XPS and SEM/EDX data, three important observations were made:

(a) In the WN-1 solution, in the absence of clays, UO_2 samples were more oxidized under irradiation than in its absence.

(b) The presence of clays tended to limit the oxidation of $UO_{2.15}$ surfaces, both in the presence and absence of radiation.

Reduction of $UO_{2.15}$ to $UO_{2.1}$ appears to have occurred in the presence of illite and gamma radiation.

(c) In bicarbonate solutions, UO_2 oxidation proceeded no further than a surface composition of approximately $UO_{2.33}$ for both gamma-irradiated and unirradiated samples. Although no more oxidized than the unirradiated sample, the gamma-irradiated sample had clearly undergone substantially more dissolution (compare Figs. 5H and 5I).

3.2.3. Discussion and Conclusions

The previous observations can be explained by considering the interaction of UO_2 with species produced by solution radiolysis and with species released from the clays. Gamma radiolysis of complex solutions produces a large number of species that potentially can interact with UO_2 and clays. It is not possible to establish with certainty the species responsible for the observed oxidation (or reduction) of the UO_2 surfaces. The results obtained in the presence and absence of clays, however, suggest that some clay components can act to remove oxidizing species. Table 4 indicates that the illite contained substantially more Fe(II) than the bentonite. It is postulated that the reduction of the $UO_{2.15}$ to $UO_{2.1}$ in the presence of illite was due to the release of Fe(II) into solution. Theoretical calculations by Christensen and Bjergbakke, (1982) predict that Fe(II) would act to remove, from solution, species that could oxidize UO_2. In addition, the radiolytic yield of hydrogen in the presence of dissolved Fe(II) is significantly higher than in its absence. Although molecular hydrogen is a poor reducing agent at temperatures below $100^{\circ}C$ (Tremaine and Leblanc, 1980), over long periods of time at $100^{\circ}C$ it is probably quite an effective reducing agent. The observed oxidation behavior in the absence of clays suggests that the oxidizing species produced by solution radiolysis are kinetically more reactive than the reducing species. While the number of equivalents of oxidizing and reducing species produced by radiolysis must initially be equal, the reaction rates of the various species with UO_2 and with other solution species are expected to be quite different. In addition, the escape of hydrogen into the gas phase would ensure that solutions without Fe(II) would be oxidizing.

The oxidation behavior of UO_2 in 10^{-2} M $NaHCO_3$ solutions is in agreement with work of Shoesmith et al. (in preparation), who postulated the reaction scheme shown in Fig. 6 for UO_2 oxidative dissolution. In the presence of a high concentration of complexing species, such as carbonate, surface oxidation proceeds no further than $UO_{2.33}$. At this point, UO_2^{2+} is removed to solution as the dicarbonate complex. As shown in Figs. 5H and 5I, much greater dissolution occurred in the presence of gamma radiation than in its absence, perhaps because of the oxidizing power of the CO_3^- radical (Gromov, 1981).

The results described here illustrate clearly that gamma-radiolysis of leaching solutions may be an important factor influencing used-fuel leaching. This is supported by the work of several researchers (Johnson, 1982; Forsyth et al., in press; Norris, 1979), who have reported attempts to perform fuel-leaching studies at temperatures below 100°C using hydrogen gas as a reducing agent. Dissolution rates were reported to decrease by a factor of 5 to 30, relative to rates in air-saturated water. Based only on the lower oxygen concentrations achieved in those studies, a dissolution rate decrease of a factor of 10^2 to 10^3 would have been predicted assuming a linear dependence of rate on oxygen concentration (Grandstaff, 1976). This, however, ignores further reduction of the dissolution rate which should have occurred if the hydrogen reducing agent were stabilizing the UO_2. The results reported in the present study indicate that oxidation due to gamma-radiolysis (ignoring beta- and alpha-radiolysis, which may be even more significant factors) is, in itself, sufficient to prevent the attainment of reducing conditions, and could explain the anomalous results from the aforementioned studies.

The effect of Fe(II), in mitigating the effects of radiolysis, may be an important factor with regard to the disposal of used fuel in clay buffer materials or in any situation where iron-based container materials are used. Whereas the presence of Fe(II) may be of less significance in the case of alpha-radiolysis, because the radiolysis reactions will occur at the fuel-water interface, the effects of species such as Fe(II) in modifying the radiation chemistry of leaching solutions clearly warrants further study. The approach developed here will be applied to investigating the effects of alpha-radiolysis on UO_2 dissolution in the presence and absence of Fe(II) and clay buffer materials.

3.3. Effects of Alpha-Radiolysis on UO_2 Dissolution

3.3.1. Introduction

Alpha radiation is densely ionizing (alpha particle range ~ 30 μm) and considerable yields of radiolysis products are to be expected at the surface of the fuel, especially in pores and cracks. Consequently, oxidation and dissolution of UO_2 via reactions with alpha-radiolysis products is a distinct possibility.

3.3.2. Experimental

An electrochemical cell was used to monitor the effects of alpha-radiolysis on the corrosion potential of a UO_2 electrode. In this cell the UO_2 electrode can be brought to within ~ 20 μm of a gold-plated alpha-source (^{210}Po; $t_{1/2}$ = 138 days), the potential of which can also be monitored. A three electrode cell arrangement is used so that conventional electrochemical experiments, such as voltammetry, can be conducted on the UO_2 and, possibly, also on the gold surface of the plated alpha-source. Measurements of the UO_2 corrosion potential, with no alpha-source present, in the presence of added H_2O_2, or in O_2-saturated solutions, have also been made in order to provide a data-base with which to compare and interpret the effects of alpha-radiolysis.

3.3.3. Results

Fig. 7 shows the corrosion potential of UO_2 in close proximity to a 3.7×10^7 Bq alpha-source (dose rate ∿ 580 Gy/h) in Ar-degassed 0.1 mol/L $NaClO_4$ (pH = 9.55). With a separation of ∿ 30 µm, a potential of +65 mV (vs SCE) is achieved after ∿ 20 h of exposure. By comparing this value to the value of ∿ -200, increasing to -60 mV (vs SCE) measured in the absence of the alpha-source, and attributable to oxidation by residual traces of dissolved O_2, it is evident that the radiolytic decomposition of water establishes a more oxidizing condition at the UO_2 surface. Cathodic stripping voltammetric experiments show that significant film formation occurs in the potential region -600 to -50 mV (vs SCE), so that by the time the potential reaches +65 mV a layer of undetermined composition, UO_{2+x}, exists on the surface of the UO_2 electrode.

When the electrode separation is increased to ∿ 750 µm, the volume of solution between the electrodes is increased by a factor of 25, thereby sweeping the radiolysis products away from the UO_2 surface. Consequently, the corrosion potential falls to ∿ -40 mV (vs SCE). When the electrode separation is again decreased to 30 µm, the oxidizing conditions are reestablished as the concentration of radiolysis products builds up, and this is reflected in the anodic shift in potential, Fig. 7. Even after a further 4 h the potential decreases to ∿ -50 mV when the electrodes are separated, suggesting very little irreversible surface oxidation over and above the formation of UO_{2+x}, which is also observed in the absence of the alpha-source. This is supported by cathodic stripping voltammetric experiments of the UO_{2+x} film caused by exposure to the alpha-source. Whether or not there is a change in the composition of the film needs confirmation by X-ray photoelectron spectroscopy.

3.3.4. Discussion

Assuming the "active" radiolysis product is H_2O_2, then the following reactions involving H_2O_2 are possible at the UO_2 surface:

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \tag{1}$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e \tag{2}$$

$$4UO_{2.25} + 2H^+ \rightarrow 4UO_2^{2+} + H_2O + 6e \tag{3}$$

plus the sequence of film-formation reactions:

$$UO_{2.25} \rightarrow UO_{2.33} \rightarrow UO_{2.5} \rightarrow UO_{2.67} \tag{4}$$

where $UO_{2.25}$ is assumed to be the composition of the initially formed UO_{2+x} surface layer. The irreversible oxidation reactions ((4) above), which generally accompany dissolution in non-complexing solutions (Sunder et al., 1981), do not appear to occur, and of the other three reactions, a coupling of (1) and (2) leading to H_2O_2 decomposition, i.e.,

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{5}$$

appears to predominate over uranyl ion dissolution. This is illustrated by the data in Fig. 8, which shows the corrosion potential of UO_2 in 0.1 mol/L $NaClO_4$ (pH $\sim$ 9.7) solutions containing various concentrations of H_2O_2. Over the concentration range 10^{-5} to 10^{-3} mol/L the potential is independent of peroxide concentration, as expected for the coupling of reactions (1) and (2) (i.e., the Nernst relationship predicts potential shifts of equal magnitude but opposite sign for the two reactions). For concentrations $>10^{-3}$ mol/L, the potential shifts to more anodic values and UO_2 dissolution is accelerated by the coupling of reactions (1) and (3). This conclusion is borne out by our own and other (Needes and Nicol, 1973) electrochemical experiments.

From these results we can conclude that alpha-radiolysis of water leads to the establishment of oxidizing conditions at the UO_2 surface due to the build-up of H_2O_2, but that peroxide decomposition tends to predominate over the oxidative dissolution of UO_2. The relative importance of these two reactions has not yet been determined. Also, the time scale for these studies was relatively short (~ 30 h), and hence we cannot yet say whether UO_2 oxidation will become more important with time.

Obviously there is a need to determine the relative importance of UO_2 dissolution compared to H_2O_2 decomposition, and whether significant UO_2 attack occurs over long periods of time. Presently we are using published models for the alpha-radiolysis of water to estimate the expected concentrations of H_2O_2 as a function of dose rate within the gap between the UO_2 electrode and the alpha-source. Our model takes into account the loss of H_2O_2 by diffusion out of the gap. Simultaneously we are attempting to analyze the actual H_2O_2 concentration in the gap by applying a voltammetric sweep to the gold-plated alpha-source, and taking the value of the current as a measure of H_2O_2 concentration. Also, we intend to study the change in composition of the UO_2 surface using X-ray photoelectron spectroscopy. By a combination of these approaches, we hope to clarify the extent of UO_2 attack and how it is related to the alpha dose rate. Finally we intend to extend our studies to chloride- and carbonate-containing solutions, which could produce other oxidizing species such as Cl_2, ClO_2, $Cl^{\cdot}$, Cl_2^-, Cl_3^-, and CO_3^- in the presence of an alpha-field.

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TABLE 1. Release of Stable Xenon and ^{137}Cs from Used CANDU Fuel

Used Fuel* Identity	Reference**	% Stable Xenon in Gap		% ^{137}Cs Leached at 25°C	Average % ^{137}Cs Leached at 25°C
		Calculated	Measured		
F21271C, O.E.	(1)	2.35	2.75	0.8-2.1	1.35
F21271C, Int. E.	(1)	0.07	0.13	0.03-0.07	0.05
	(2)	0.07	0.13 (assumed)	0.010-0.015	0.013
F21271C, Inn. E.	(1)	0.05	0.07	0.01	0.01
	(2)	0.05	0.07 (assumed)	0.004-0.018	0.012
F21271C, C.E.	(1)	<0.1 (estimated)	N.D.	0.01	0.01
	(2)	0.05	N.D.	0.012-0.019	0.016
A01789, O.E.	(1)	0.26	0.96	0.07-0.65	0.316
A01790, O.E.	(1)	0.46	1.76	0.10-0.71	0.4
15527C, O.E.	(1)	5.9	8.9	3.1-4.0	3.55
A01756, O.E.	(1)	0.4	N.D.	0.4	0.4
A13894W, O.E.	(2)	0.64	1.28	0.39-1.52	0.96
A07993W, O.E.	(2)	0.42	4.31	5.58-11.67	8.63

* O.E. = outer element
Int. E. = intermediate element
Inn. E. = inner element
C.E. = centre element
N.D. = not determined

** (1) Johnson et al., 1983
(2) this work

TABLE 2. Release of Stable Xenon and ^{129}I from Used CANDU Fuel

Used Fuel Identity*	Reference**	% Stable Xenon in Gap Calculated	% Stable Xenon in Gap Measured	% ^{129}I Leached at 25°C	Average % ^{129}I Leached at 25°C
F21271C, O.E.	(1)	2.35	2.75	2.5	2.5
A13894W, O.E.	(2)	0.64	1.28	1.18-2.36	1.77
A07993W, O.E.	(2)	0.42	4.31	4.7-10.4	7.55

* O.E. = outer element

** (1) L.H. Johnson et al., 1983

(2) S. Stroes-Gascoyne, this work

TABLE 3. Composition of WN-1 Groundwater Used in Gamma-Irradiation Dissolution Studies

Species	mg/L
Na	1910
K	14
Mg	61
Ca	2130
Sr	24
Fe(III)	0.56
HCO_3	68
Cl	6460
SO_4	1040
NO_3	33

TABLE 4. Composition of Clays

	"ILLITE" wt.%	"BENTONITE" wt.%
Montmorillonite	-	79
Illite	40	9.5
Quartz	30	5
Plagioclase feldspar	3	3
Gypsum	-	2
Carbonate	7.5	1.5
Chlorite	14	-
Vermiculite	5	-
Organic matter	0.6	0.12
Fe(II)*	2.2	0.3
Fe(III)*	4.9	3.3

* Fe is contained both within the indicated mineral phases and as discrete oxides. All wt.% values are approximate.

TABLE 5. Test Conditions and Final UO_2 Surface Compositions for Gamma Radiolysis Experiments

Groundwater	Clay	Radiation Field[1]	UO_2 Surface Composition[2,3,4]
WN-1	none	no	$UO_{2.38}$, $UO_{2.40}$
WN-1	none	yes	$UO_{2.49}$, $UO_{2.46}$
WN-1	bentonite	no	$UO_{2.19}$, $UO_{2.39}$
WN-1	bentonite	yes	$UO_{2.20}$, $UO_{2.22}$
WN-1	illite	no	$UO_{2.22}$, $UO_{2.25}$
WN-1	illite	yes	$UO_{2.09}$, $UO_{2.10}$
10^{-2} mol/L $NaHCO_3$	none	no	$UO_{2.31}$, $UO_{2.30}$
10^{-2} mol/L $NaHCO_3$	none	yes	$UO_{2.35}$, $UO_{2.34}$

[1] Gamma dose rate = 4.1 Gy/h
Cumulative dose = 4.8×10^4 Gy

[2] All experiments run in duplicate

[3] Analytical uncertainty = ±0.05 in oxygen content

[4] Unreacted reference samples - $UO_{2.15}$, $UO_{2.16}$

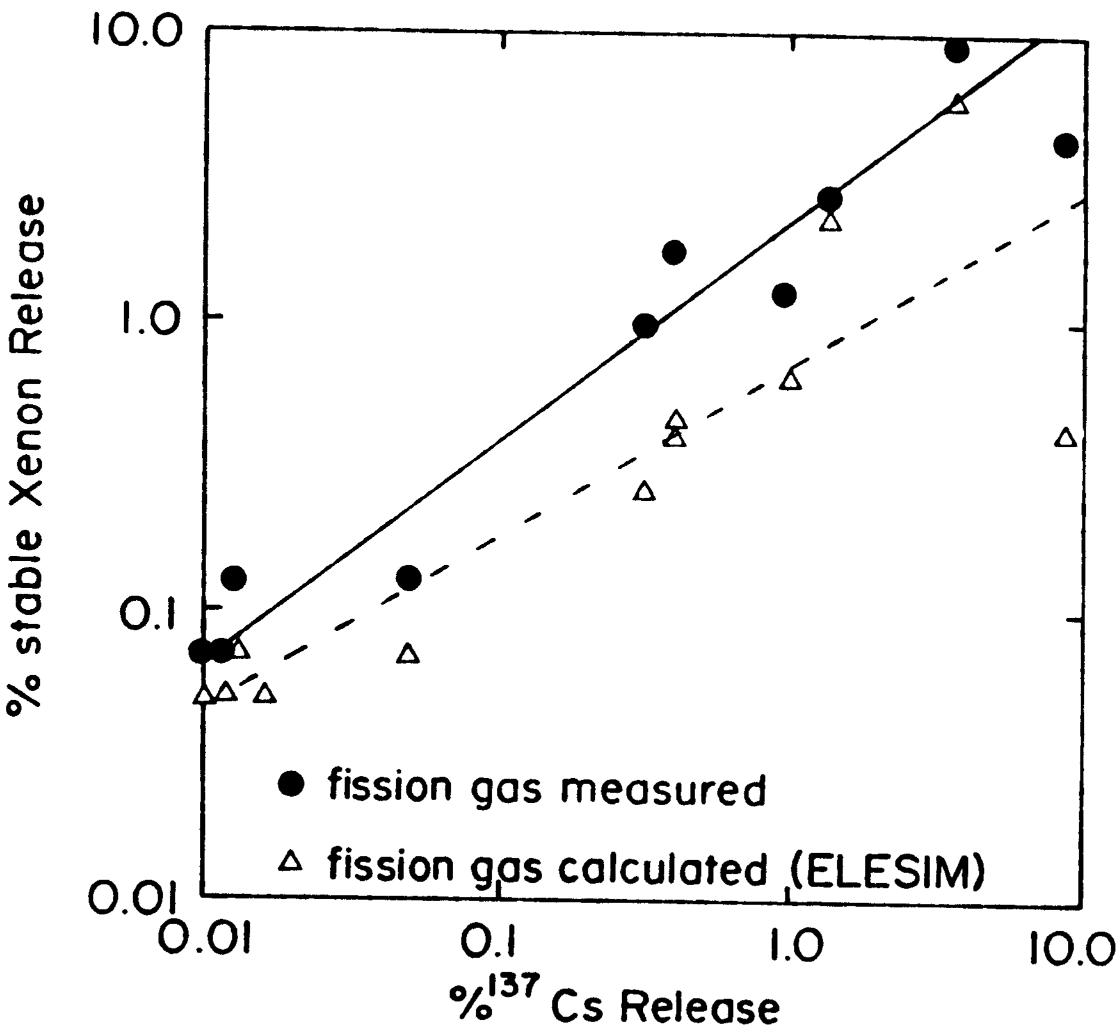


Fig. 1. Relationships between measured and calculated stable xenon release and ^{137}Cs release during leaching.

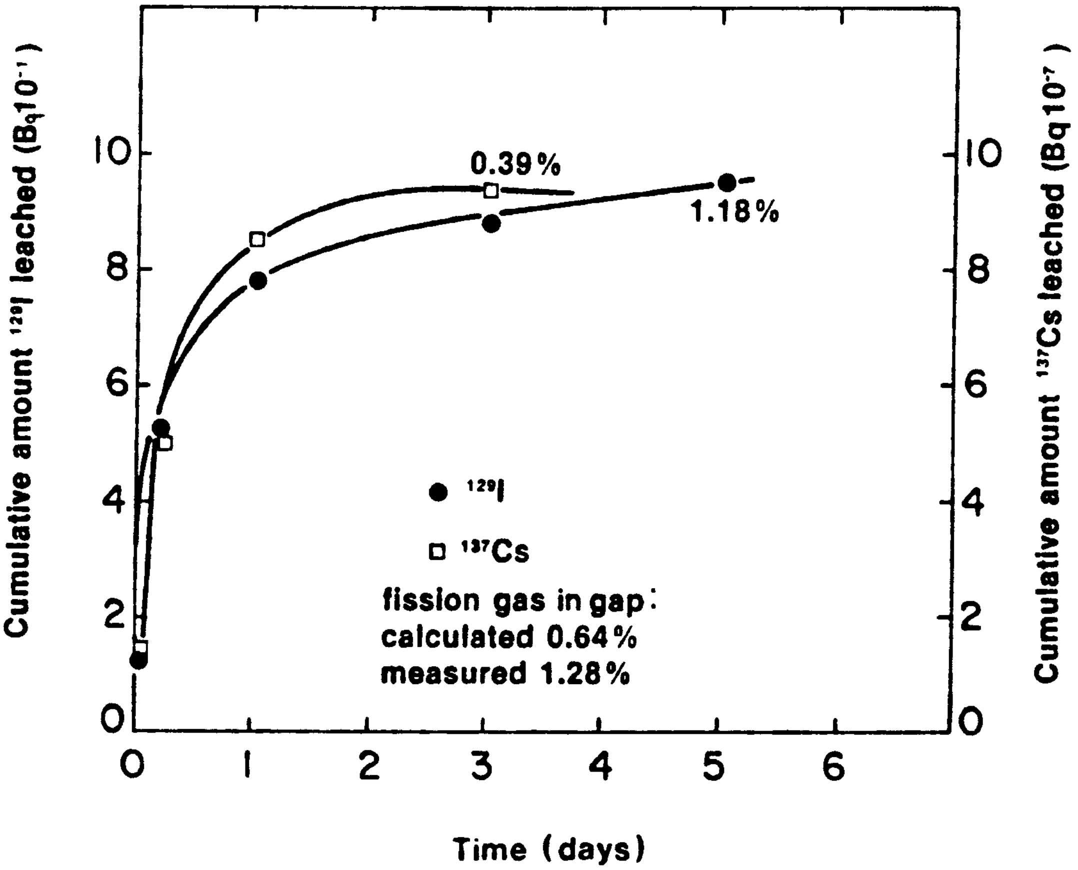


Fig. 2. Cumulative amounts of ^{129}I and ^{137}Cs leached in distilled water at 25°C from a 2-cm piece of element #9 of Pickering fuel bundle A13894W.

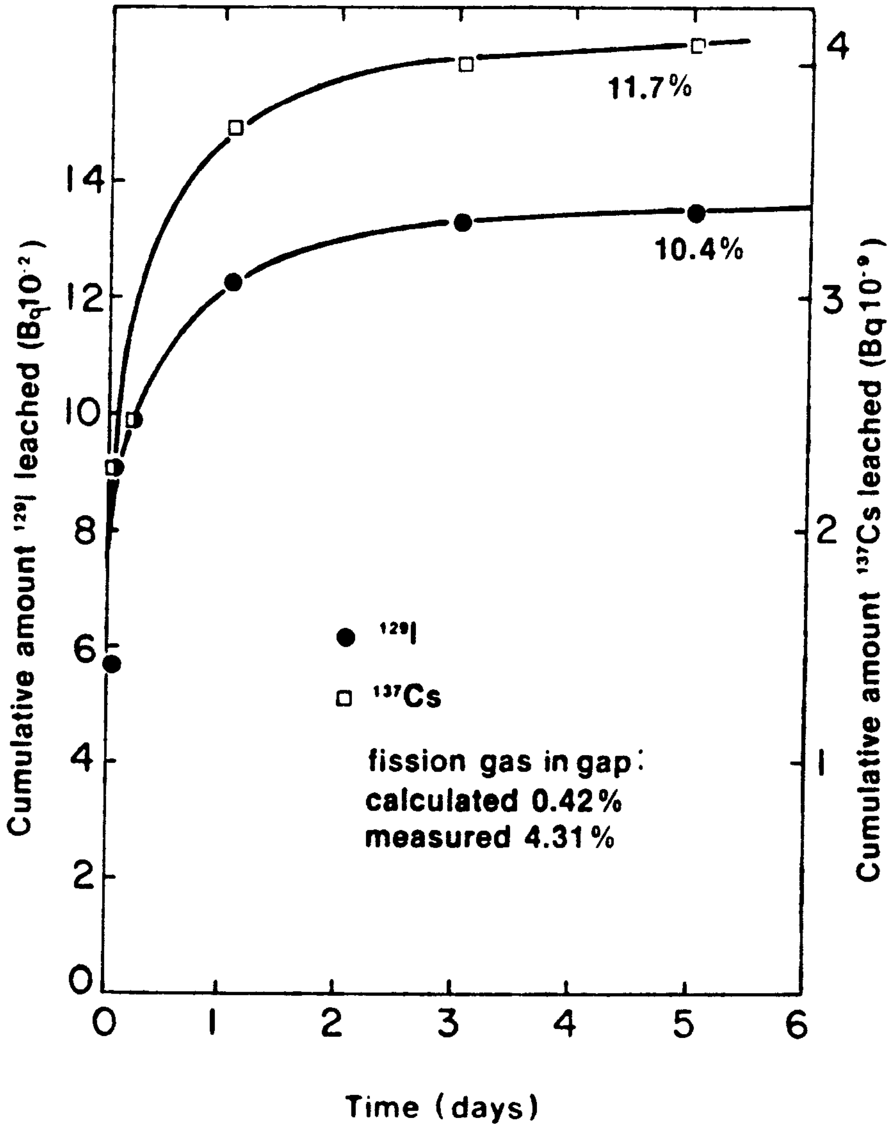


Fig. 3. Cumulative amounts of ^{129}I and ^{137}Cs leached in distilled water at 25°C from a 2-cm piece of element #9 of Pickering bundle A07993.

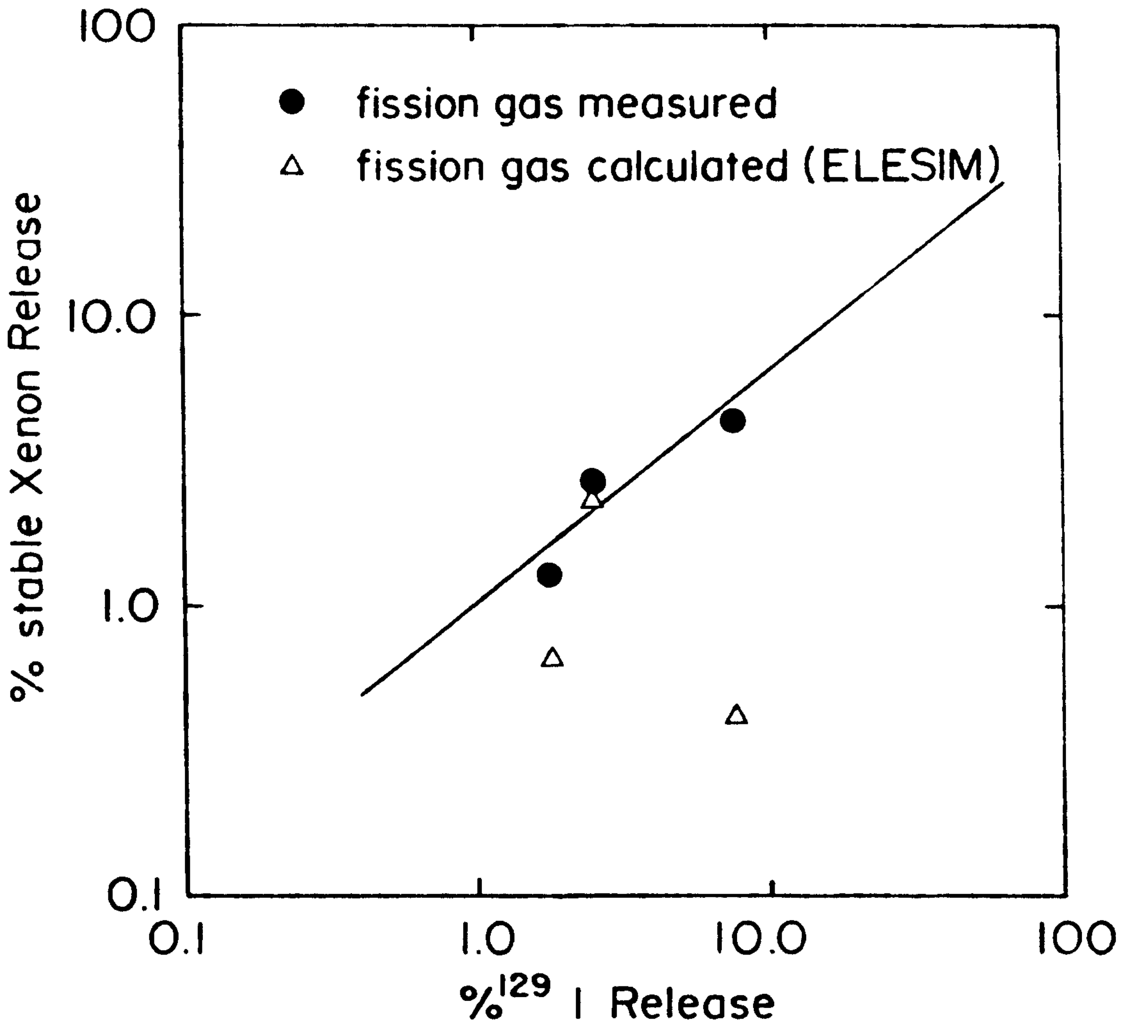
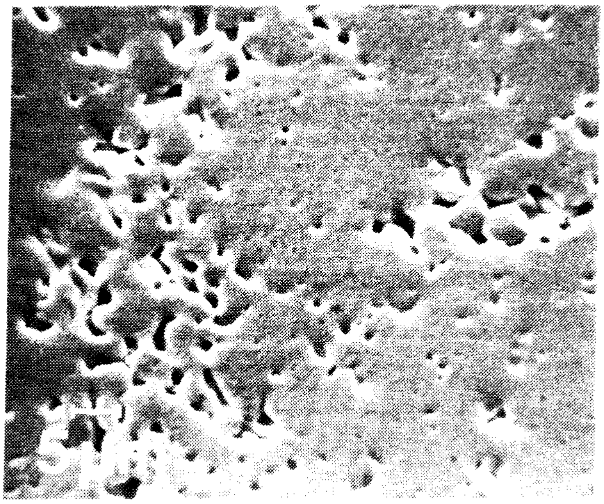
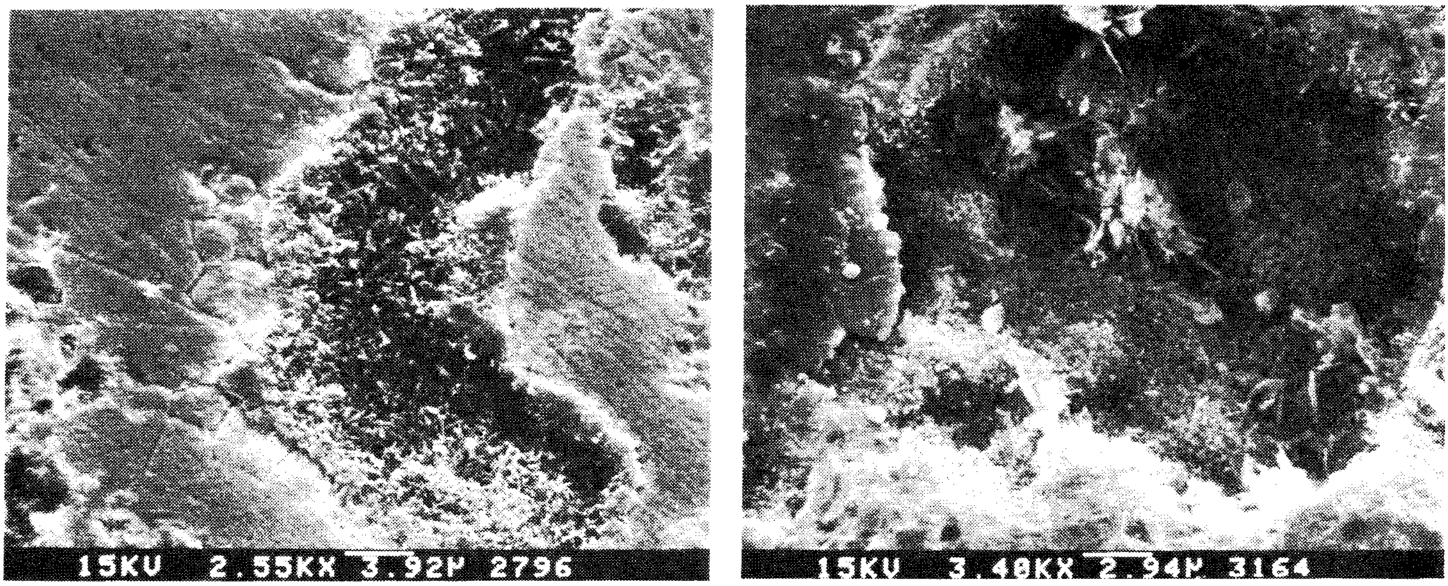


Fig. 4. Relationships between measured and calculated fission gas release and ^{129}I release during leaching.

Fig. 5. Scanning electron micrographs of UO_2 pellet samples from UO_2-gamma radiolysis experiment. See Table 5 for details

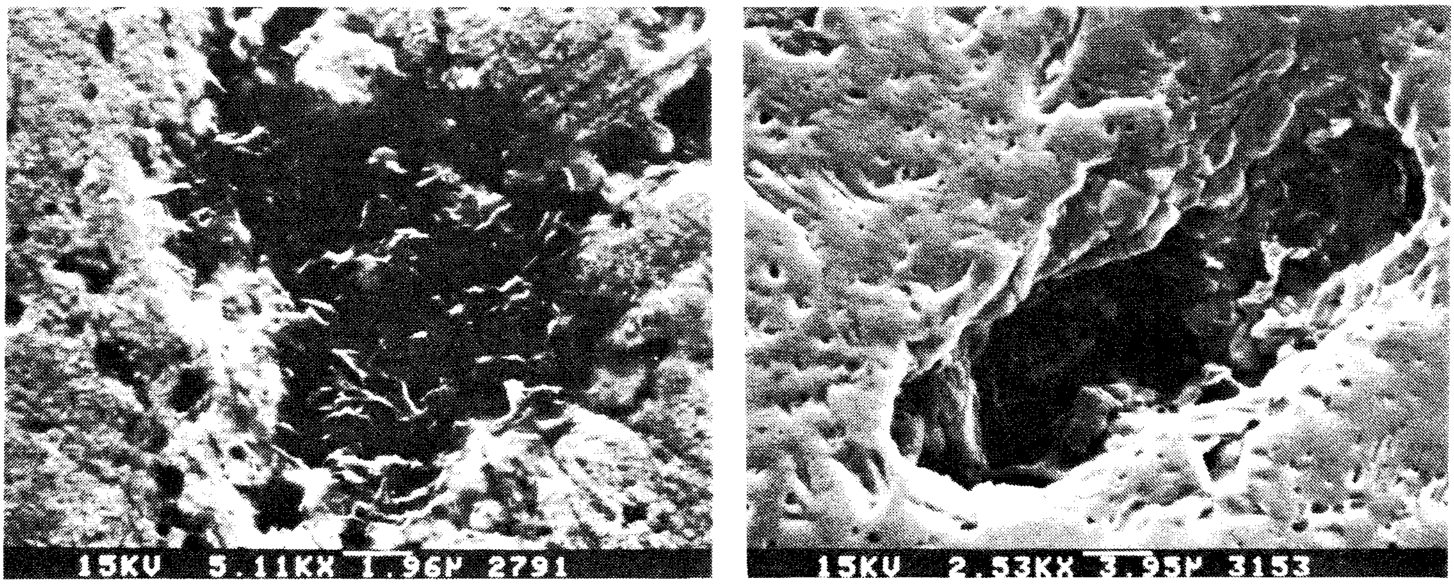


A. unreacted reference sample



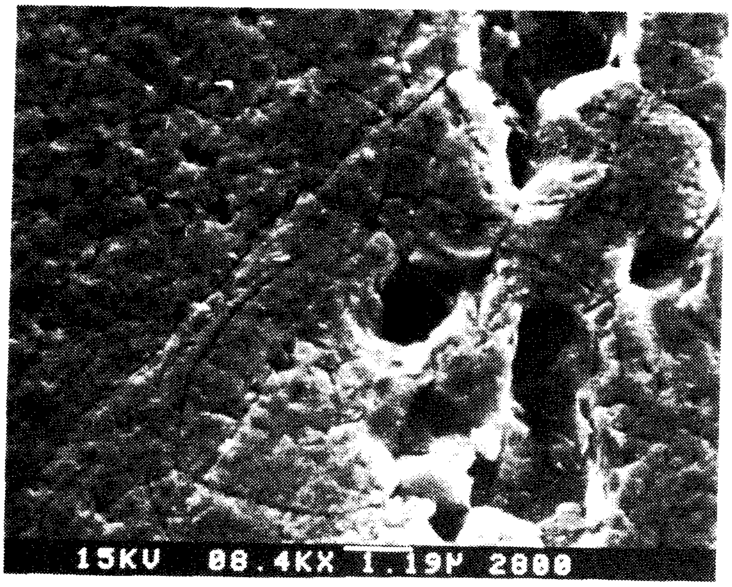
B. sample exposed to WN-1 solution, unirradiated

C. sample exposed to WN-1 solution, γ-irradiated

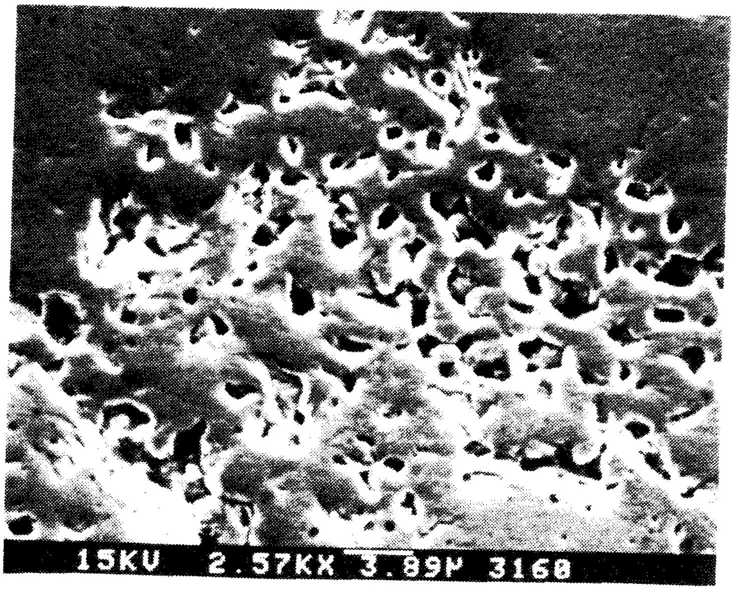


D. sample exposed to 0.2 g/mL bentonite in WN-1 solution, unirradiated

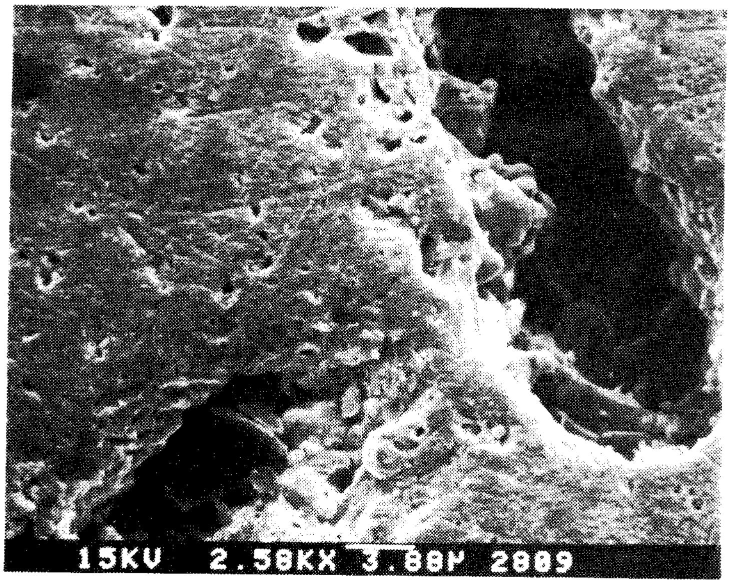
E. sample exposed to 0.2 g m/L bentonite in WN-1 solution, γ-irradiated



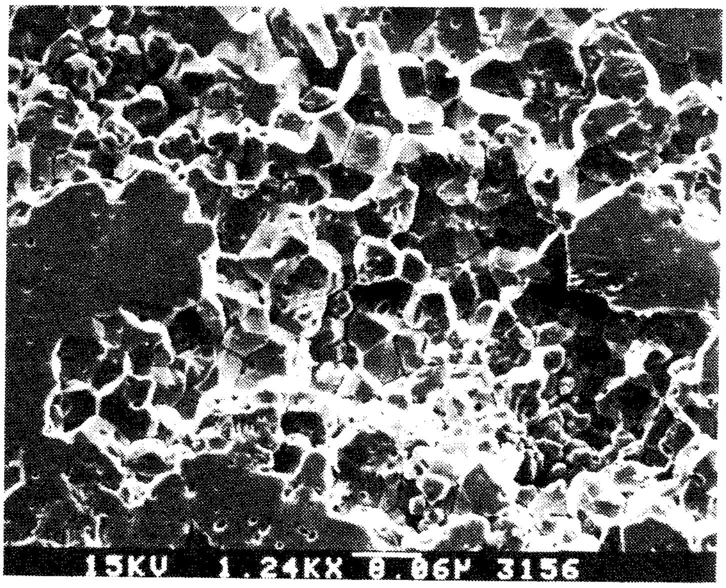
F. sample exposed to 0.2 g/mL illite in WN-1 solution, unirradiated



G. sample exposed to 0.2 g/mL illite in WN-1 solution, γ-irradiated



H. sample exposed to 10^{-2} mol/L $NaHCO_3$ solution, unirradiated



I. sample exposed to 10^{-2} mol/L $NaHCO_3$ solution, γ-irradiated

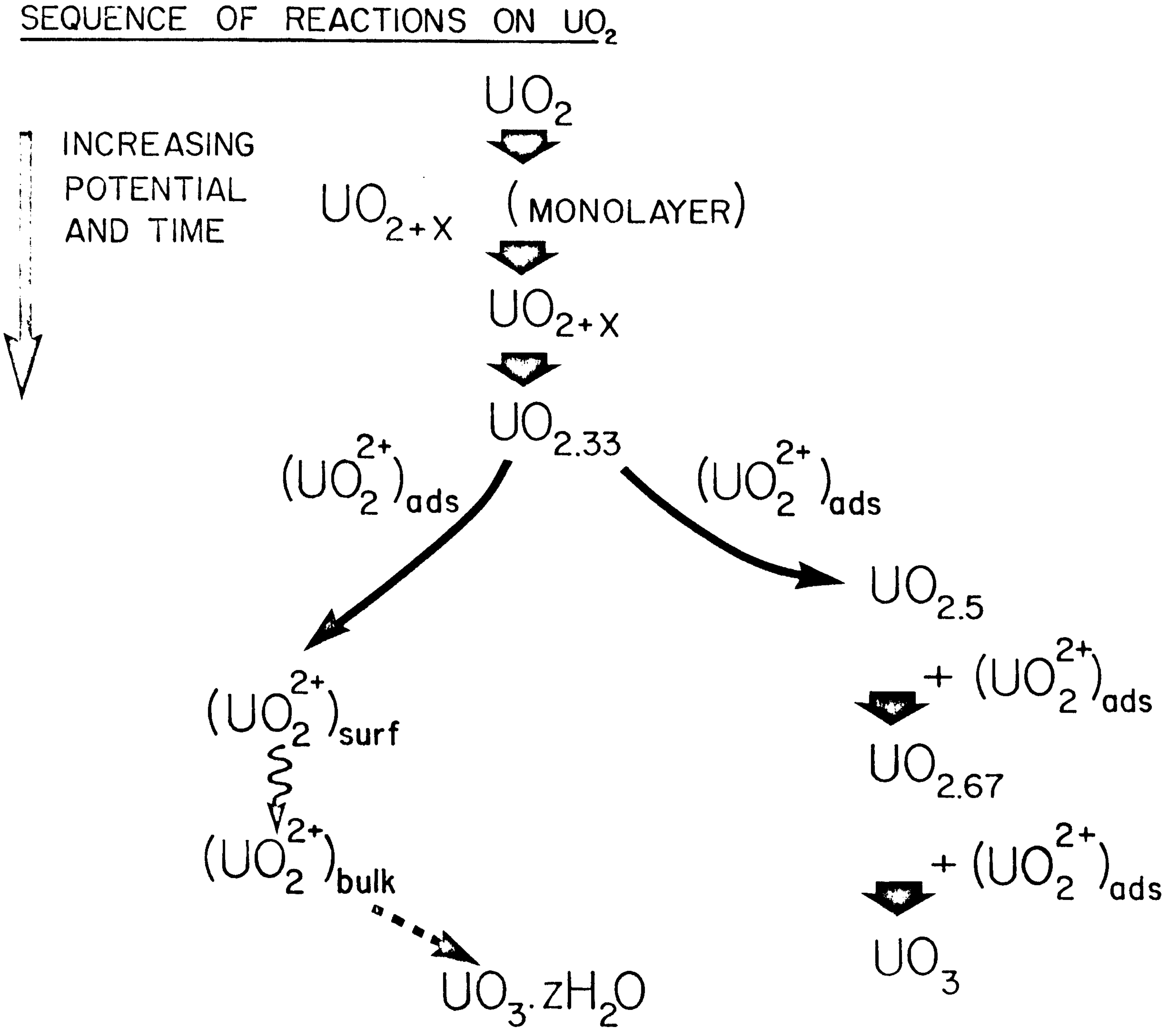


Fig. 6. Reaction sequence for UO_2 during oxidative dissolution in complexing solutions (left branch) and non-complexing solutions (right branch).

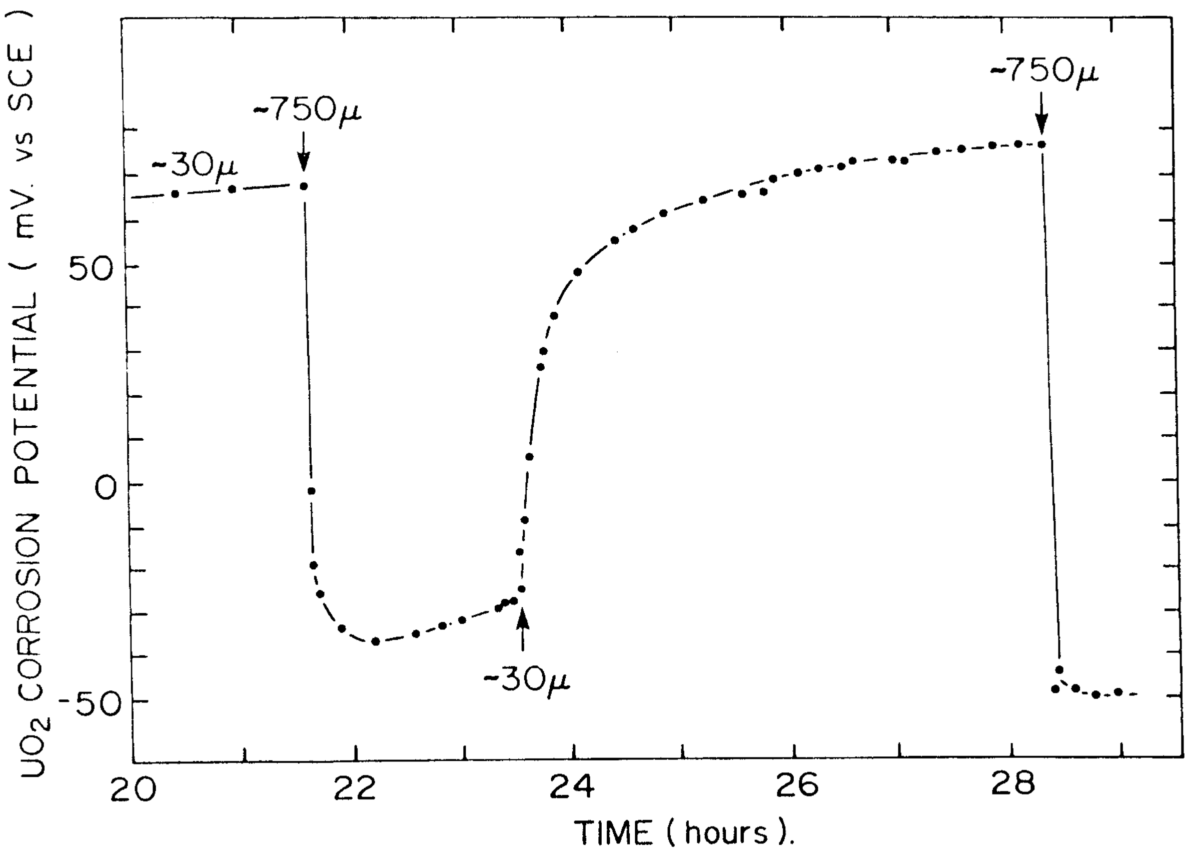


Fig. 7. UO_2 corrosion potential as a function of time for two values of electrode separation from a gold-plated 3.7 x 10^7 Bq alpha-source (estimated dose rate ∿ 580 Gy/h); 0.1 mol/L $NaClO_4$ (pH = 9.55).

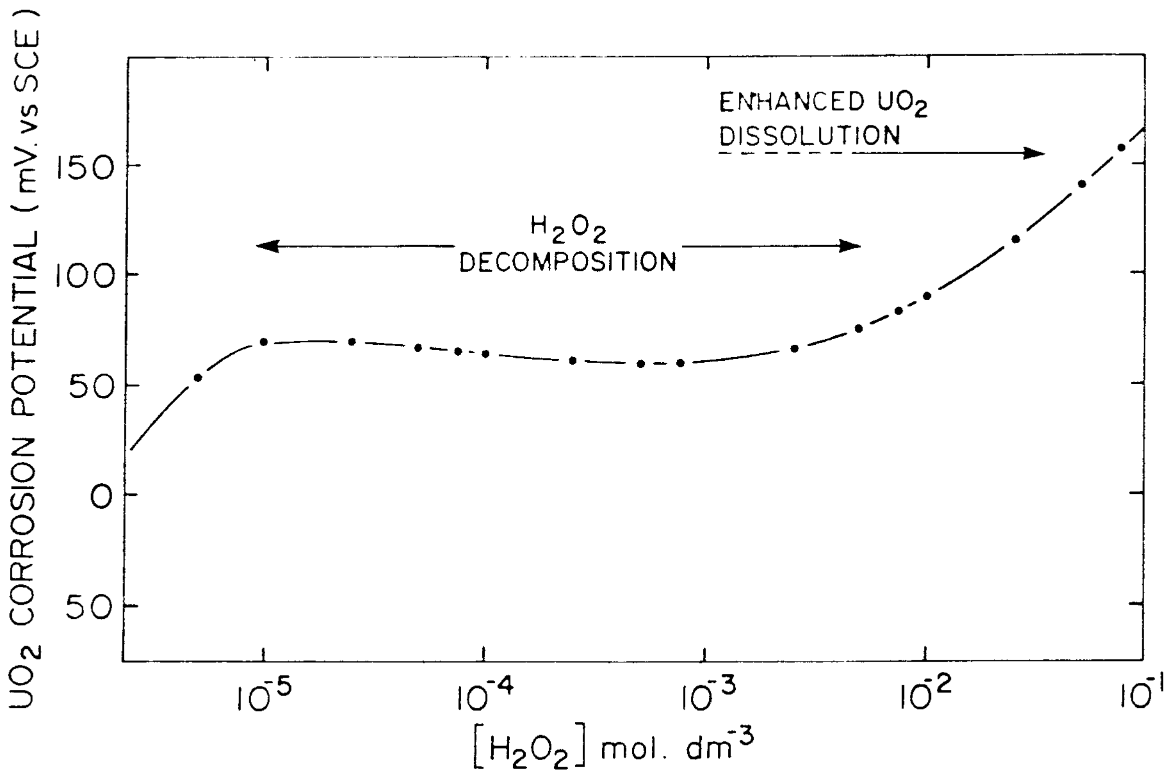


Fig. 8. UO_2 corrosion potential, as a function of hydrogen peroxide concentration, in 0.1 mol/L $NaClO_4$ (pH ∿ 9.7).

COMPARISON OF SPENT FUEL AND UO_2 RELEASE IN SALT BRINES

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ABSTRACT

Leach tests have been performed on spent fuel in synthetic Permian Basin salt brine at 25 and 75°C. Complementary tests on unirradiated UO_2 pellets have been conducted in both salt brine and deionized water in the range 25 to 150°C. Iron and/or oxidized zircaloy coupons were included in some of the tests. Uranium release from spent fuel was more than 100 times greater than from UO_2. In brine, iron had no significant effect on the total uranium release but substantially reduced the amount in solution by causing the uranium to plate out on the iron coupon and container walls and to precipitate as filterable particles.

INTRODUCTION

Spent fuel is being considered as a possible waste form for disposal in domed or bedded salt. To adequately model the release of radionuclides from a repository, it is necessary to understand the leach behavior in salt brines and the chemical interactions of the released radionuclides with their environment. Toward this end, leach tests were conducted on unclad spent fuel in salt brine; some of the tests contained coupons of ductile iron which is a candidate overpack material. In addition, the distribution of radionuclides after release from the spent fuel was investigated. That is, the proportion of radionuclides in true solution, suspended in solution as small particulates, or plated-out on the container walls or iron coupons was established.

Because of the expense of conducting experiments using actual spent fuel, other series of tests were conducted using UO_2 pellets depleted in U-235. Interactive effects of both iron and oxidized zircaloy, separately and together, were also evaluated. The latter was used to represent spent fuel cladding. Results from these tests will be used to define experiments aimed toward establishing leaching mechanisms, to identify parameters that should be taken into consideration in future spent fuel experiments, and to provide a comparative data base.

EXPERIMENTAL

Details of the experimental procedures used have been described elsewhere [1]. Briefly, two different experimental matrices were involved in the work described here--one with spent fuel at 25 and 75°C, and one with UO_2 at temperatures of 25, 75, and 150°C. The salt brine used as a leachant in all three tests was a synthetic one made up to simulate the saturated solution produced by dissolving salt from the G. Friemel Hole No. 1 in Deaf Smith County, Texas, which is located within the Permian Basin. The composition of the brine is given in Table I. The ratio of specimen surface area to leachant volume was $SA/V = 10\ m^{-1}$ in all cases.

TABLE I. Salt Brine Composition

	Permian Brine Composition	
Ion	25°C Equilibrated	150°C Equilibrated
Na^+	127,000 ± 300	123,000
K^+	40 ± 2	39
Ca^{2+}	1,580 ± 40	1,100
Mg^{2+}	132 ± 23	122
Sr^{2+}	34 ± 1	35
Zn^{2+}	8 ± 2	8
Cl^-	191,300 ± 600	191,000
SO_4^{2-}	3,260 ± 100	1,910
HCO_3^-	28 ± 15	23
Br^-	27 ± 6	24
BO_3^{3-}	<10	<10

Ductile iron coupons and/or short sections of oxidized Zircaloy-4 tubing were included in some tests. Ductile iron was used to represent a candidate overpack material, and the oxidized Zircaloy-4 tubing was meant to simulate average fuel pin cladding as discharged from the reactor. Surface areas of the iron coupons and zircaloy tubes were made the same as the spent fuel or UO_2 specimen in each individual leach test. Other aspects of the experimental procedures are described separately for the three different matrices.

Spent Fuel Tests at 25 and 75°C

The spent fuel used in this study was discharged from the H. B. Robinson II reactor on June 6, 1974, with an average burnup of 28 MWd/kgM. Unclad fuel fragments from more than one fuel rod were combined and used for testing. Each leach specimen consisted of a single fuel fragment with a surface area of about 2 cm^2.

Static leach tests were conducted in brine at 25°C for periods up to 60 days and at 75°C for 5 and 28 days, and a parallel series of tests was conducted with iron coupons. Each time-temperature test consisted of a single spent fuel specimen (i.e., there were no duplicate tests).

All leach tests were performed in sealed quartz containers. At the end of each test, the solution was cooled (if required) and the pH was measured. The leachants were passed through a 1.8 nm filter and the filtrates were analyzed for U, Pu, Tc, and Cs. Material plated out on the container walls was removed with a 5 $\underline{M}$ HNO_3, 0.05 $\underline{M}$ HF solution. This same type of solution was used to clean the filters. Aliquots of the plate-out and filter solutions were analyzed for the same elements listed above. The iron coupons were stripped with 6 $\underline{M}$ HCl and these solutions were also analyzed for the same four elements.

UO_2 Tests at 25, 75, and 150°C

Cylindrical pellets of UO_2 depleted in U-235 with surface areas of about 3.6 cm^2 were used in these tests. Four combinations of specimens were tested--UO_2 pellets only, UO_2 plus iron, UO_2 plus oxidized

Zircaloy-4, and UO_2 with both iron and oxidized Zircaloy-4. (The last combination was not tested at 150°C.) Each combination (except as noted) was leach tested in brine at all temperatures for periods up to 60 days. Each combination was also tested in deionized water for periods up to 14 days at 25 and 75°C and up to 60 days at 150°C. All these leach tests were performed in sealed Teflon containers.

Following the leach tests, the leachates were handled in a manner similar to that described for the spent fuel tests. An exception was that each leachate was analyzed both before and after passing through a 1.8 nm filter rather than analyzing the residue left on the filters. Also, the various solutions were analyzed only for uranium.

RESULTS

Leach data have been plotted here in terms of normalized uranium mass loss with units of grams per square meter of specimen surface area. The normalization calculation involves simply dividing the total mass loss by the fraction of uranium originally present in the sample, 0.88 in the case of UO_2. In most cases, only a single sample was run for each time-temperature, and the lines on the graphs were drawn through these points (not shown). In the few cases where two or three samples were run, the lines were drawn through the average of the data for that particular time-temperature point. Figure 2 shows some results where only data points (no lines) were drawn because there is only one point (sometimes two).

Data presented here (Figs. 1-5) have been selected from a large volume of data [1] to illustrate the following points:

1. The leaching characteristics of uranium from both UO_2 and spent fuel in brine are nearly independent of temperature over the range studied. This can be seen by comparing Figures 1 and 3. Little more (if any) uranium was released in brine at 150°C than at 25°C. Data not shown for both spent fuel and UO_2 at 75°C support this conclusion.

2. The leaching characteristics of both UO_2 and spent fuel in brine are nearly independent of time. This is illustrated by Figs. 1, 3, and 5. Within the scatter of the data, most of the uranium is released within the first few days. This suggests that the uranium release is restricted by solubility limitations or that there exists a surface phase that is more readily soluble than the bulk material. This is a point that will be returned to later.

3. Unlike brine, leaching of UO_2 in deionized water is dependent on temperature, at least when iron was not present. Fig. 2 compares results from brine and deionized water. Clearly, uranium release values in deionized water, in the absence of iron, are higher at $75^{o}C$ than at $25^{o}C$. Fig. 4 shows that when iron was not present, more uranium was released at $150^{o}C$ than at $75^{o}C$.

4. Considerably more uranium leaches from UO_2 in deionized water than in brine at $150^{o}C$; the difference is less pronounced at $25^{o}C$. Fig. 2 shows that, in the absence of iron, the difference between the uranium released in deionized water and brine is small at $25^{o}C$ but increases at $75^{o}C$. Comparing Figs. 3 and 4 shows that this trend continues at $150^{o}C$ to the point where the release in deionized water is greater than that in brine by more than one order of magnitude. When iron is present, there is little difference between deionized water and brine at 25 and $75^{o}C$, although some difference prevails at $150^{o}C$.

5. Uranium leached from spent fuel in brine is more than 100 times greater than from UO_2. This can be seen by comparing Figure 5 with Figures 1 and 3. Spent fuel results at $75^{o}C$ are similar to those at $25^{o}C$, although the data are not shown here.

6. The presence of iron coupons reduces solution concentrations of uranium; the uranium plates out on the iron and container walls or precipitates as filterable particles. All five figures illustrate this point. Iron has no effect on the total uranium released in brine, but it causes a substantial reduction in solution concentration of uranium probably because it lowers the oxidation

potential, thereby lowering uranium solubility. Although the data are not presented here, the same trend is true for plutonium and technetium in the spent fuel tests. Cesium, the only other element analyzed in the spent fuel tests, was not affected by iron.

7. Oxidized zircaloy coupons have no effect on UO_2 leaching characteristics. Figures 1-3 illustrate this point.

DISCUSSION

Much of the discussion in previous articles on mechanistic investigations [2-4] of UO_2 and spent fuel leaching has involved the effect of the redox potential of the leach solution and the fact that U(VI) is much more soluble than U(IV) [5]. Some of the prominent features of the present study (viz., the effect of iron, the fact that uranium release from spent fuel is at least 100 times higher than from UO_2, and the general tendency for most of the uranium release to occur within the first few days) suggest that more is involved than only solubility limitations based on redox potential. The situation is further complicated by the differences between brine and deionized water. Unlike the case with brine, iron does affect the total uranium released when deionized water is the leachant, and the amount released does depend on temperature.

Restricting the discussion to brine for the moment, iron would be expected to reduce the oxidation potential and thereby lower the uranium solubility. Uranium concentrations in solution were, in fact, found to be considerably lower when iron was present. However, there was no effect on the total uranium released, and one must keep in mind that the total released was more than a factor of 100 higher for spent fuel than for UO_2. It would seem that if solubility limitations were the dominant factor, then either (1) the total uranium released should vary with the presence or absence of iron, or (2) the total release should continue to increase with time when iron is present (since uranium dissolved from the source pellet is removed from solution). Both possibilities are contrary

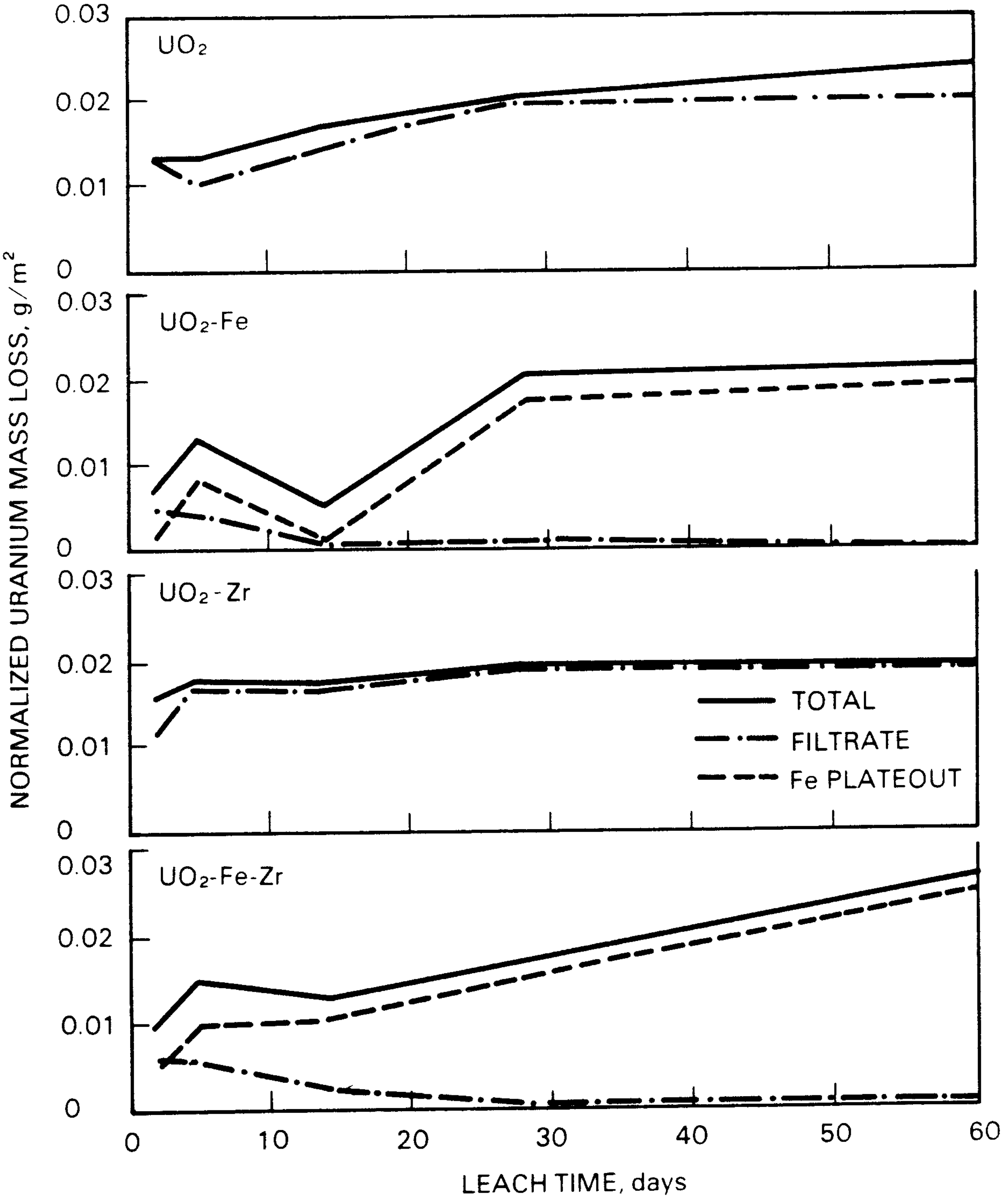

FIGURE 1. Comparison of results between leach systems incorporating UO_2 at 25°C in brine. (Filtrate results are after passing through a 1.8 nm filter)

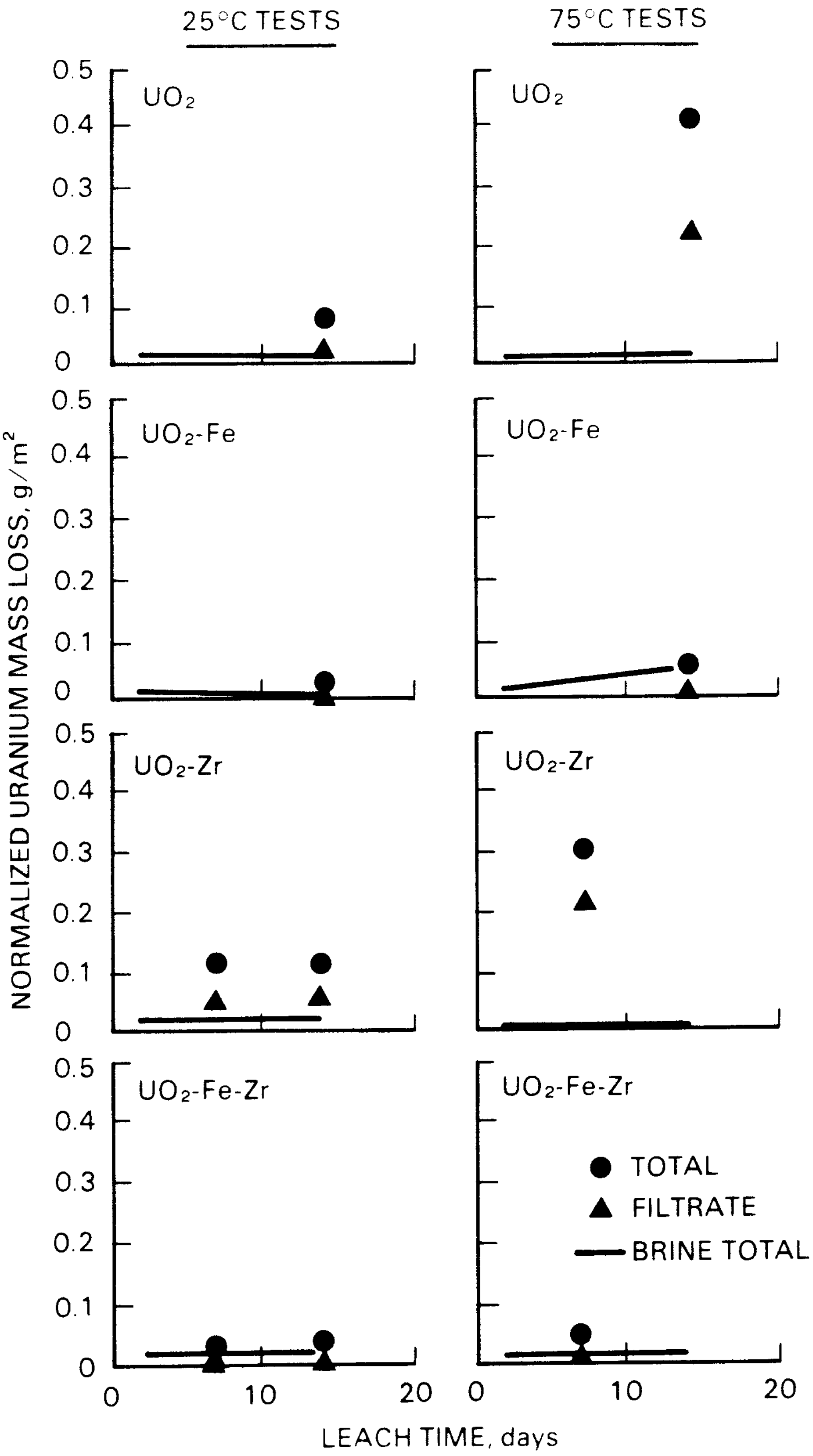

FIGURE 2. Comparison of results between leach systems incorporating UO_2 at 25 and 75°C in deionized water. (Filtrate results are after passing through a 1.8 nm filter.)

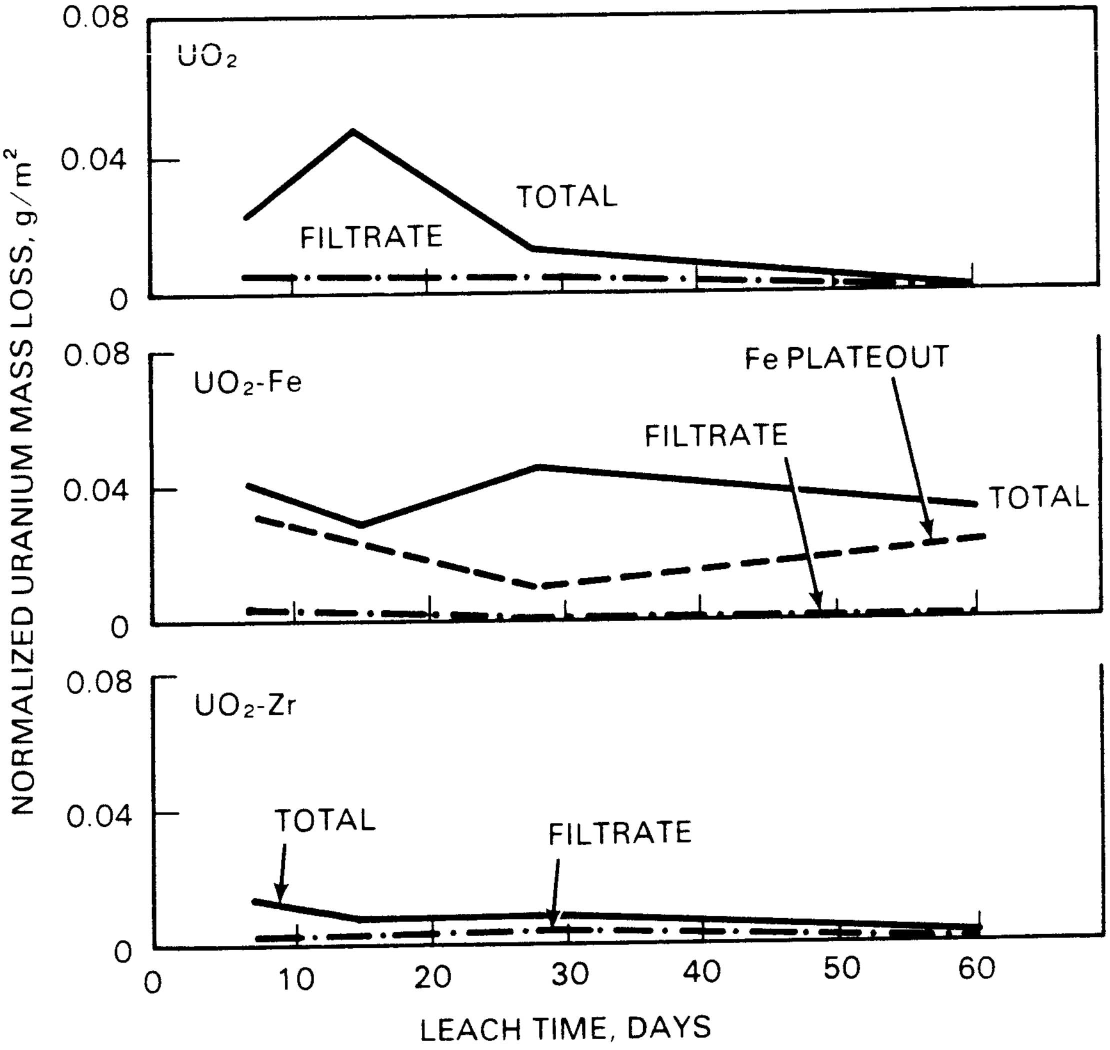

FIGURE 3. Comparison of results between systems incorporating UO_2 at 150°C in brine. (Filtrate results are after passing through a 1.8 nm filter)

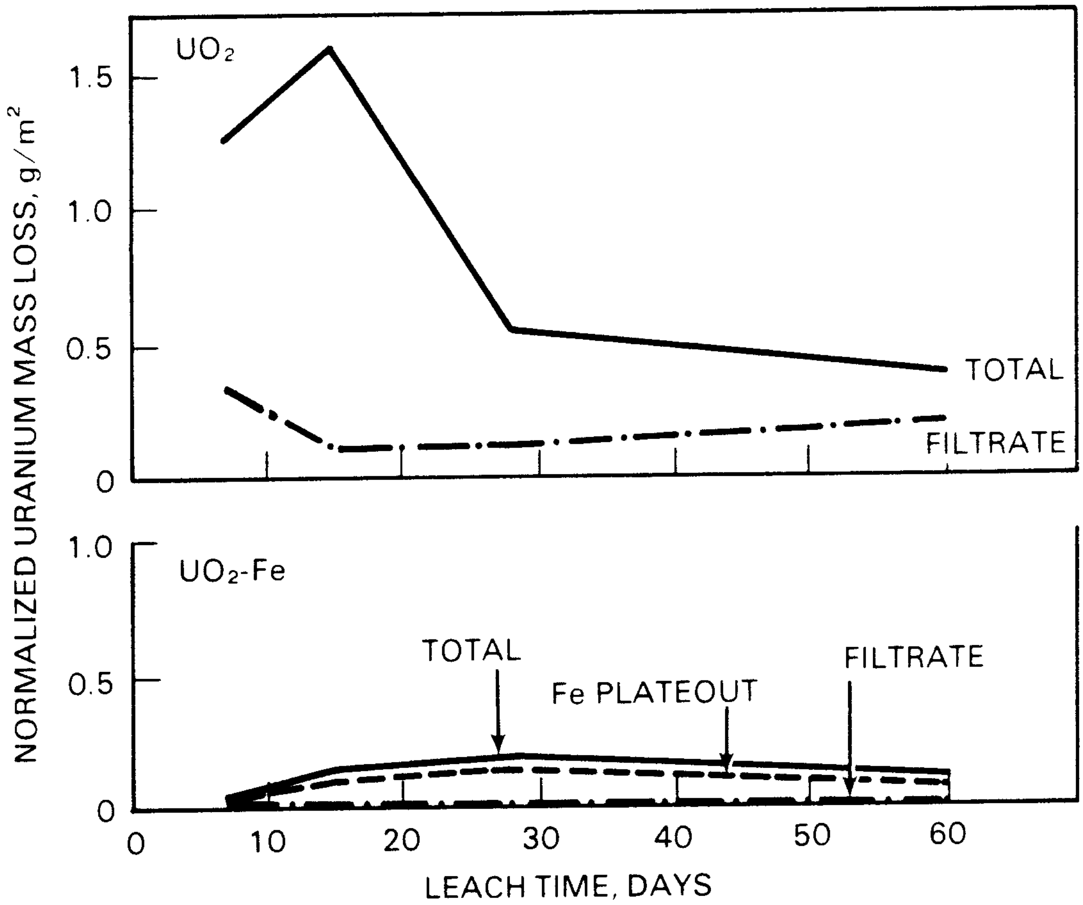

FIGURE 4. Comparison of results between leach systems incorporating UO_2 at 150°C in deionized water. (Filtrate results are after passing through a 1.8 nm filter.)

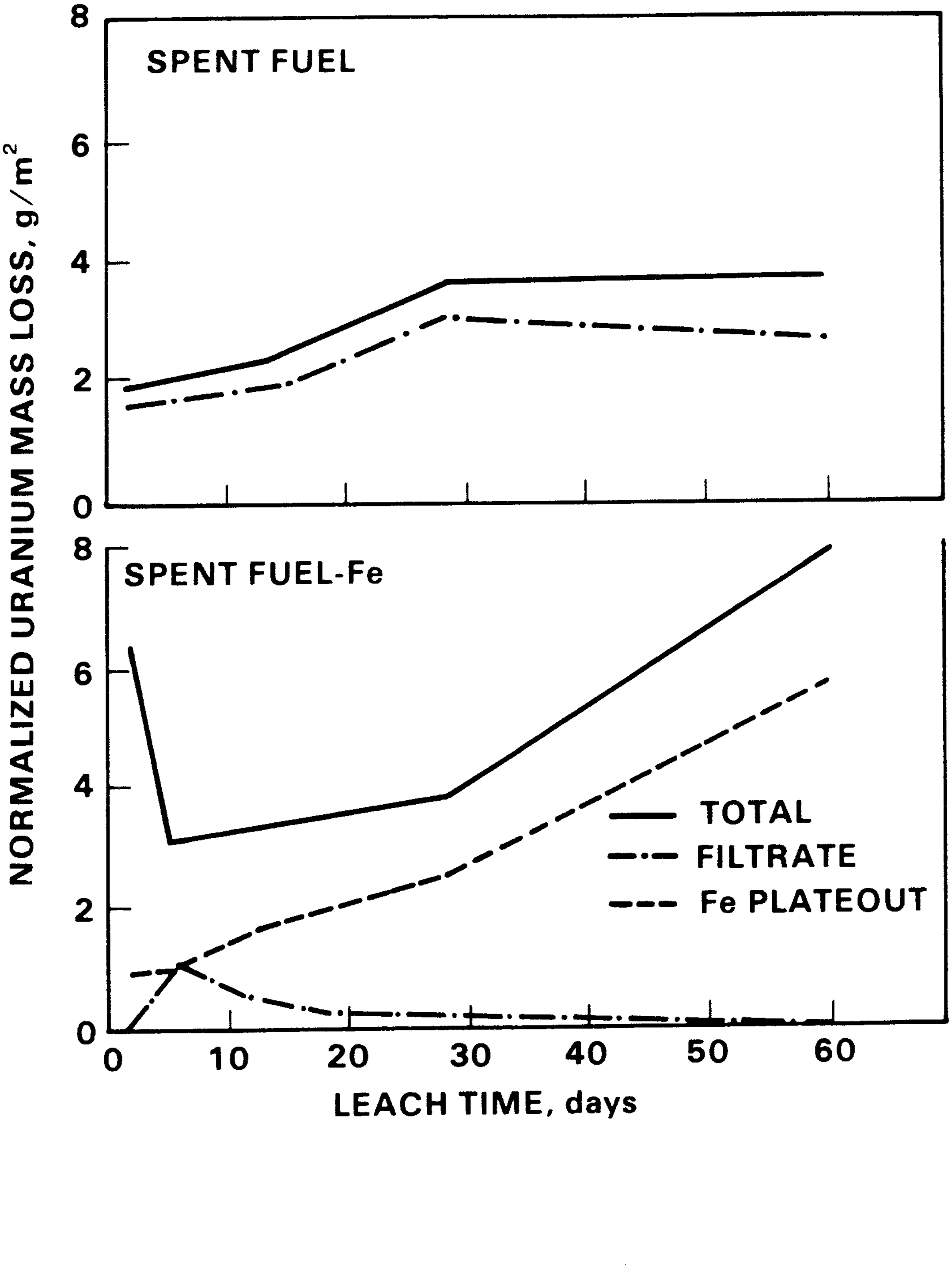

FIGURE 5. Comparison of uranium released in systems incorporating spent fuel at 25°C in brine. (Filtrate results are after passing through a 1.8 nm filter)

to observation. Rather, data presented here seem to imply that a small portion of the UO_2 pellet is much more soluble than the bulk and that the spent fuel fragments have at least 100 times more of this soluble phase. Perhaps the near surface region is more highly oxidized, say U_3O_8, prior to start of the leach tests. It would seem reasonable to expect greater uranium release from spent fuel since spent fuel surfaces may have been oxidized to a greater depth because of radiation damage and because storage temperatures (after removal from the fuel pin) would be somewhat elevated due to radioactive decay heat. Once the soluble phase has dissolved, then one is left with the relatively insoluble and leach resistant UO_2. When iron is present, it simply reduces the uranium in solution, which precipitates but has no effect on the amount originally dissolved. Not only total release but also solution concentrations of uranium in the spent fuel tests were considerably higher (a factor of 100 or more) than those in the UO_2 tests. This could reflect a higher redox potential due to radiolysis [6]. Competition between iron and the radiolytic effects could result in an overall redox potential higher than in the absence of radiolysis.

The products of alpha radiolysis of saturated Permian brine are given in Table II for experiments performed using aqueous ^{244}Cm as an alpha source. The experiments were performed in a glove box with a nitrogen atmosphere. In contrast to gamma radiolysis where H_2/O_2 ratios were 2:1, the ratios were nearly 10:1 following alpha radiolysis. A ratio of exactly 2:1 would indicate a redox potential unchanged by irradiation, essentially as found for gamma radiolysis. The large H_2/O_2 imbalance found after alpha radiolysis would predict that the brine should become quite oxidizing. It is also apparent that nitric acid may be formed under these conditions. Since all of the energy from alpha decay was absorbed in the solution, the reaction must have occurred in the solution phase. The Eh/pH data of Table II are plotted in Figure 6 with expected environmental bounds for groundwater systems [7]. The effect of alpha radiolysis for total doses of approximately $0.9 - 3.6 \times 10^6$ rad is to raise the redox potential by approximately +1.0 volt over unirradiated brines. Actinide solubilities may be significantly enhanced by the action of alpha radiolysis in concentrated brines. Further work is proceeding on determining solubilities for specific actinides under these conditions.

TABLE II. Results of Alpha Radiolysis on a Cycle 4 Synthetic Permian Brine using ^{244}Cm*

Days of Equilibration	^{244}Cm (μg)	pH	pe	Gas Composition (%) H_2	H_2O	N_2	O_2	Nitrate mgN/ℓ
45	174	2.87	21.1	41.4	3.4	47.6	4.5	0.292
45	174	2.87	21.1	43.5	3.1	44.7	4.9	0.292
43	44	6.08	19.0	15.9	0.9	80.7	2.2	0.290
43	44	6.17	18.9	24.7	2.4	69.3	3.1	0.290

*48 ml solution, nitrogen atmosphere

Differences observed between the brine and deionized water results are difficult to interpret on the basis of our present knowledge. Differences in UO_2 alteration products may be involved. For example, the existence of sodium uranates is likely in the brines but not possible with deionized water. Differences in ionic strength may also play a role.

Summarizing the more noteworthy observations derived from the leach tests performed in brine: (1) the presence of iron coupons had no effect on total release of uranium from either spent fuel or UO_2 but did reduce solution concentrations, and (2) in excess of 100 times more uranium was released from spent fuel than from UO_2.

We have speculated about some possible causes for the effects we have noted. To test these ideas, experiments are planned to determine whether alpha and/or gamma radiation can be responsible for the differences in spent fuel and UO_2 leaching characteristics. Other experiments on UO_2 will be performed to test the idea that a more highly oxidized surface layer (e.g., U_3O_8) leaches away quickly, regardless of whether iron is present, so

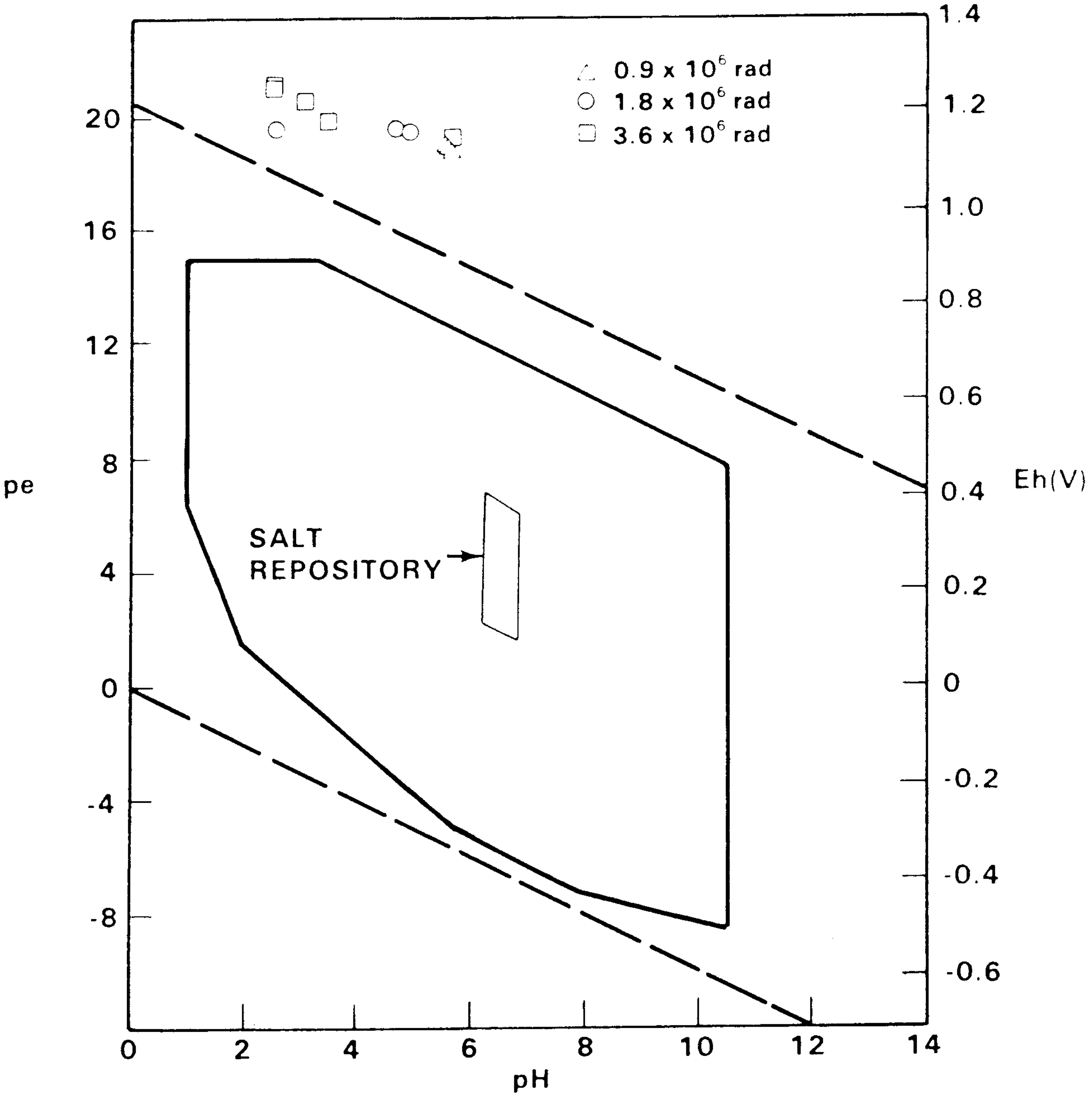

FIGURE 6. Measured and expected pe versus pH in a synthetic saturated Permian brine, Table I. The dark solid lines represent the range of conditions typical of groundwaters [7]. Alpha radiolysis of the saturated brines by ^{244}Cm in a nitrogen atmosphere yielded very oxidizing conditions.

that the total release seems nearly independent of time after the first few days. In addition, a new series of spent fuel leach tests will be initiated and extended to times up to six months to determine whether the markedly reduced leach rates observed between about 10 and 60 days hold for longer periods.

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SPENT FUEL WORKSHOP

Boston Park Plaza Hotel
November 10-11, 1983
8.00 a m - 5.00 p m
Back Bay Room (Room 410)

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TR 82–28

The KBS Annual Report 1982.

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1983

TR 83–01

Radionuclide transport in a single fissure A laboratory study

Trygve E Eriksen
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TR 83–02

The possible effects of alfa and beta radiolysis on the matrix dissolution of spent nuclear fuel

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