

- 1. The application of PIE techniques to the study of the corrosion of spent oxide fuel in deep-rock groundwaters**
- 2. Spent fuel degradation**

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Studvik Nuclear

January 1991

1. THE APPLICATION OF PIE TECHNIQUES TO THE STUDY OF
THE CORROSION OF SPENT OXIDE FUEL IN DEEP-ROCK
GROUNDWATERS

2. SPENT FUEL DEGRADATION

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

Information on SKB technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20), 1986 (TR 86-31), 1987 (TR 87-33), 1988 (TR 88-32) and 1989 (TR 89-40) is available through SKB.

FOREWORD

During the autumn of 1990, papers summarizing work performed at Studsvik as part of the SKB research programme designed to study the corrosion behaviour of spent nuclear fuel in deep-rock groundwaters were presented at two scientific meetings:

1. "The application of PIE techniques to the study of the corrosion of spent oxide fuel in deep-rock groundwaters."
IAEA Technical Committee Meeting on Post-Irradiation Examination Techniques for Reactor Fuel. Workington, England, 11-14 September, 1990.
2. "Spent Fuel Degradation."
Symposium on the Scientific Basis for Nuclear Waste Management XIV, Boston, U.S.A., 26-29 November, 1990. (To be published in Volume 212 of the Material Research Society Symposium Proceedings Series.)

Since the papers were presented to different groupings of the "nuclear community", they emphasize different aspects of the programme. Further, the presentations unavoidably overlap somewhat, but it is felt that they complement each other and together represent a better view of the present project status. They are therefore re-published together in the SKB Technical Report Series.

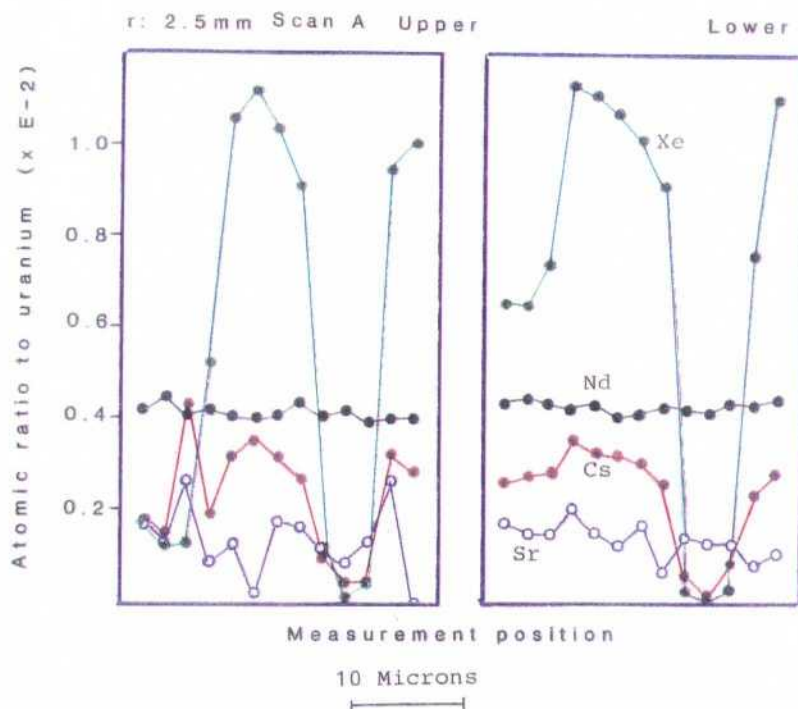
Roy Forsyth Studsvik 16 January 1991.

(Note: The requirement of successive printings has caused a shortage of some original photographs, and it has been necessary to substitute new but equivalent SEM photographs for the original photographs in Figures 9 and 10 of the first paper.)

Studsvik Report

THE APPLICATION OF PIE TECHNIQUES TO THE STUDY OF THE CORROSION OF SPENT OXIDE FUEL IN DEEP-ROCK GROUNDWATERS

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Studsvik Nuclear

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CORROSION OF SPENT OXIDE FUEL IN DEEP-ROCK GROUNDWATERS

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ABSTRACT

The direct disposal of spent fuel is an increasingly favoured alternative to fuel reprocessing and subsequent vitrification of the highly active waste solutions for the closure of the nuclear fuel cycle. The direct disposal route is based on a multi-barrier concept, one barrier being the corrosion resistance of the fuel itself. Corrosion of spent fuel in groundwaters is being studied in several countries, and the results currently available suggest three, partly overlapping, processes, of which two in particular are dependent on structural changes and migration effects produced in the fuel during reactor irradiation. Thus, in order to be able to define and quantify these processes for the purpose of safety analysis, it is necessary that, in addition to extensive leachant analysis after corrosion tests, PIE techniques are applied to the detailed study of spent fuel both before and after water contact. This paper presents results and observations from the Swedish programme which illustrate the problems involved.

1. INTRODUCTION

There are two principal methods for the closure of the nuclear fuel cycle: reprocessing followed by vitrification of the high-level waste solutions, and direct disposal of the spent oxide fuel after an intermediate storage which permits substantial decay of fission product activities. Research programmes in support of the direct disposal route have been in progress for 10-15 years in Canada, Sweden, Finland and the U.S.A., and later, in the Federal Republic of Germany and Spain.

In Sweden, the currently favoured method [1] involves encapsulation of the LWR spent fuel assemblies in thick-walled copper canisters, which, surrounded by annuli of compacted bentonite, are placed in wells in the tunnel floor of a repository located at a depth of 500 m or more in the granitic bed-rock. After final closure of the repository and its slow re-filling with groundwater, the most probable chemical environment (depending on the chosen site) is a groundwater with a bicarbonate content in the 100-150 ppm range, and with a very low E_H value. Under these conditions, corrosion of the copper canister is extremely slow, and thus, the primary barrier to release of fission products and actinides to the environment, is the long-life canister. The multi-barrier approach used in the repository concept, however, also requires an evaluation of the corrosion of the fuel itself under the same conditions.

One of the reasons for the selection of uranium dioxide, in the form of densely sintered pellets, as the fuel form for water reactors was, of course, its relatively high chemical stability to corrosion by water or steam in the event of the breach of the Zircaloy cladding sheath, and a great deal is already known about the in-reactor performance and subsequent pool storage of defective fuel rods. In-reactor corrosion of defective fuel, however is chronologically limited to periods of the order of an irradiation cycle, and is terminated by removal from the core, and the nuclear industry has therefore directed most interest to the definition and avoidance of the causes of clad breaching, whether outside the rod by abrasion by small objects or by water chemistry, or by the thermo-mechanical behaviour of the fuel rod itself.

A safety analysis for the direct deposition route, however, must span a time-scale of perhaps 10^6 years, governed by the decay of long-lived fission products and actinides. Clearly, against this background, the extrapolation of experimental results from corrosion tests alone is an inadequate basis for safety analysis, which must be firmly based on the definition and good understanding of the corrosion processes involved and the identification of solid corrosion products which may determine solubilities in the long term.

In addition to corrosion tests and solution analysis, this requires the application of PIE techniques to the detailed study of high burnup fuel both before and after contact with groundwater, but with analytical goals and detection limits somewhat different from those relevant to the study of in-reactor fuel performance. This paper will present results and observations from the Swedish programme which illustrate the problems involved.

2. CORROSION TESTS: SOLUTION ANALYSIS

Most of the corrosion tests in the Swedish programme are performed on fuel fragments and on 20 mm long segments of fuel and clad from reference BWR and PWR rods of burnup 41-41 MWd/kgM. The reference case simulated groundwater has a composition about mid-range of the real groundwaters recovered from deep bore-holes. (pH:8.2, 123 ppm bicarbonate). Details of experimental technique and a summary of early results have been reported earlier [2]. Since the main interest in this paper is in PIE techniques, the principal results obtained from leachant analysis after corrosion tests on spent fuel will be briefly summarized here.

Fig. 1 shows that even after short contact times between fuel/clad segments and groundwater under oxic conditions, uranium leachant concentrations appear to saturate at a few mg/litre, but approach the concentration obtained with a bare unirradiated fuel pellet as corrosion proceeds. With the fuel weights and experimental conditions used, the amount of uranium in solution represents a fraction of the total uranium inventory of the order of 10^{-5} . Parallel tests using Deionized water (DIW) gave uranium concentrations of a few ppb, about the detection limit of the laser fluorescence analytical method used.

The results for plutonium show an apparent saturation concentration of about 1 ppb (somewhat higher for distilled water), although in this case the plutonium concentration decreases with contact time. Only small amounts of plutonium are found in the colloidal form or adsorbed on the vessel walls. Since the fate of plutonium in the corrosion process is an essential ingredient in any safety analysis, these are important observations: a solution ratio for Pu/U of about 0.001 is appreciably lower than in the spent fuel itself, and this suggests the formation of a plutonium phase or an alteration product enriched in plutonium on or in the fuel.

Saturation of uranium and plutonium in the leachant does not, of course, mean that the corrosion process ceases: fission products such as cesium, iodine, strontium, technetium and molybdenum are continuously released to the leachant, although their release rates (the unit used is fraction of the total inventory/day) decrease rapidly with time. Comparison of results from long-term static tests with those from sequential leaching procedures

demonstrate that, under otherwise identical experimental conditions, the rates of release are dependent upon the total contact time. Not all of these elements or their nuclides are of significance for safety analysis purposes: knowledge of their behaviour, however, can be useful for determining the mechanisms of corrosion.

Fractional release rates for Cs-137 and Sr-90 are presented in Figs. 2 and 3. In the case of Cs-137, high release rates are observed during the first weeks of water contact: this, the so-called Instant Release Fraction, represents the well-established release of cesium from the higher temperature zone of the fuel during reactor operation and its migration to fuel/clad surfaces and fuel cracks. During this phase, Sr-90 release rates are more or less constant.

Later in the corrosion process, the release rates for both Cs-137 and Sr-90 decrease with time in about the same way, although the Cs-137 release rates are higher by a factor of 2-5. (Note that the rates are independent of whether corrosion occurred in the bicarbonate groundwater or in deionized water).

The total fractional release of Cs-137 from the reference BWR and PWR rod fuel specimens was about 1% after a few years of corrosion, of which 80-85% was released during the first weeks, agreeing well with the integral FGR values for the whole rods of 0.9 and 0.7% respectively. For Sr-90, the total fractional release values were only of the order of 0.1%.

The results presented above refer to experiments performed under oxidizing conditions - a conservative case - since the deep-rock groundwaters are known to be extremely reducing. Experimentally, it is difficult to establish and maintain low E_H conditions in a hot-cell environment, but about 20 experiments have been carried out using groundwaters reduced by circulation over crushed rock from bore samples, or by H_2 gas in the presence of a palladium catalyst. Successful establishment of a reducing environment is demonstrated by a marked reduction in uranium and actinide leachant concentrations to about or below their detection limits. It is found, however, that the release rates for Cs-137 and Sr-90 are only lowered by about one order of magnitude. Reducing conditions do not appear to affect the size of the Instant Release Fraction for Cs-137, which is strong evidence that this represents the rapid solubilization of cesium compounds, and does not require significant oxidation and dissolution of the UO_2 itself.

3. THREE - PROCESS CORROSION HYPOTHESIS

Since results generally similar to those reported here have been obtained in other spent fuel corrosion programmes, the current view of most workers active in this field is that the corrosion of spent oxide fuel in aqueous media can be described by:

- a) the rapid dissolution of fission product species which were released to the fuel surfaces and fuel rod internal void during reactor operation. This, the so-called Instant Release Fraction, applies to cesium and iodine nuclides, and since their migration and release from the fuel grains can be correlated to that of krypton and xenon, fission gas release models can be applied to quantitatively describe the process.

- b) selective attack, non-oxidative or oxidative, at the sites of fission product segregation, or at grain boundaries.
- c) general matrix dissolution, involving oxidation of UO_2 to higher valence forms, soluble or insoluble, with the simultaneous release of fission products and actinides to the aqueous phase.

The first two of these processes are particularly dependent on the irradiation history of the fuel with regard to fission product migration and grain boundary porosity and interlinkage, and distinction between these processes is fairly arbitrary.

A clear distinction between the last two processes is necessary for quantification and projection of the corrosion rate in the long term, but can be difficult experimentally. The lanthanides and actinides, which are in solid solution in the UO_2 matrix and therefore homogeneously distributed at the grain level, have very low solubilities in the groundwater, and can, therefore, not serve as monitors of matrix dissolution.

4. GRAIN BOUNDARY SEGREGATION

Certain fission products - the fission gases Kr and Xe, Te, I and Cs, and the 4d metals Mo, Tc, Ru, Rh and Pd - are known to migrate to the fuel grain boundaries. The fission gases are only of indirect interest for the study of spent fuel corrosion: the 4d metals will be discussed later.

It was mentioned above that, following completion of the first phase of corrosion (Instant Release Fraction), the release rate of Cs-137 decreases rapidly with time, but is always larger than the corresponding value for Sr-90.

The scatter in the data is appreciable but there appears to be a trend towards convergence of the rates as corrosion proceeds.

If Sr-90 could be shown to be homogeneously distributed in the fuel matrix, measurement of its release would constitute a measure of matrix dissolution. The cumulated difference in the release of Cs-137 and Sr-90 would then represent the enrichment of Cs-137 at grain boundaries.

Some of the results from the Swedish programme [2,3], however, appear to indicate Sr-90 segregation: fuel specimens from the two reference BWR and PWR rods, with the same nominal burnup but from different locations in the fuel column, showed consistently different release rates for Sr-90 over a period of several years, suggesting the effect of local power history variations. There are few literature reports of Sr-containing segregated phases in LWR fuel [4,5], and search for such phases or zones in the reference fuel used in the Swedish programme (burnup 41-42 MWd/kgM) has so far been unsuccessful.

EPMA-WDS examination of power-ramped fuel (burnup 37 MWd/kgU): max. ramp power 43 kW/m) has also been performed [6]. Even in zones where grain-boundary sweeping had caused abrupt changes in Xe and Cs contents (Fig. 4), any variations in local Sr content are concealed by the poor precision of the analytical method at this detection level.

Because of its long half-life and mobility in groundwaters, Tc-99 is a significant nuclide for safety analysis of spent fuel repositories. Fractional release fractions for Tc and Mo determined in corrosion tests on spent fuel are of the same order as those for Sr-90, while those for Ru, Rh and Pd, the other constituents in the metal inclusions, are very low. Clearly it is of interest to determine the abundance of these inclusions in LWR fuel, and their corrosion properties.

In ceramographic specimens from the reference BWR and PWR rods in the Swedish programme, optical microscopic examination showed the resolvable particles to be small and restricted to about a quarter of the fuel volume. By quantitative image analysis it could be estimated that the inclusions represented only about 0.1 mg/g of bulk fuel for both fuel types, i.e., only about 1% of their total inventories as calculated by ORIGEN-2. The value of 0.1 mg/g fuel only refers to inclusions over about 0.5 μm in size, the resolution of the optical microscope. Thomas et. al. [7], however, have shown by transmission electron microscopy that spent PWR fuel contained inclusions down to sizes of tens of nanometers, the larger of which were located at or close to the grain boundaries.

An experimental programme was performed at Studsvik [8] in 1987-89 in attempt to determine the amount of 4d metals held even in these smaller inclusions. Four whole pellet specimens from each rod were dissolved in cold 6M HNO_3 for a week or more: the ratio of HNO_3 to fuel was about 30 l/kg fuel. The heavy black residues, well-known from the analytical procedure for burnup analysis, were filtered through glass sinters and air-dried to constant weight.

Residue weights of 4.54 ± 0.43 mg/g fuel (BWR) and 4.89 ± 0.23 (PWR) were obtained. The residues were examined by gamma spectrometry through a collimator in the cell wall and subsequently small residue flakes were directly mounted on plastic tape for SEM/EPMA examination. The filtrates were analysed in order to determine mass balances. XRD analysis showed that residues were predominantly amorphous.

The appearance of the "filter cake" of one of the residues is shown in Figs. 5 and 6. In the latter, it can be seen that the residue consisted of agglomerates of small particles which, hopefully, indicates that the inclusions had been converted directly to oxides or hydrated oxides during the fuel dissolution process.

EDS examination of the upper and lower surfaces of several residue flakes showed no difference in composition, demonstrating that particle segregation by sedimentation during filtration was insignificant. By WDS examination (the EDS software tended to give lower values for the smaller peaks), it was shown that about 80% (BWR) and 86% (PWR) of the residues consisted of 4d metals. Minor component were uranium, actinides, Cs, Sr, Sb and Co. The 4d metal compositions of the residues (average of four specimens) are given in Table 1, and are very similar to those reported recently by Kleykamp [9] from similar experiments.

Samples of the two types of residue were then contacted with 700 ml of the bicarbonate groundwater for a period of 434 days. Samples were removed on four occasions, centrifuged through membrane filters, and analysed. It was found

that Mo and Tc solution concentrations attained saturation quite rapidly in the leachant, giving maximum concentrations of about 1.5 and 0.5 mg/litre respectively. These values are about five and three times higher than the maximum achieved in spent fuel corrosion tests.

A more systematic study of known and possible segregation effects is now in progress. Fig. 7 shows the sampling plan for a programme of corrosion tests and fuel characterization on the lower segment of a stringer rod irradiated in the Ringhals 1 BWR. Fuel burnup along the rod varies between 24 and 47 MWd/kgM. Results from the programme will be reported elsewhere, but Fig. 8 is presented here to illustrate some of the early results. The cumulative release fractions for Cs-137 over the first 91 days of corrosion show the expected dependency on burnup and/or local linear power, increasing rapidly for fuel of burnup about 32 MWd/kgM, and levelling out at burnups about 40 and higher. The time dependence of cesium dissolution, however, is seen to vary along the rod: the higher burnup specimens in particular lost most cesium to the leachant during the second contact period. This is possibly due to the effect of fuel structure on water penetration and will be investigated further.

5. CORROSION SITES

It is clear from the discussion above that there is currently no firm identification of the sites for corrosive attack. If Sr-90 is indeed not segregated in LWR fuel, and therefore its release can serve as a monitor of matrix conversion or dissolution, its cumulative release fraction of the order of 0.1% over several years of water contact, would indicate that in a 10 g fuel pellet, only 10 mg of fuel would have been converted or dissolved. Identification of such small amounts in highly-active fuel specimens is obviously experimentally difficult.

It is, however, reasonable to assume that corrosion is most probable in fuel zones with extended networks of inter-linked porosity, such as at the fuel pellet rim, and quantitative microscopy is being applied within the Swedish programme to the study of high burnup fuel specimens both before and after aqueous corrosion in an attempt to quantify these effects [10]. Fig. 9 shows the appearance of the fuel at the rim in a fuel fragment exposed to a bicarbonate groundwater (240 ppm bicarbonate) for about 4 years. It can be seen that there has been material loss. Fig. 10 is a higher magnification photo micrograph of a portion of the corroded crust removed from a second fuel fragment in the same test, and shows the presence of rounded particles at a grain corner. Identification of this material by XRD has so far been unsuccessful.

It is also far from clear that these particles represent an alteration product formed during corrosion, releasing fission products and actinides to the leachant, since the fuel at the rim of uncorroded high burnup fuel also contains apparently similar material, perhaps formed by intensive fission fragment bombardment of the fuel surface immediately surrounding intergranular porosity.

The enhanced fission rate at the fuel rim is also associated with a build-up of actinides as seen in autoradiographs of high burnup fuel. Since under the anoxic conditions typical of deep-rock groundwaters, it is probable that the

driving force for fuel oxidation and dissolution is radiolysis of the groundwater by the alpha and/or beta gamma radiation fields, it is important to attempt to quantify this effect.

Fig. 11a is an autoradiograph of a fuel section from the same BWR fuel as used in the test described above. Fig. 11b presents the results of quantitative image analysis (alpha particle etch pit counts) on enlargements (x200) of another autoradiograph of the fuel but with only 3 seconds exposure time.

The results of a calculation with Studsvik's MICBURN code for the radial distribution of alpha activity at the same date as when the autoradiograph was performed (about 11 years after end of irradiation) are given in Fig. 11c. After such a decay time, only 5 nuclides are responsible for almost all the alpha activity. At shorter decay times, however, such as at the start of the BWR fuel corrosion tests in 1982, Cm-242 was a major contributor. Use of the results in Fig. 11 together with quantification of the interlinked porosity in the fuel could hopefully permit calculation of the alpha dose to the groundwater within the fuel structure, and its variation over long time periods.

6. CONCLUSIONS

The aim of this paper has been to present some of the problems involved in the study of the corrosion of spent nuclear fuel in groundwaters and to illustrate the necessary coupling of the results from corrosion tests with fairly standard PIE methods for their solution, by means of work performed in the Swedish programme.

7. ACKNOWLEDGEMENTS

Many of the staff of Studsvik's Hot Cell Laboratory have been engaged in experimental work described. The author gratefully acknowledges their contributions. Thanks are also due to Dr. L.O. Werme for useful discussions.

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To be published.

Table 1 Relative 4d metal compositions in the residues

		w/o			
	Mo	Tc	Ru	Rh	Pd
BWR	18,7	9.3	54.8	7.0	10.2
PWR	20.4	10.4	52.2	7.2	9.8

Fig 1. URANIUM CONCENTRATIONS IN GROUNDWATER

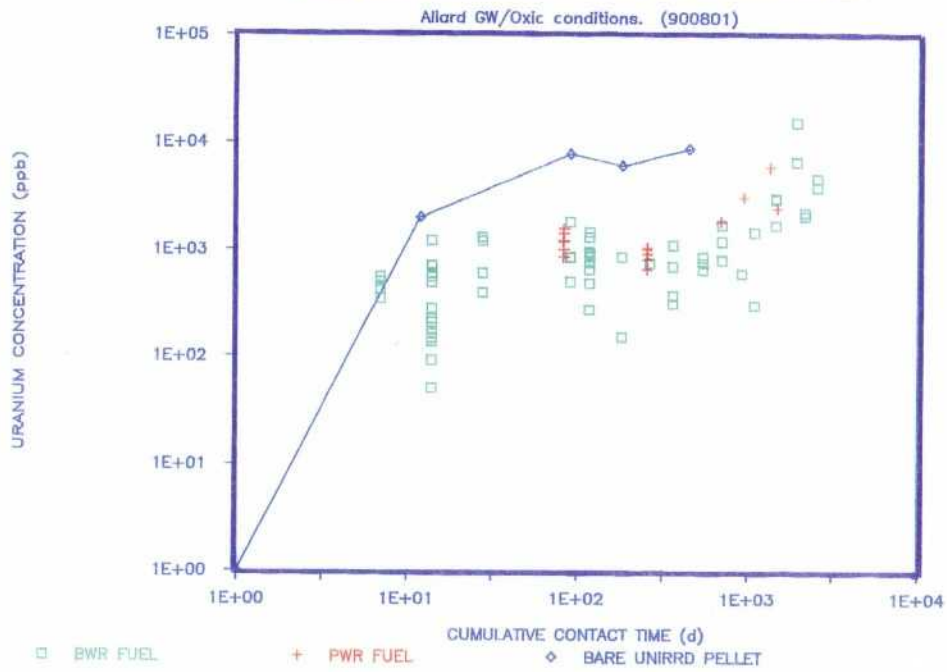


Fig 2 FRACTIONAL RELEASE RATE: Cs-137

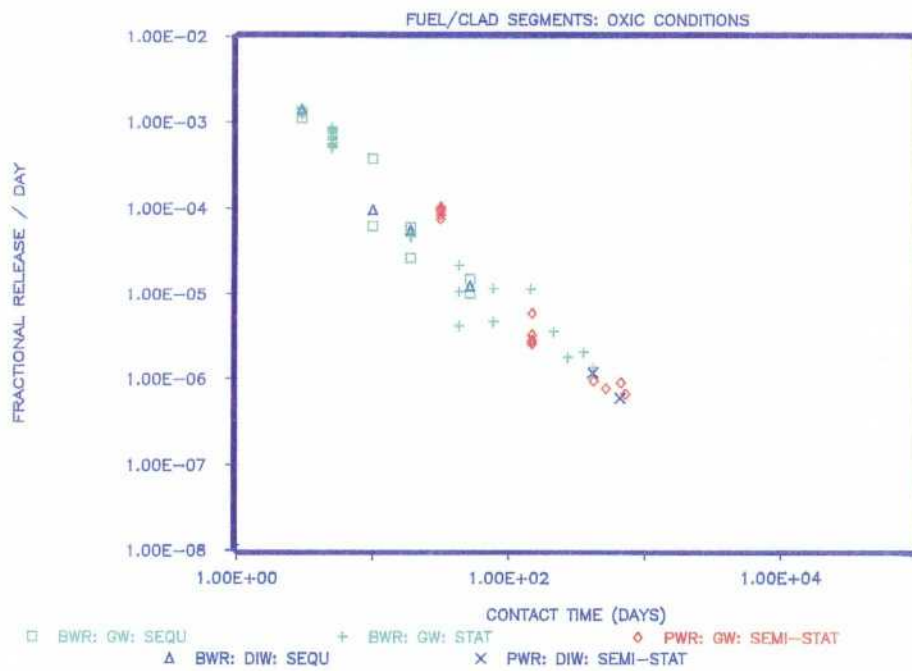


Fig 3.

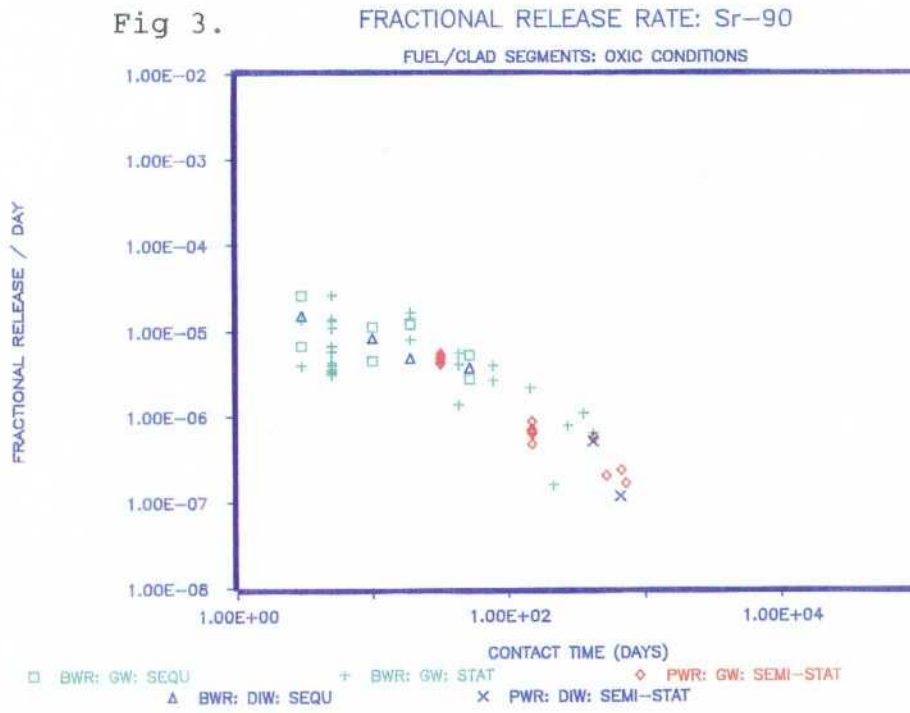
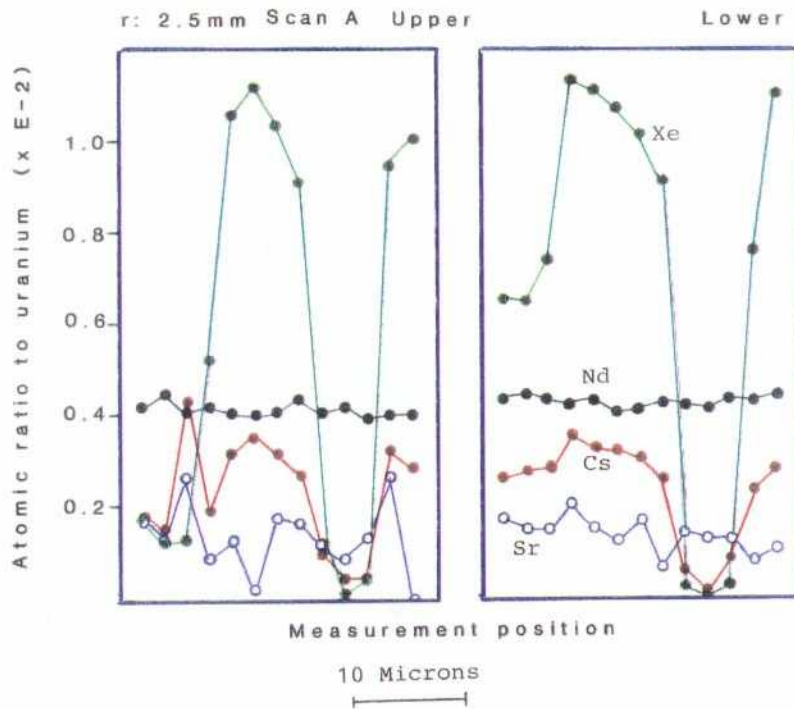


Fig 4. EPMA results on grain-boundary swept zone. Note poor precision for Sr.



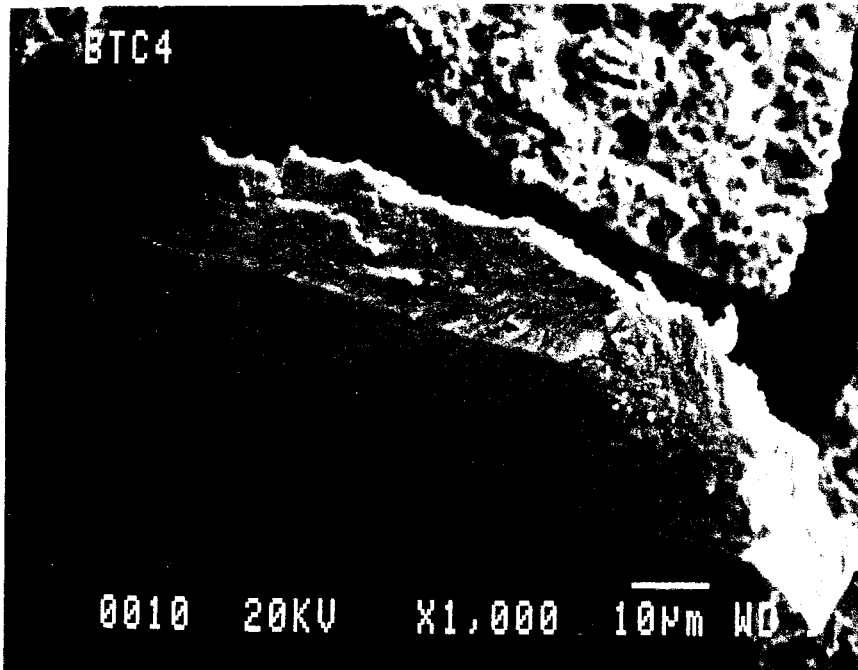


Fig 5. "Filter cake" of 4d metal fission products.

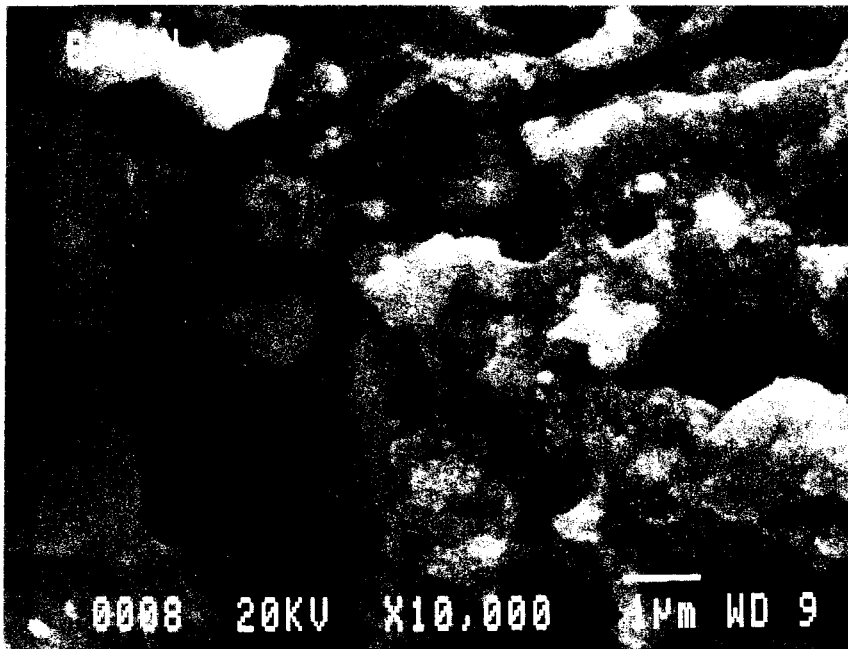


Fig 6. Detail 4d metal residue showing preservation of inclusion geometry.

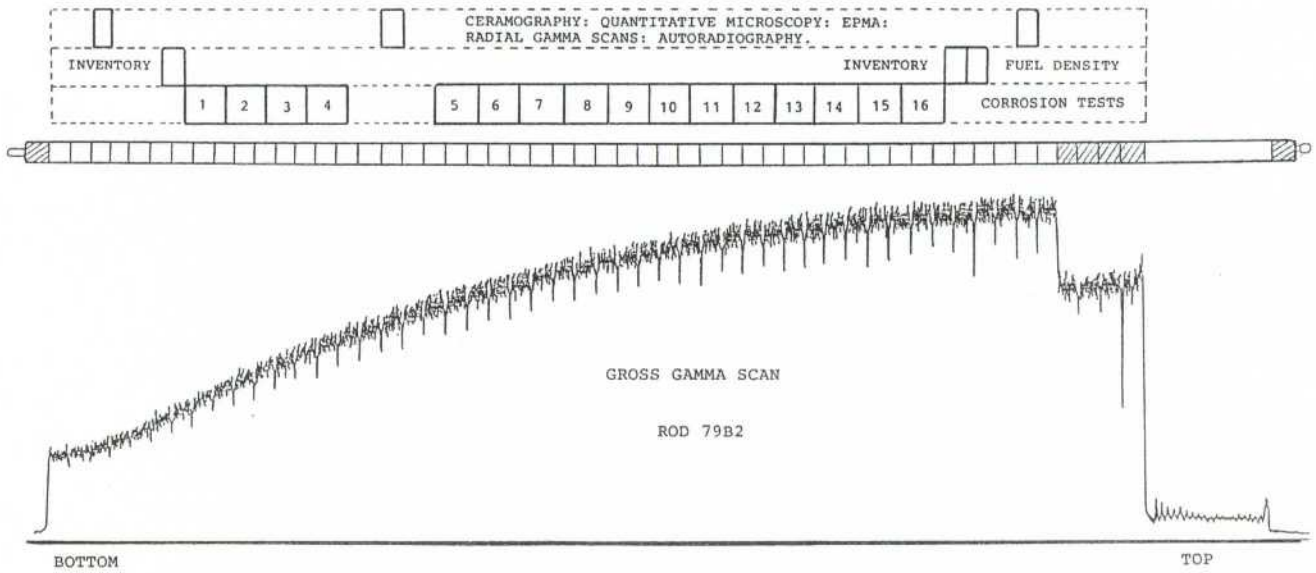


Fig 7. Sampling plan for stringer rod used for studying the relationship between burnup/linear power and corrosion properties.

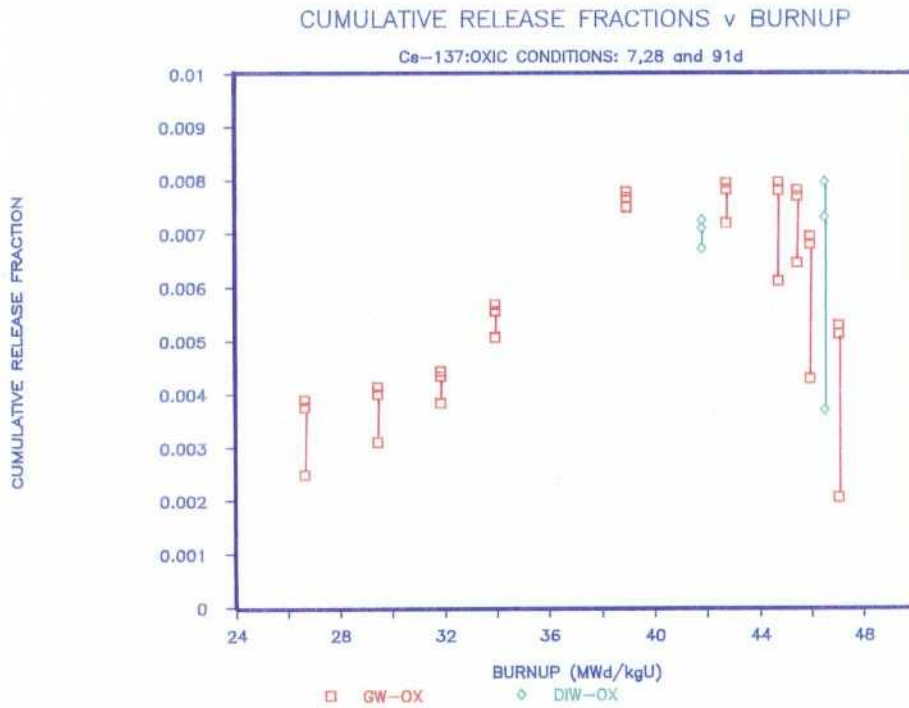


Fig 8. Cs-137 Cumulative release fractions during Instant Release phase.



Figure 9

Corrosion at the rim of a BWR fuel fragment exposed to groundwater for 3.9 years. (X2000)



Figure 10

"Alteration product" at the grain boundary. (Specimen from corroded fuel crust).

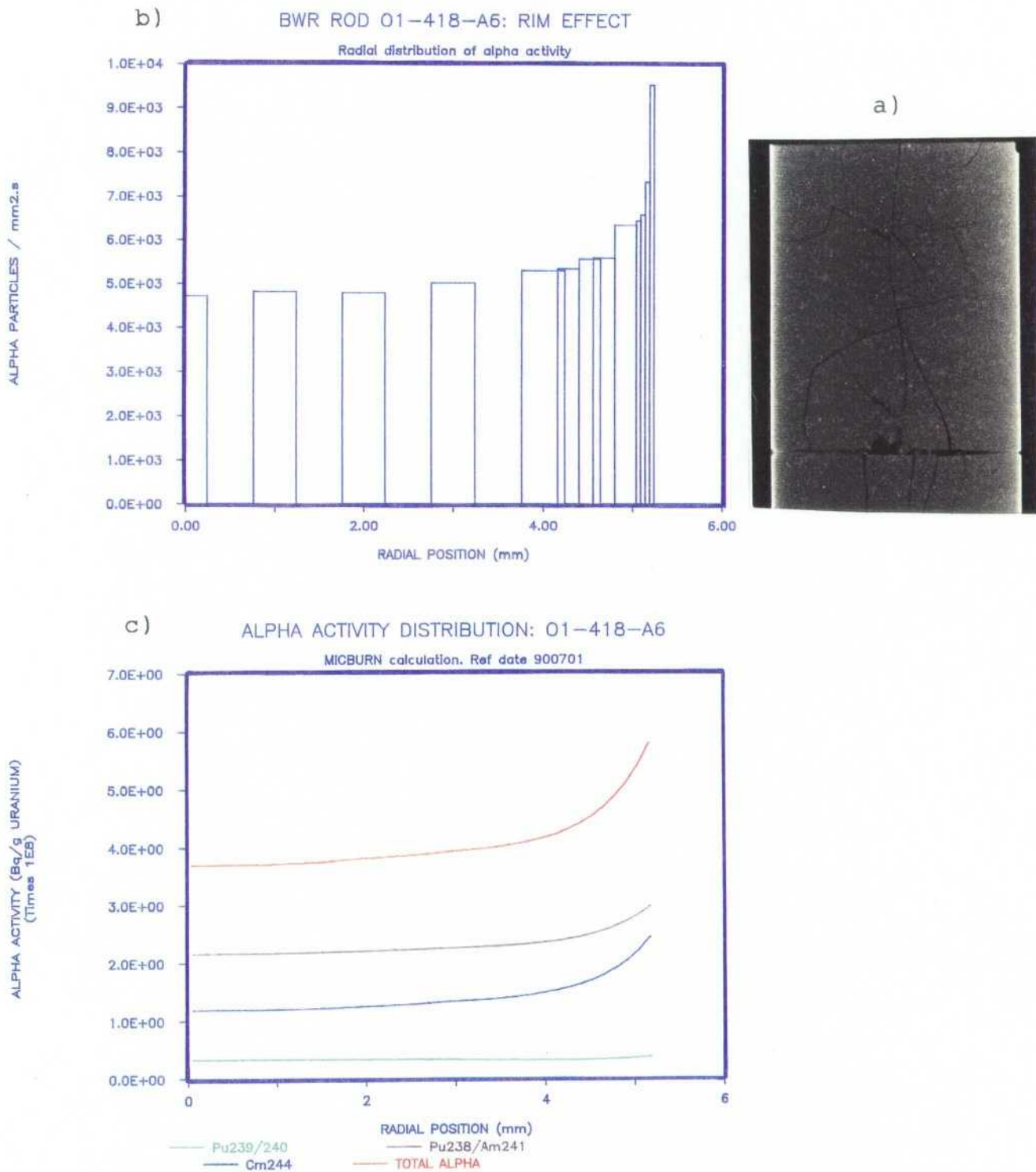


Fig 11. Investigation of the rim effect for the BWR reference fuel.
 a) alpha autoradiograph
 b) results of etch pit density counting
 c) MICBURN calculation of alpha activity distribution

STUDSVIK/NF(P)-90/43

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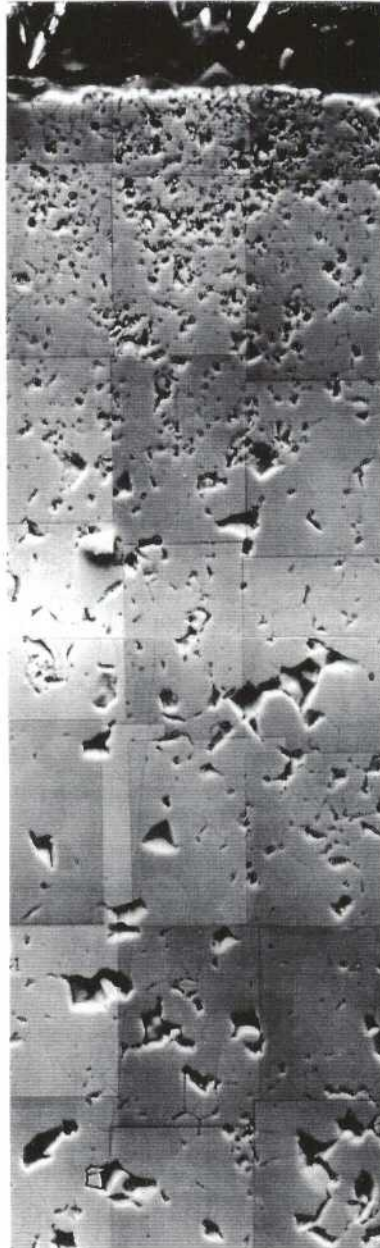
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Studsvik Report

SPENT FUEL DEGRADATION

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Presented at Symposium: Scientific Basis for Nuclear Waste Management XIV,
Materials Research Society, Boston, USA, November 26-29, 1990

Studsvik Nuclear

1990-12-21

SPENT FUEL DEGRADATION

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(Frontispiece: Scanning electron micrograph mosaic of the peripheral zone - 55 μm x 165 μm - of a spent fuel pellet exposed to DIW for 1521 days).

Approved by: *Roy Forsyth*

Presented at Symposium: Scientific Basis for Nuclear Waste Management XIV, Materials Research Society, Boston, USA, November 26-29, 1990.

1990-12-21

SPENT FUEL DEGRADATION

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ABSTRACT

The degradation and dissolution of spent nuclear fuel in groundwaters occurs by three partly concurrent processes: dissolution of mobile species which have migrated to the fuel rod void, grain boundary attack and matrix dissolution. Of the first two processes, both clearly dependent on the irradiation history of the fuel, the first is fairly well understood, but there is currently insufficient data on the migration of key nuclides to grain boundaries during reactor operation and their release kinetics during subsequent water corrosion to enable satisfactory modelling of this process to be performed.

This paper presents results from recent experiments included in the Swedish programme which are relevant to this issue.

INTRODUCTION

Research programmes directed at the identification and quantification of the mechanisms responsible for the degradation of spent nuclear fuel in groundwaters have been in progress for 10-15 years in the U.S.A., Canada and Sweden and for somewhat shorter periods in Finland, the Federal Republic of Germany and Spain. Much progress has been made in establishing a good understanding of the processes involved and there is now an extensive reference literature, not least in the various annual Proceedings of this meeting.

There are, however, a number of areas where a detailed, fundamental knowledge of the dissolution mechanisms is not yet at hand. These key areas have been recently identified and discussed by Johnson et al [1] in an excellent review of progress in the field. One such area is the interpretation of the experimentally-observed leaching behaviour of Sr-90 in spent fuel corrosion tests under both oxidizing and reducing conditions. Since the build-up of lanthanide fission products and actinides (including uranium) in neutral or alkaline groundwater appears to be solubility limited, and other fission products such as cesium, iodine and technetium are known to relocate and segregate in fuel during reactor operation, Sr-90 has been considered as a possible monitor of the on-going degradation process.

Early results [2, 3] from the Swedish programme on the corrosion of reference BWR and PWR fuel, however, showed a difference in Sr-90 leaching behaviour between fuel specimens of similar burnup (about 41 MWd/kgU) but taken from different locations in the rods. This appeared to suggest that even Sr-90 can be relocated during power operation and therefore subject to preferential dissolution during subsequent corrosion tests, although this was rather surprising since the fuel specimens in question had experienced irradiation histories where the local linear power had always been less than 25 kW/m. Further, the observed integral fission gas release values for the two rods - 0.7 % and 1.06 % respectively - suggested the absence of significant thermal feed-back effects, fuel restructuring and fission product migration.

1990-12-21

The present paper represents an up-dated reporting of results obtained in the Swedish programme relevant to preferential dissolution effects, including interim results from recently started experiments specifically designed to study possible correlations between corrosion behaviour and fuel properties conditioned by burnup and/or local power variations. Recent observations during the search for corrosion sites in fuel exposed to corrosion for about 4 years are also presented.

CORROSION PROCESSES : SOLUTION ANALYSIS

The results obtained in the programme up to 1988, and details of experimental parameters and procedures were summarized in a recent status report [4] but it is useful in the following to briefly review the principal findings in the light of later observations.

Uranium and plutonium

Figure 1 presents the centrifugate concentrations of uranium found during the leaching of short fuel/clad segments of the BWR and PWR reference fuel in Allard groundwater (123 ppm bicarbonate: pH 8.0-8.2) plotted against cumulative contact time. This shows a trend of increasing apparent saturation solubility as corrosion proceeds, possibly because of improved leachant access to the fuel surfaces, and approaches the value attained during leaching of a bare, unirradiated fuel pellet.

It is interesting to note that the scatter in the BWR fuel results at contact times up to a few hundred days can be assigned to clear differences in behaviour between fuel segments sampled from different parts of the fuel column, although with the same nominal burnup. The segments showing lower uranium concentrations (and plutonium: see below) also released less Cs-137 and Sr-90. In experiments where fuel segments, BWR and PWR, were exposed to deionized water (DIW), the uranium concentrations were at or below the detection level of a few ppb. These segments, however, as will be shown later, released Cs-137 and Sr-90 at rates comparable to similar specimens leached in the bicarbonate groundwater.

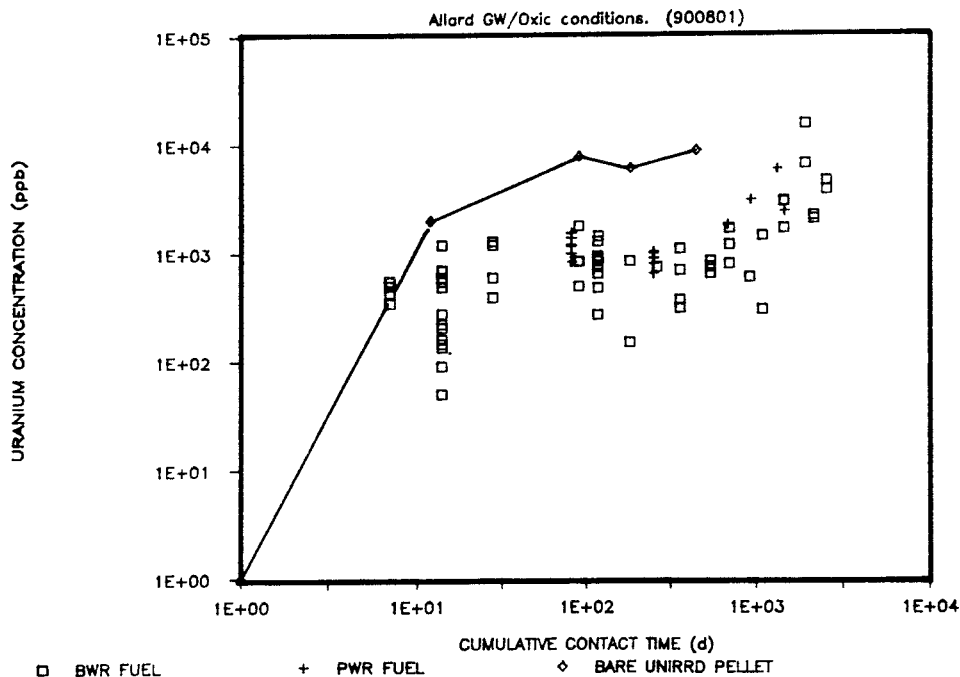


Figure 1 Uranium concentrations in centrifugates from leach tests on fuel/clad segments in GW.

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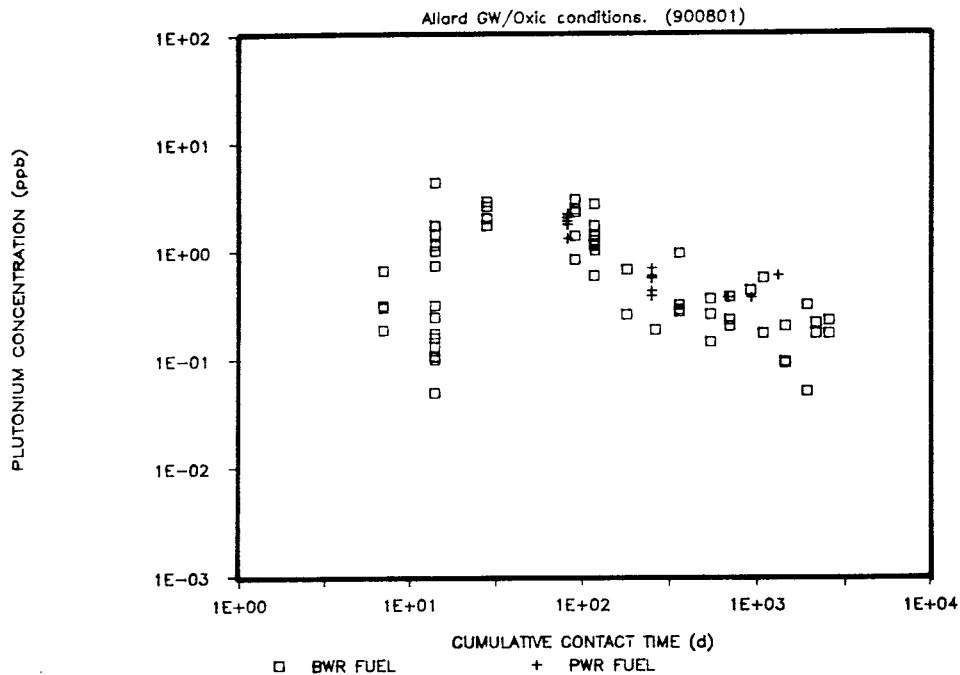


Figure 2 Plutonium concentrations in centrifugates from leach tests on fuel/clad segments in GW.

The corresponding results for plutonium concentrations in Allard GW are given in Figure 2. Recent results from experiments on the PWR fuel confirm the previous observation that the plutonium concentration decreases from about 2 ppb to about 0.3 ppb with increasing residence time in solution. Since no corresponding increases in plutonium collected on the membrane filters or enriched in the strip solutions were observed, it appears that the "missing" plutonium was preferentially adsorbed or precipitated on clad and/or fuel surfaces.

In DIW experiments, solution concentrations of 5-10 ppb were obtained. Thus, plutonium release, like uranium release, seems to be solubility controlled in both GW and DIW. It can be noted that plutonium/uranium ratios in GW solution are always lower than the ratio in the uncorroded spent fuel.

Choppin [5] has found satisfactory agreement between these measured solubilities under oxic conditions and available thermodynamic data, assuming that UO_2^{2+} and PuO_2^+ are the relevant solution species. The corresponding solubility limiting solids would be schoepite and $\text{Pu}(\text{OH})_4$.

A surface deposit which had been formed during air-storage of PWR fuel exposed to DIW contact has recently [6] been identified as dehydrated schoepite, nominal composition $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$. The plutonium content as measured by EPMA was less than the estimated detection level of 0.3 w/o. No evidence of $\text{Pu}(\text{OH})_4$ formation as a separate phase, or of schoepite-type compounds in GW experiments has yet been found in the Swedish programme.

Cesium : strontium : technetium and molybdenum

These fission products, which appear to be fairly readily solubilized under oxic conditions, show release behaviours which vary with time in different ways, and it is these differences, together with established or postulated correlations with spent fuel characteristics, which have led to the definition of the two preferential dissolution modes which are included in current models of spent fuel degradation.

Fractional release rates for Cs-137 and Sr-90 from corrosion tests on fuel/clad segments from the reference BWR and PWR rods are presented in Figure 3. This shows the now-familiar so-called Instant Release phase for

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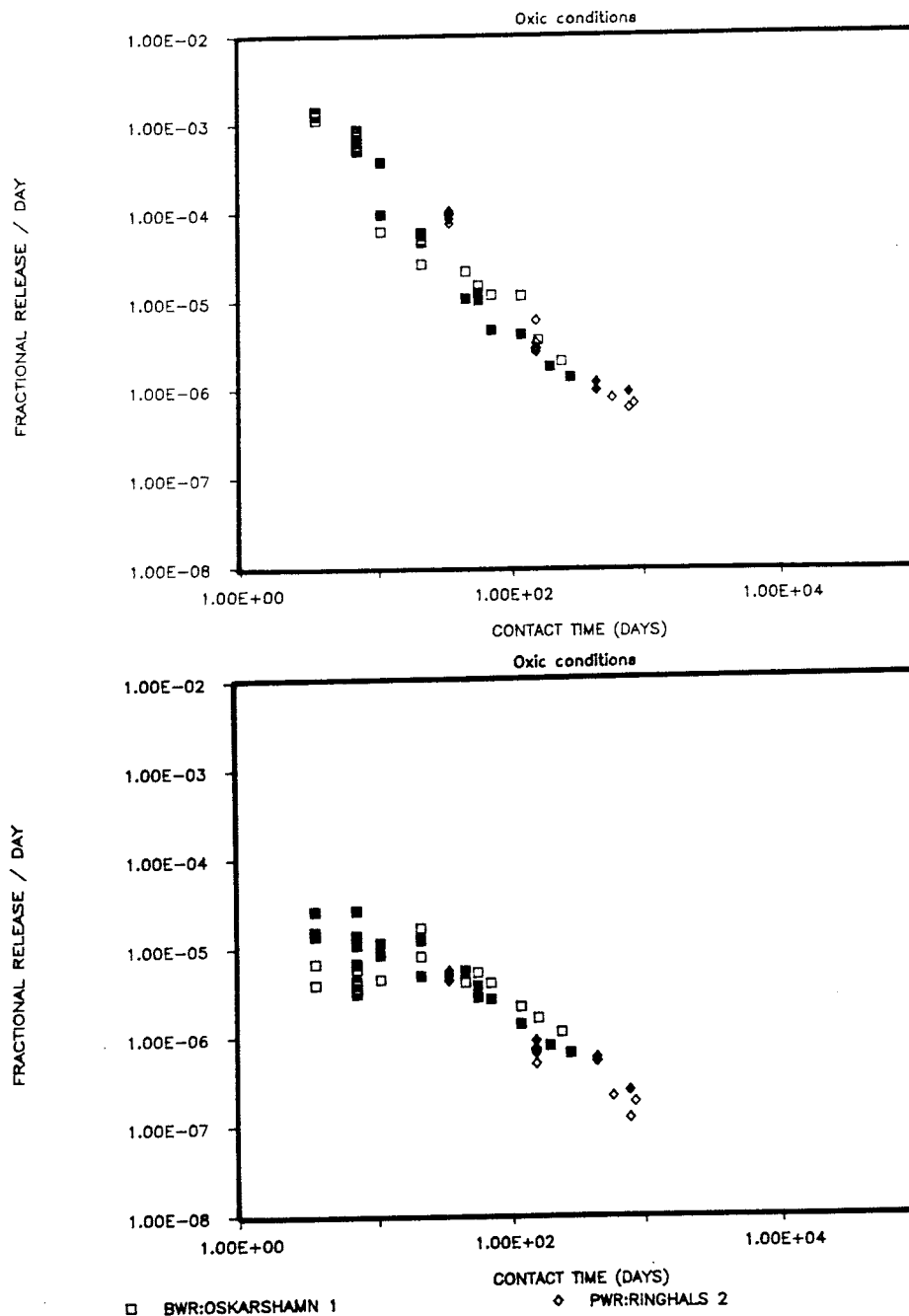


Figure 3 Fractional release rates for Cs-137 (above) and Sr-90 (below) for fuel/clad segments in Allard GW and DIW

Cs-137, during the first few weeks of water contact, during which time the Sr-90 release rate is fairly constant, followed by a rapid decrease in the rates for both nuclides. The Cs-137 release rates, however, are always higher than the corresponding values for Sr-90.

Release rates for Tc-99 and Mo, which are probably selectively leached from the 4d metal fission product inclusions known to be present in the central fuel zone and at the peripheral rim (see later), are about the same as those for Sr-90 during the initial contact period but decrease slightly to a level of somewhat above $1.E-06/\text{day}$, which appears to be maintained subsequently.

An apparent difference in Sr-90 release behaviour between fuel specimens of similar burnup, mentioned above, has been attributed to the effect of local differences in irradiation history, which had caused different degrees of Sr-90 segregation, for example at the grain boundaries.

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This was first observed in the early results [2] from corrosion tests on the BWR reference fuel. The effect can be seen on inspection of the Sr-90 release rates in Figure 3, where the filled and empty symbols represent specimens from two different parts of the fuel column.

However, a faster release rate of both Sr-90 and Cs-137 during the early stages of corrosion seems to be followed by a slower rate at longer contact times. In consequence, it can be observed that for a given cumulative release fraction for Sr-90 ("reaction progress"), the ratio between the Cs-137 and Sr-90 cumulative release fractions is approximately the same for both parts of the fuel column. This, in turn, can be explained by differences in water penetration behaviour rather than Sr-90 segregation.

A distinct difference in release behaviour between specimens from different parts of the fuel column has also been observed for the PWR reference rod, as shown in Table I, which presents cumulative release fractions from 6 fuel/clad specimens exposed to sequential corrosion tests under oxidic conditions for 3 contact periods. All specimens were exposed to corrosion in Allard GW for 2 periods of 82 and 170 days respectively, followed by a third period in DIW (7.1 and 7.2) or GW (7.3-7.6).

Table I
Cumulative release fractions from PWR fuel/clad segments.
(Odd and even numbered specimens were taken from different parts of the rod.)

Specimen No.	Cumulative time (days)	Cumulative Release Fractions					Mo
		U	Cs-137	Sr-90	Tc-99		
7.1	688	4.4E-05	9.9E-03	8.0E-04	5.5E-04	2.0E-04	
7.3	688	7.2E-05	9.3E-03	8.2E-04	8.7E-04	5.8E-04	
7.5	1331	1.7E-04	9.5E-03	8.1E-04	3.3E-03	1.1E-03	
7.2	1331	4.4E-05	8.8E-03	6.1E-04	4.4E-04	2.6E-04	
7.4	938	1.0E-04	7.4E-03	5.8E-04	1.4E-03	8.2E-04	
7.6	1469	1.0E-04	9.2E-03	7.2E-04	3.9E-03	1.5E-03	

The cumulative release fractions for Cs-137 and Sr-90 are clearly different for the two specimen groups, while Tc and Mo release is more directly correlated to the cumulative contact time, with the exception of those specimens, 7.1 and 7.2, which had a final exposure in DIW. Note that, as corrosion proceeds, the total release of Tc and Mo exceeds that of Sr-90, and approaches that of Cs-137. (See comments above on Tc and Mo release rates).

The Sr-90 release behaviour, however, is rather surprising. The two fuel specimen zones in the BWR rod had experienced slightly different irradiation histories due to control rod movements. Although the local linear power had always been less than 25 kW/m, it is conceivable that Sr-90 segregation by migration either as strontium or as Rb-90 precursor could have occurred to an extent necessary to explain the results: the cumulative release fraction for Sr-90 represents only of the order of 0.1 % of the total inventory after several years of corrosion.

The PWR fuel specimen zones, however, were immediately adjacent to each other between the 3rd and 4th spacer grids, where such time-dependent power effects would be very similar. It was therefore decided to examine the relationship between fission product release and burnup/local power in a separate experiment.

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EFFECT OF BURNUP/LINEAR POWER ON CORROSION PROPERTIES

Rod 79B2 is the bottom segment of a stringer rod irradiated for 8 cycles in the Ringhals 1 BWR. The local burnup along the fuel column, excluding the end pellets, varies between 20-47 MWd/kg U, and only during the first irradiation cycle did the maximum-rated pellet experience a linear power as high as 25 kW/m. The preliminary integral fission gas release value for the rod is 1.1 %. Fuel/clad specimens taken from different burnup positions along the rod are being corrosion-tested in a programme which includes detailed characterization of the fuel at 3 burnup levels.

Since the differences in release behaviour between nominally identical fuel specimens from the reference BWR and PWR rods were observed after short contact periods, close attention is being paid to this phase. The release fractions for Cs-137 and Sr-90 for rod 79B2 fuel specimens (series 11) under oxidic conditions for cumulative contact times of 7, 28, 91 and 182 days are presented in Figures 4 and 5.

Inspection of the figures leads to a number of observations:

- 1) Even though some of the effects noted are surprising, the results form a consistent set.
- 2) That for both Cs-137 and Sr-90, a step-increase in leachability occurs at a rod position with a burnup of about 32 MWd/kg U.
- 3) That after the step-increase (about 39-40 MWd/kg U), there was no further increase in "leachability" with increasing burnup and fuel temperatures under reactor operation. Indeed, the release behaviour over the 4 contact periods suggest instead that water access to the fuel surface, or certain parts of the fuel surface, has been hindered.

Support for the hypothesis is afforded by the observed Tc-99 release behaviour. Although it is usually assumed that Tc release is effected by oxidative attack on the 4d metal inclusions situated at grain boundaries, and that formation of the inclusions is enhanced at higher burnups and fuel temperatures, the measured cumulative release fractions for Tc-99 were lower for the high burnup specimens (>40 MWd/kg U) than for the lower.

Hopefully, future results from this on-going programme, particularly those on fuel characterization, will furnish satisfactory explanations for these effects.

CORROSION SITES

So far in this paper, interest has been concentrated on possible fission product segregation or concentration-enhancement, particularly for Sr-90, at grain boundaries in low-powered LWR fuels. Another necessary condition for explanation of the release behaviour observed in this and other programmes is, of course, the exposure of such enhanced zones to leachant attack at an early stage of the corrosion process, when Sr-90 release rates are highest. For short initial contact periods, say 7 days, Sr/U leachant ratios are always greater than unity, even when uranium has not reached solution saturation.

There is little published information on the identification of corrosion sites in spent fuel exposed to water corrosion. Some early results on LWR fuel are available [7] and Johnson et al [1] have inferred extensive grain boundary attack from grain pull-out during ceramographic examination of CANDU fuel exposed to aggressive corrosion in a saline leachant. The observed grain pull-out occurred from $r/r_0 = 0.7$ out to the pellet periphery.

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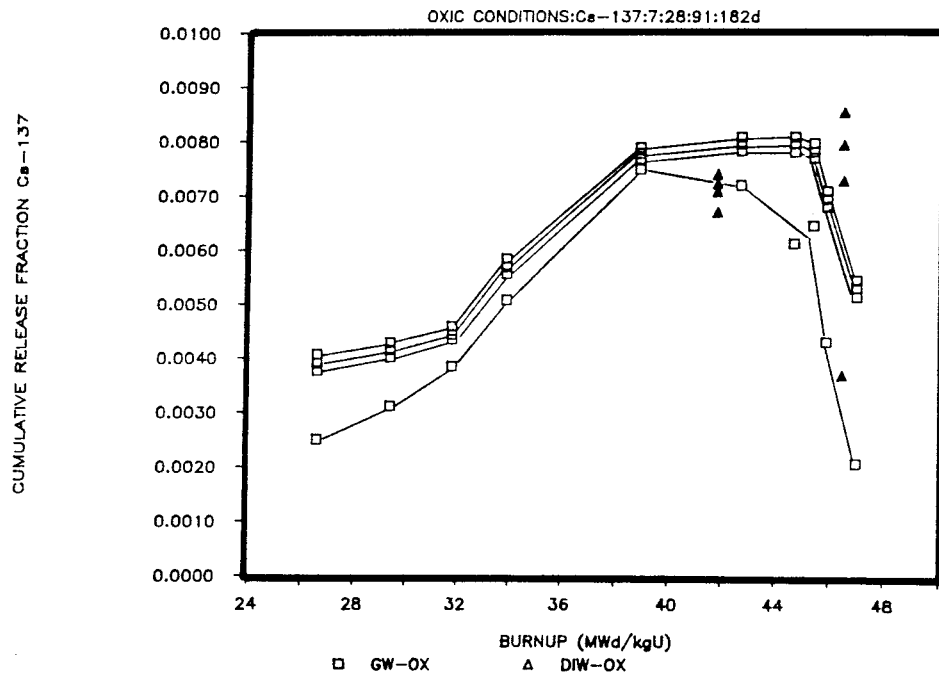


Figure 4 Cumulative release fractions (7, 28, 91 and 182 days) for Cs-137 under oxitic conditions.

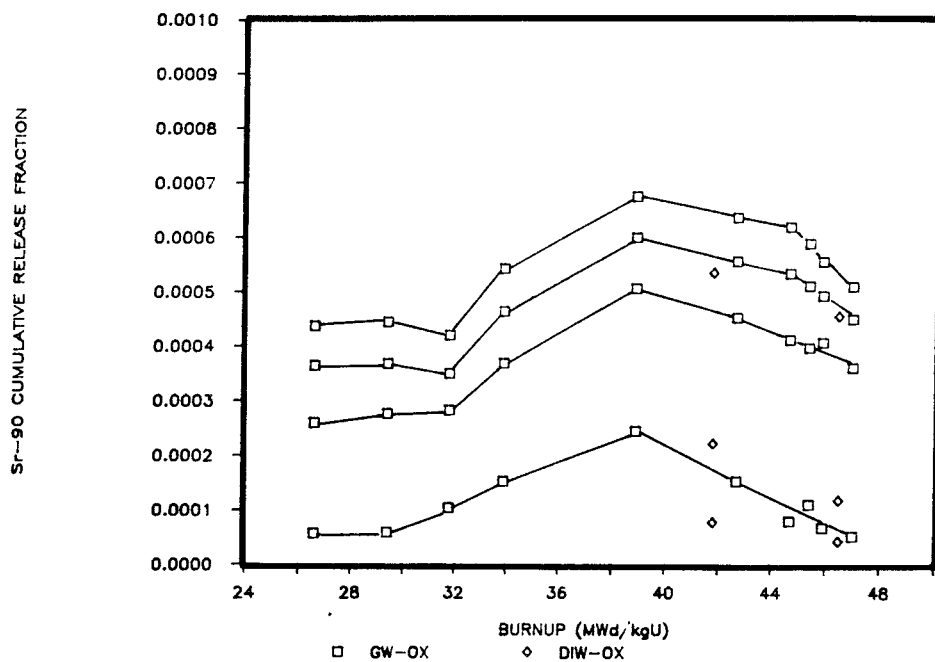


Figure 5 Cumulative release fractions (7, 28, 91 and 182 days) for Sr-90 under oxitic conditions.

At Studsvik, results are now becoming available from an on-going programme where selected fragments of the reference BWR fuel, exposed to DIW and modified Allard GW (varied bicarbonate concentration) for 4 years or more, are subjected to systematic examination for comparison with the original material.

A large weight fraction of the fuel fragments from spent BWR and PWR fuel pellets consists of sectors of the fuel cross-section, the sector

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sides being delineated by the pellet periphery and two radial cracks. Selection of suitable fragments permits systematic study of the corrosion process both at the fuel periphery and at a series of radial positions representing different fuel characteristics, for example, porosity.

Because of space limitations, results from experiments performed under reducing conditions, i.e., the most relevant for fuel disposal in granitic deep-rock repositories, have not been discussed here. However, it is known from this and other experimental programmes, that under such conditions, fractional release rates for Sr-90, and also for Cs-137 after the instant release phase, decrease by only about an order of magnitude. This effect is usually attributed to local oxidative attack at the fuel surfaces due to alpha and/or beta-gamma radiolysis of the leachant.

For LWR fuels, the specific alpha activity (defined here as total alpha Bq/g U) increases as a function of burnup mainly due to increased formation of americium and curium nuclides. In segment rod 79B2 discussed above, for example, the specific alpha activity in the bulk fuel at the start of the experiments increases by a factor of about 3.3 along the fuel column, while the corresponding factor for burnup (and, approximately, for beta-gamma activity) is only 1.8. At the outer rim of the fuel, however, due to neutron spectrum effects, there is a further steep increase in both fission rate and actinide build-up. The latter can be clearly seen as a thin halo in alpha autoradiographs of fuel cross-sections.

This alpha rim effect has recently been quantified by alpha etch pit counting on alpha autoradiographs of the reference BWR fuel used in these experiments [8]. Fuel porosity changes even more abruptly at the fuel rim. Values of the total porosity as a function of radial position [9], together with the corresponding values of relative alpha activity are given in Table II.

Table II

BWR reference fuel: radial variation of fuel porosity and actinide inventory.

Radius (mm)	0	2	4	4.5	4.9	5.05	5.10	5.15	5.20
Porosity (%)	0.82	0.57	0.88	1.05	0.98	1.59	1.81	1.81	5.03
Alpha act ^y (relative)	1.00	1.01	1.12	1.18	1.34	1.37	1.40	1.55	2.02

As mentioned above, there is also a fission rate increase at the fuel rim, where it is a factor of about 2 higher than in the bulk fuel. Thus, the outer porous 50 microns of the fuel, which represents about 1.9 % of the pellet volume, contains about .4 % of the fission product inventory.

Solution analysis results from two fragment corrosion experiments are presented in Table III.

Table III

Cumulative release from fragments of BWR fuel leached in:
specimen 3.25 : 240 ppm HCO₃ GW. Specimen 3.26 : DIW.
Oxic conditions.

Specimen No.	Cumulative time (days)	Cumulative Release Fractions				
		U	Cs-137	Sr-90	Tc-99	Mo
3.25	1427	2.2E-03	1.2E-02	3.3E-03	4.7E-03	5.0E-03
3.26	1521	5.1E-06	1.2E-02	4.6E-03	1.1E-02	1.5E-03

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In these experiments, a higher water/fuel ratio (about 200 g/g) was used than in the fuel/clad segment experiments described earlier (13-20). In experiment 3.25, where the leachant was a modified Allard GW, with 240 ppm bicarbonate, this had the effect of ensuring that larger than "normal" amounts of uranium could be held in solution, while in experiment 3.26 (DIW), any alteration product formed, for example schoepite, would be retained on the fuel surface or in the accessible porosity.

Inspection of Table III, however, shows a general agreement with earlier results: corrosion (as measured by Sr-90 release) proceeds at least as readily in DIW as in bicarbonate GW.

On removal from their respective leachants, the fuel fragments from both experiment were black: no trace of surface deposit was observed on the 3.26 experiment fragments. However, about 30 minutes later, during inspection under the cell periscope, a yellow surface covering formed almost immediately on the fragments exposed to DIW.

The fuel fragments from both experiments have been subjected to systematic ceramographic examination (OM and SEM) on both polished and fracture surfaces at a series of radial positions and compared with the original fuel. Although there was evidence of some grain boundary corrosion (grain pull-out) at all radial positions, the peripheral zones showed the most pronounced evidence of corrosive attack. Strips from SEM microphotomosaics (originally 4000x) of the fuel rim for the two experiments and uncorroded reference fuel are presented in Figure 6.

Comparison of Figure 6a (reference material) and Figures 6b and 6c (specimens 3.25 and 3.26 respectively) clearly shows that there has been pore enlargement and interlinkage, and loss of material in the outermost 20 microns or so of the fuel rim. Further in, grain boundary attack is evidenced by the development of chains of porosity and grain pull-out. The effect is more pronounced for specimen 3.26 (DIW) which also showed a larger release fraction for Sr-90. Note also for this specimen the crystals of UO_3 hydrate which have grown out from the fuel surface (see above).

A feature of the microphotographs of the corroded fuel is the presence of numerous rounded particles, a few hundred nanometres in size, in zones at the fuel rim, and clearly visible at pore surfaces further into the fuel. Although similar particles are also seen in the porosity of the reference fuel, their distribution seems to be much less extensive.

This impression, however, is illusory. Examination by SEM of fracture surfaces of reference fuel shows that the particles are extremely prevalent at the outermost fuel rim, decorating grain corners and edges and covering pore surfaces. They are also present, but with decreasing frequency, far into the fuel, but characterization of the fuel in this respect is still in progress.

Figures 7a and 7b present SEM micrographs of the fracture surface of the reference fuel, at the periphery and at 100 microns from the periphery, while Figures 8a and 8b are corresponding micrographs from the rim of experiment 3.25 fuel. While the particles discussed above appear to be associated with larger porosity, other smaller particles are also visible in Figures 7 and 8 in or near the sites of small fission gas bubbles on grain faces. It is suggested here that these smaller particles are inclusions of the 4d metals (Mo, Tc, Ru, Rh, Pd). Production (and inventories) of these elements is much higher at the fuel rim than elsewhere in the fuel, partly because the fission rate is higher at the rim, and partly because their fission yields are higher for fission of plutonium nuclides than for U-235. It is possible, therefore,

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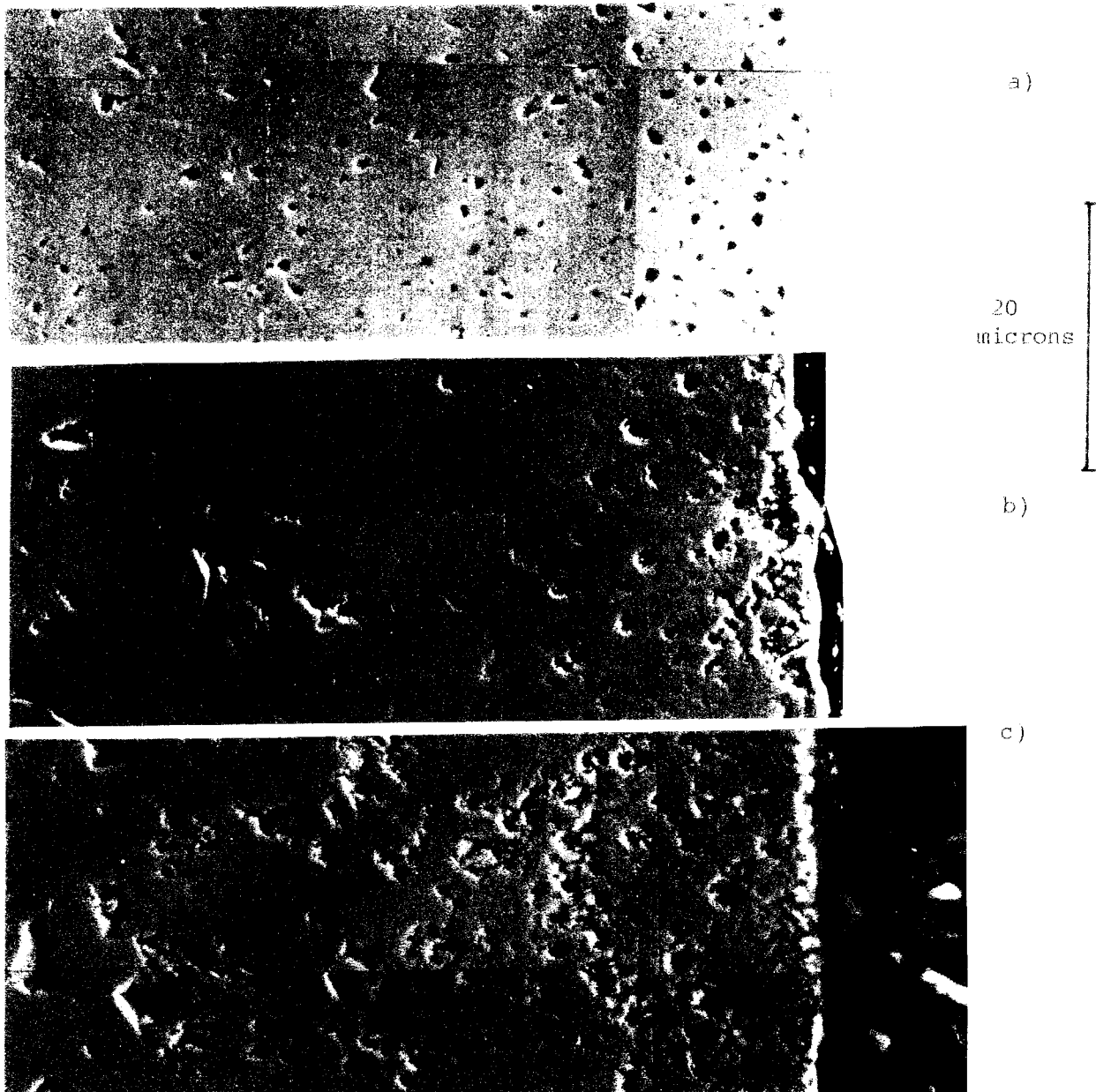


Figure 6 SEM mosaics of the rim of the BWR reference fuel.
a) Uncorroded.
b) Expt. 3.25. (1427d in 240 ppm bicarbonate GW.)
c) Expt. 3.26. (1521d in DIW.)

that the Tc and Mo release fractions reported earlier in this paper, at least in part, are due to selective oxidative attack on these inclusions since access of leachant through the interlinked porosity is relatively easy.

With respect to the larger particles, however, any hypothesis regarding their identification is even more speculative. The results of XRD analysis of small specimens selectively removed from the corroded rims of specimens 3.25 and 3.26 have hitherto shown no other phase present than UO_2 . EPMA examination of reference fuel and corroded fuel is at present underway at Studsvik but results will not be available for some time. TEM examination would obviously be useful.

The rim effect in high burnup fuels is currently not well understood, and has only attracted serious attention in recent years with the trend towards higher discharge burnups for commercial LWR fuel.

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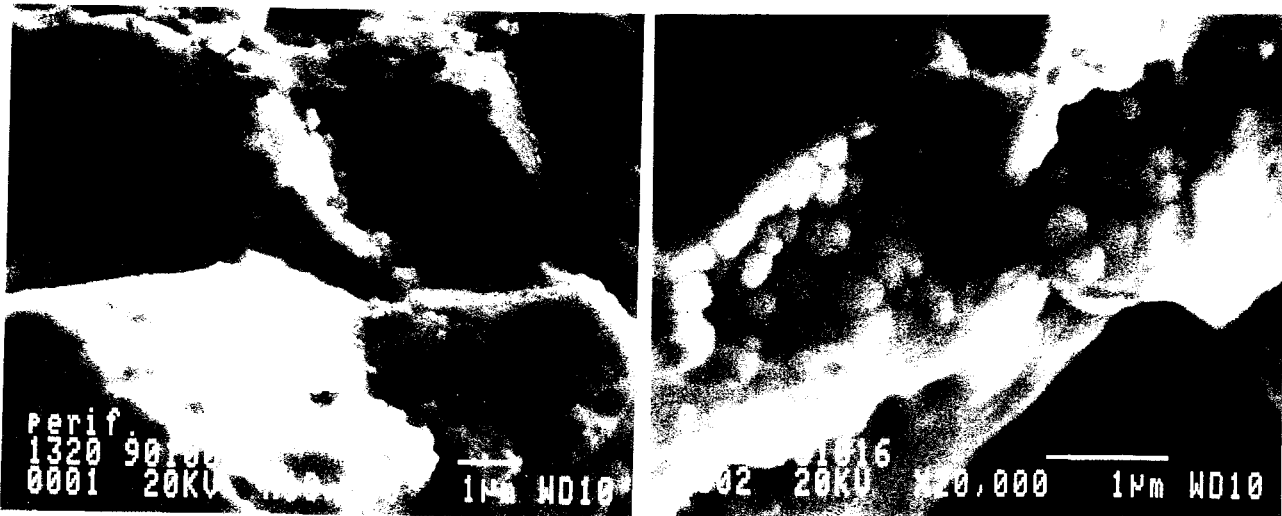


Figure 7 Scanning electron micrographs of the fracture surface of the uncorroded reference fuel.
 a) At the periphery.
 b) 100 microns from the periphery.

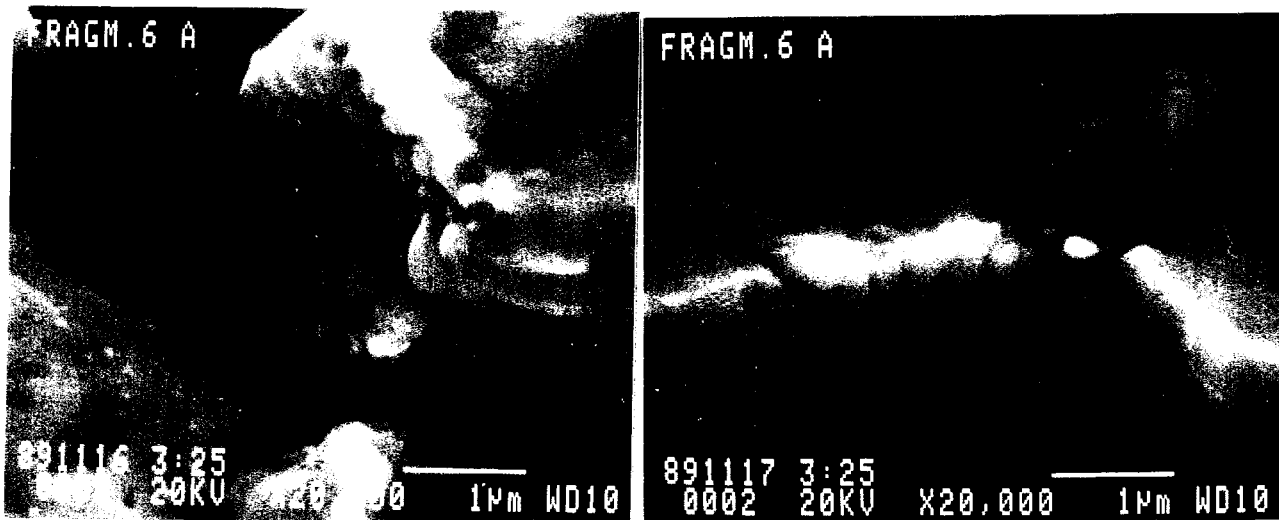


Figure 8 Scanning electron micrographs of the fracture surface of fuel corroded in 240 ppm bicarbonate groundwater. (3.25.)
 a) At the periphery.
 b) 100 microns from the periphery.

The location of the particles at, or in, the surfaces of voids - pores and grain boundaries - and the apparent decrease in fluorite crystallinity at the fuel rim, however, suggests tentatively that the effects observed may be caused by the high fission fragment flux in combination with development of increased porosity as burnup proceeds.

During standard PIE work at Studsvik about 10 years ago on the thickness and growth of zirconium oxide layers on inner clad walls, it was observed that, particularly at higher burnup, the oxide layer displayed unusual morphological features, such as wrinkles, spherical nodules and wormlike structures. Although further investigation of the effect was not pursued, a

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critical review [10] of the experimental results and possible causes, suggested fission fragment damage as one of the more possible explanations of the phenomenon.

The ceramographic and SEM observations on the corroded fuel in the 3.25 and 3.26 experiments, although they suggest some material loss at pores and grain boundaries, are not sufficiently quantitative to indicate whether the "altered" fuel particles are subjected to preferential dissolution or not. However, a possible loss of fluorite structure caused by intense and localised fission fragment damage may mobilise and redistribute the contained fission products and increase their availability for leaching.

ACKNOWLEDGEMENTS

Many of the staff of Studsvik's Hot Cell Laboratory have been engaged in the experimental work reported here. The author gratefully acknowledges their contributions. Thanks are also due to Dr. L.O. Werme, Swedish Nuclear Fuel and Waste Management Co., for many helpful discussions and suggestions.

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