

SPENT FUEL AS A WASTEFORM.
THE SWEDISH PROGRAM FOR STUDIES AND EVALUATION OF SPENT FUEL FOR DIRECT DISPOSAL

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ABSTRACT

Direct disposal of spent nuclear fuel is currently considered as the main option for nuclear waste management in Sweden. Technical characteristics as well as the safety of the once-through alternative of the nuclear fuel cycle have been studied since 1977. Within the program, dissolution mechanisms and dissolution rates of spent fuel in contact with groundwater have been investigated as well as the chemistry of the radionuclides.

The mechanisms for release of radionuclides from a spent fuel matrix are far from fully understood, but available data from the experimental program show that the actinides and many of the fission products (with exception of e, g, I, and Cs) are mobilized congruently with the matrix dissolution. Current information on the chemical properties of the radionuclides in the groundwater system as well as experimental studies of spent fuel dissolution strongly indicate that the release of most radioactive species to the near field is controlled by solubility limits and sorption mechanisms.

The speciation and solubilities of radionuclides in groundwater systems are not finally established as yet. Also the importance of some phenomena, such as alpha radiolysis, influencing the dissolution rate of the spent fuel matrix requires further studies. However, conservative estimates show that direct disposal of spent fuel in deep geological formations is a technically viable option.

INTRODUCTION

Direct disposal of spent nuclear fuel is currently considered as the main option for nuclear waste management in Sweden. Technical characteristics, as well as economical and safety aspects of the once-through alternative of the nuclear fuel cycle have been studied since 1977. The methods, proposed in Sweden and elsewhere, have in common a multibarrier concept to radionuclide release to the environment. The innermost barrier is the UO_2 -matrix itself. Within this concept, dissolution mechanisms and dissolution rates of spent fuel in contact with groundwater have been investigated, as well as the chemistry and behavior of the radionuclides in the near and far fields.

BACKGROUND

The waste package, which consists of a metallic overpack or container enclosing the otherwise unconditioned fuel elements, should provide zero-release for a desired period of time, the length of which is dictated by considering the half-lives of the radionuclides in the spent fuel and other constraints imposed by the overall design of the repository. After the containers have been breached, the release of radionuclides to the environment will be controlled by the dissolution rate of the wasteform, the solubilities of the individual radionuclides and the retardation or fixation in the geosphere.

In the Swedish concept, the acceptability of the disposal system is evaluated based on its overall performance, considering the spent fuel wasteform as the innermost barrier. However, no criteria for acceptability of wasteform performance per se has been developed or applied. Nevertheless, the behavior of the wasteform in the repository environment after contact

with groundwater must be established by experiment, since the release from the wasteform constitutes the source term for the radionuclide migration through the geosphere.

Compared to other wasteforms, such as borosilicate glass comparatively few laboratories have devoted substantial efforts to the study of spent reactor fuel as a wasteform^{1,2,3,4}. It has, therefore, been considered important that a comprehensive experimental program is carried out in Sweden to provide data complementary to data obtained elsewhere as well as data specific to the Swedish disposal concept. This program has now been implemented for nearly four years and results from the studies have also been published^{5,6}.

EXPERIMENTAL STUDIES

The experimental program aims at a deeper understanding of fuel dissolution and solubility limitations as well as the effects of radiolysis on fuel dissolution. The details of the experimental program as well as the procedure are described elsewhere^{6,7}. Both static and sequential (IAEA-type) leach experiments are performed using D.I. water and synthetic groundwater (see Table I for composition) to study kinetics and mechanisms of fuel dissolution. To date, contact times up to over 900 days have been evaluated. These studies are supplemented with shorter exposures in groundwater solutions with different pH-values, as well as solutions where reducing conditions have been imposed. The purpose of these latter experiments is to further elucidate the solubility constraints and the oxidative dissolution of the UO_2 -matrix.

TABLE I

Composition of 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.

Procedure

All leach experiments were performed in 250 ml Pyrex flasks, the fuel specimen, as short segment of fuel and clad from a BWR rod and containing about 16 g UO₂, being suspended almost vertically in a platinum wire in 200 ml of the leachant. All tests were carried out at the ambient temperature in the hot cell, 20-25°C.

After completion of the contact period, pH was measured and about 20 ml of the leachant was centrifuged through membrane filters with apertures of 1.5-2.0 nm in order to obtain a "true" solution. The material retained on the filters are arbitrarily defined as "colloidal". Both centrifugate and filters are then subjected to analysis. All samples were analyzed for uranium, Sr-90, gamma-emitting fission products and alpha-emitting nuclides.

Because of the difficulty in defining the surface area of the highly cracked spent fuel, the experimental results are expressed in fractions of the initial inventory of the nuclide in the specimen. Also, since the amount of the nuclide in the leaching vessel is the result of interacting processes (i.e., selective leaching, dissolution, colloid formation, precipitation, etc.) the neutral term Fraction of Inventory in the Aqueous Phase (FIAP) is used. The term Apparent Leach Rate (ALR) in FIAP/day is used as the corresponding definition of rate.

Cesium

As has been already confirmed in previous work, Cs is released in reactor operation from the warmer central region to the fuel/clad gap. In the case of the high burn-up BWR fuel used in these experiments, about 1% of the total Cs inventory was dissolved rapidly in the leachant. A value in good agreement with the reported value for the release of fission gases from the whole fuel rod. Plots of the FIAP versus cumulative contact time are shown in Fig. 1, for two parallel series with specimens cut from two different parts of the fuel rod having the same burnup. As can be seen, the static tests agree well with the sequential tests for the same cumulative contact times.

It can also be seen that after an initial phase, corresponding to the dissolution of cesium compounds in the neighborhood of the fuel/clad gap, the dissolution rate drops substantially.

Strontium

Figure 1 also presents the cumulative FIAP values for Sr-90. Here the ALR show a continuous decrease as a function of contact time, approaching $2 \cdot 10^{-7}$ FIAP/d after about one year. The figure also illustrates the different Sr behavior in specimens cut from different part of the rod having the same burn-up and inventory but different irradiation history.

However, after about 100 days, these initial differences have more or less disappeared.

The cumulative FIAP values from sequential and static leach tests agree well, suggesting that saturation has so far not been reached.

Uranium, Plutonium and Curium

These nuclides have interesting similarities and differences. The cumulative FIAP values versus cumulative contact time for sequential leaching are shown in Fig. 2. It can be seen that the Uranium results generally lie about one order of magnitude below the Sr-90 results (the discrepancy indicated in the figure as Uranium deficit) and for Plutonium and Curium about two orders of magnitude.

If the Uranium and Plutonium concentrations from the centrifuged solutions are plotted versus contact time, a different pattern can be observed. Figure 3 and 4 show that already after about 14 days, an apparent solubility limit is reached and longer contact times do not result in increased concentrations of U and Pu in the solutions. Indeed, for Plutonium there is some evidence for decreasing concentrations in solution for longer contact times.

Corresponding curves for Curium have not been plotted, since the filtrations show that most of the Curium in the solution is "colloidal" as can be seen in Table II.

TABLE II

Average Values of Colloidal Fraction
(% FIAP retained on 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

DISCUSSION

Preferential Dissolution

For Cs, there is some evidence for preferential leaching even after the rapid initial release from the fuel/clad gap^{3,4}. The present work supports this observation; the ALR values for Cs-137 were higher by a factor 3-4 than those for Sr-90 even after 1-2 years.

For Sr-90 the initial differences in ARL values for specimens from different parts of the rod during the first 100 days of leaching suggest some correlation with fuel properties. However, even after 2 years contact time, the ARL values were higher than those for U by a factor of 3-4. At the present stage of inquiry, it is very uncertain that the higher ARL values represent preferential leaching of Sr, rather than other restrictions, such as solubility constraints, preventing Uranium and the actinides entering the solution.

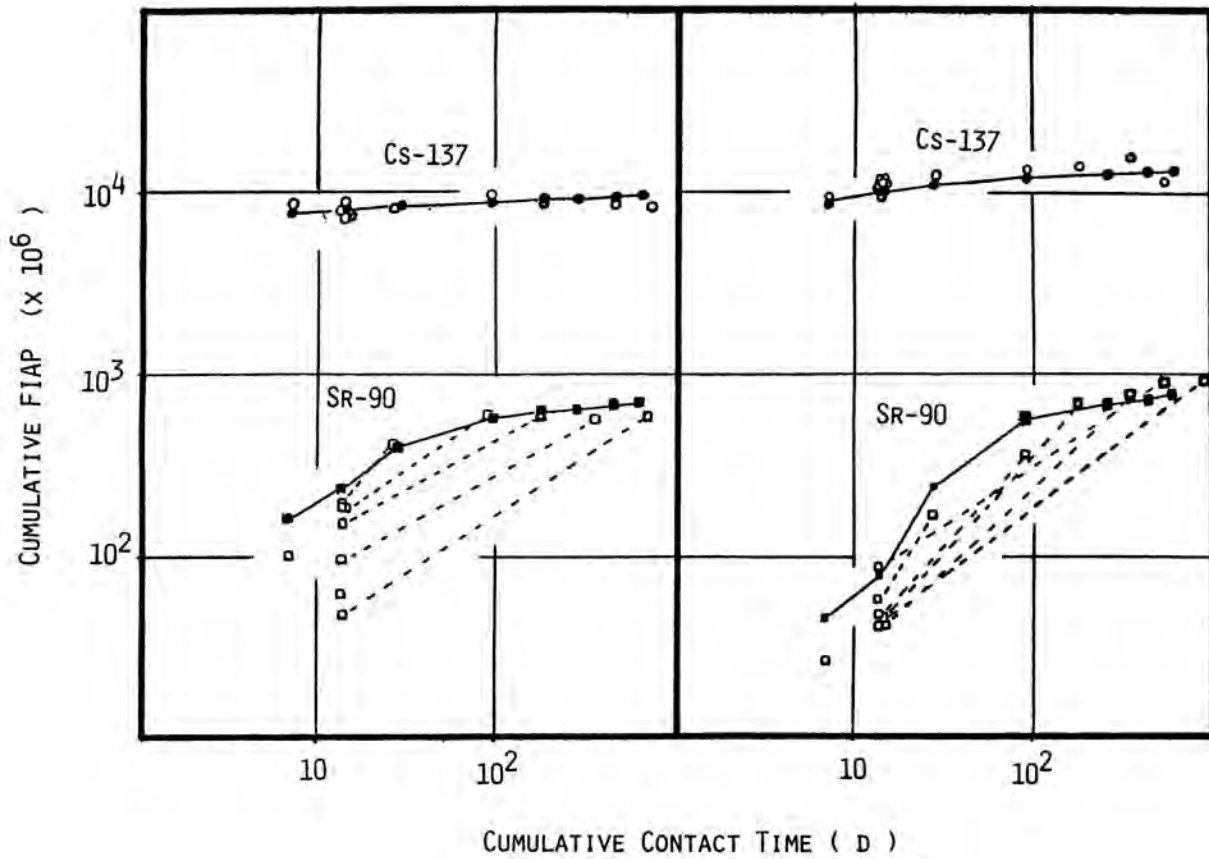


Fig. 1. Agreement between results from sequential (IAEA-type) and static tests (open symbols: static tests).

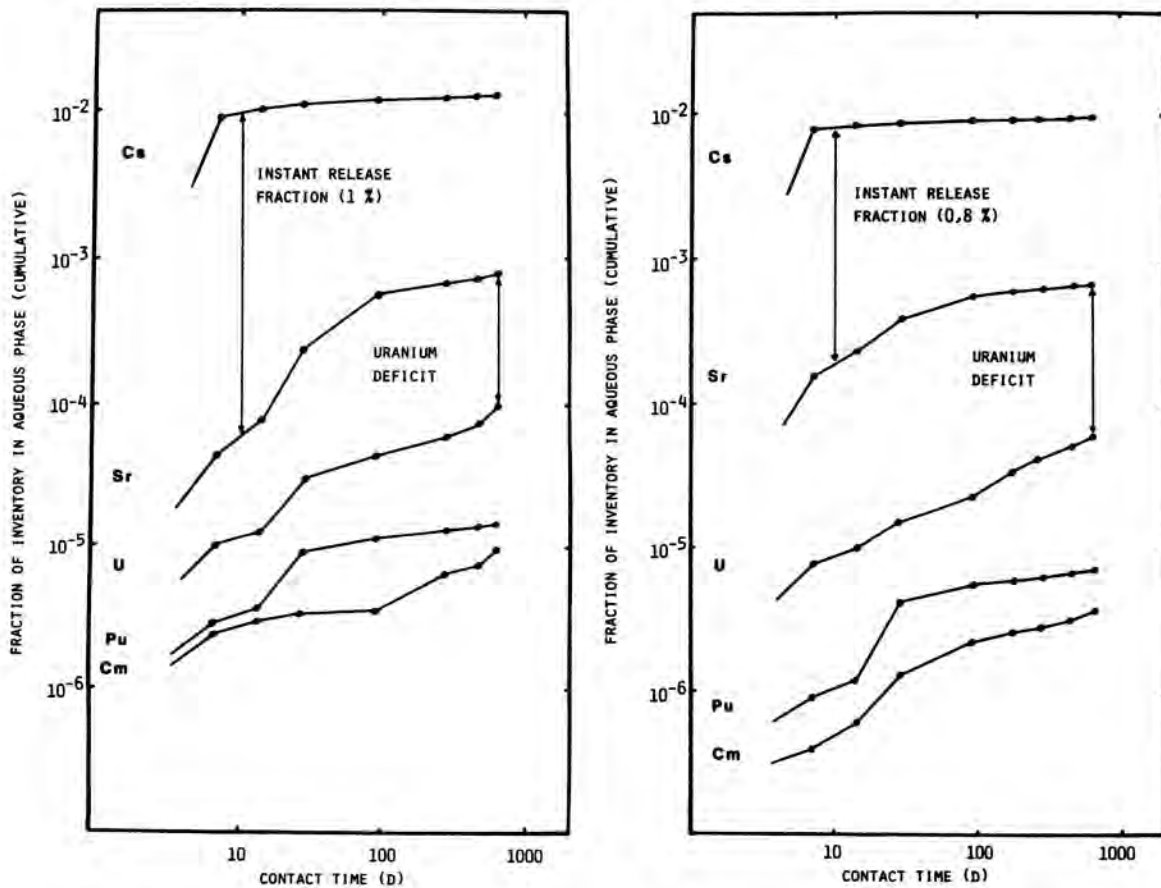


Fig. 2. Sequential leaching results for groundwater. Specimens cut from different parts of the fuel rod.

URANIUM CONCENTRATION
(centrifugate): (micrograms/liter)

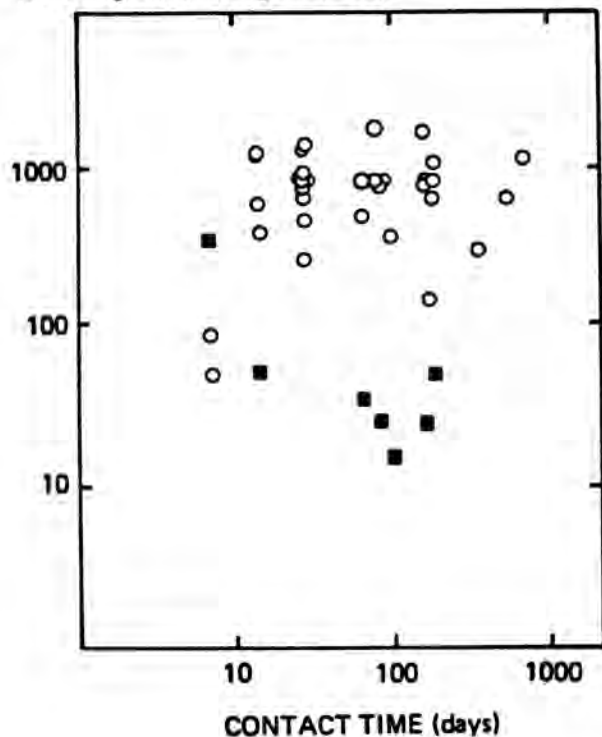


Fig. 3. Measured concentrations of U at different contact times. Open rings: exposure in synthetic groundwater at pH 8.2. Solid squares: exposure in DI H₂O (pH 7.0).

PLUTONIUM CONCENTRATION
(centrifugate): (micrograms/liter)

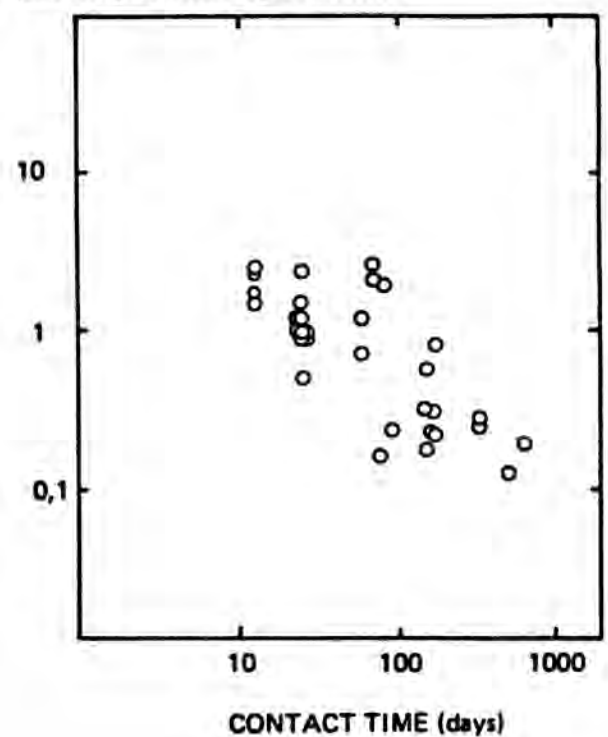


Fig. 4. Measured concentrations of Pu at different contact times.

Solubility Limitations

As was mentioned previously, plots of Uranium and Plutonium concentrations versus contact time clearly indicated an apparent solubility limitation on the release of these nuclides to the solution. In order to test the hypothesis of solubility constraints, a test of shorter contact times at lower pH was performed. The results for Uranium are presented in Fig. 5. As can be seen, the concentrations versus pH plot strikingly resembles solubility versus pH diagrams. Comparison with theoretically calculated solubilities strongly supported this assumption as can be seen by comparing the experimentally determined solubilities with the calculated ones⁶. For Plutonium, the quantitative agreement was poorer, but also for this element the calculations supported the assumption of solubility limitations.

Fuel Dissolution

Based on the experimental evidence obtained so far, it seems reasonable to assume that the initial release from the fuel sample has an important component of preferential leaching. This is certainly true for Cs (and I, although not measured in this study), but to some extent also for Sr plus possibly other nuclides not analyzed for in this study. These early releases come from the fuel/clad gap (Cs, I) but also preferential grain boundary attack may be responsible for at least some of the Cs and Se release. For a more detailed analysis of releases from these sources, a more thorough characterization of the fuel rod would be necessary. A program aiming at such studies is presently being launched in Sweden.

Throughout the leach period, Uranium and the actinides (with possible exception of Np) are controlled by their solubilities in the system. At longer cumulative contact times, whether obtained through sequential leaching or through static exposure, the release of Sr is still higher than for U and the cumulative release is independent of leach method, i.e., largely independent of the amount of U released to the solution.

The theoretical calculations show that the solubility limiting phase in the studied system is UO₂(OH)₂. A reasonable interpretation of the Sr data is that this solubility limiting phase - with which the other actinides may co-precipitate⁸ - is rapidly developed and maintains a constant Uranium concentration in the solution. However, UO₂, not being stable in the system, continues to convert to the more stable phases. (This has also corroborated by electrochemical and surface analytical studies on unirradiated UO₂.) In this process, the more soluble nuclides, such as Sr, may be released to the solution at a maximum rate equal to the rate at which UO₂ is reacted. Whether Sr in this study is a correct measure of this matrix alteration rate can at this stage not be determined, but it is reasonable to assume that it indicates a conservative upper limit for the release of more soluble species.

For the sake of comparison with other candidate wasteforms, the release rates of Uranium and the studied actinides after over two years contact time are below 10⁻⁵ per year. However, as is evident from the preceding discussions, the rates are determined by the annual waterflow rather than by the inherent properties of the wasteform itself.

URANIUM CONCENTRATION (centrifugate): (milligrams/liter)

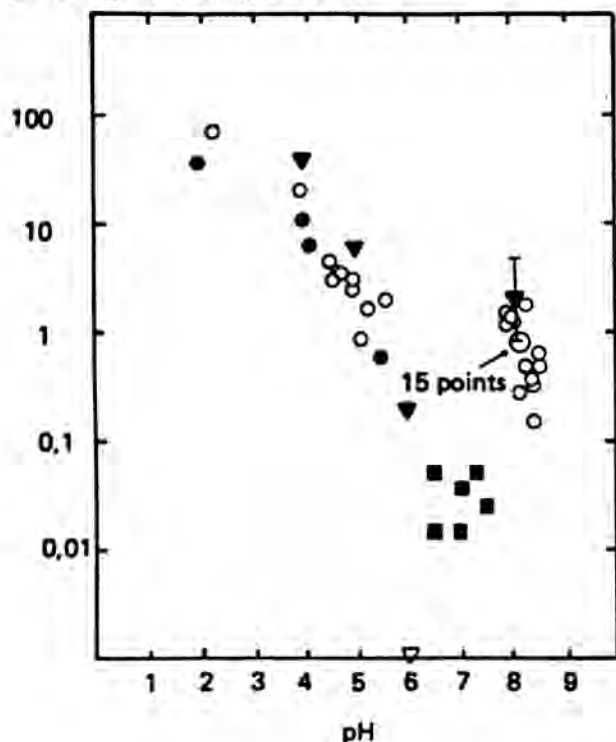


Fig. 5. Measured concentrations of U at different pH. Open rings: In the acidic range, 91 days exposure. At pH 8.2 14 days to 2 years. Solid rings: 20 days exposure. Solid squares: Exposure in DI H₂O. Solid triangles: Calculated solubility in synthetic groundwater. Open triangle: Calculated solubility in DI H₂O.

The release rate of Sr is approaching 10^{-5} per year, but within the time framework of this study still, after nearly three years, higher.

REDUCING CONDITIONS

All the experiments reported above were performed under oxidizing condition. In the deep repository projected in the KBS program, however, extremely reducing conditions - unfavorable to oxidative dissolution of UO₂ - are expected to obtain. Such conditions are difficult to establish and maintain in a laboratory, and in particular in a hot cell environment.

Adopting a method using hydrogen gas and a Palladium catalyst to obtain reducing conditions, described by Norris¹⁰ some experiments have been performed within the present program. The results must so far be regarded as preliminary, but indicate a reduced ALR for Sr with about a factor of 30. At the same time the concentrations of U dropped to near or below the analytical detection limit (about 15 ppb). An expanded experimental program studying the effects of a reducing environment is now in progress. However, it must be pointed out that the combined effect of a reducing environment and radiolysis of the solution need careful study before any precise statements can be made on the conditions at the fuel/solution interface.

Comparison with dissolution of spent UO₂-fuel of widely different burn-ups under oxidizing and

reducing conditions clearly indicate that in aerated systems, the effects of alpha-radiolysis on UO₂-dissolution are negligible compared to other sources of oxidants.

IMPACT ON SAFETY ANALYSIS

The present study clearly indicates that the releases of U and most actinides (with the possible exception of Np) are controlled by solubility constraints. This was also the approach chosen in the KBS-3 report¹⁰. However, the experimental results as well as the theory applied show that the solubilities used in KBS-3 are indeed conservative. For U the actual solubility may be overestimated with as much as a factor of 100. Even though further studies are required to unambiguously determine the release mechanisms for the radionuclides and alteration products formed when UO₂-fuel is reacted with groundwater under repository conditions, the present data and the safety analysis indicate that for the less soluble nuclides spent UO₂-fuel is indeed an adequate waste-form.

Adopting the proposed interpretation of Sr as indicator for the matrix alteration rate, the more soluble nuclides may cause some concern. However, it should be borne in mind that the experiments are conducted in a far more oxidizing environment than expected to obtain in the repository. Thus, as was mentioned before, using the Sr release rate as an indicator for the matrix alteration rate is indeed conservative.

Experimental data indicate that even a relatively soluble actinide like Np is expected co-precipitate with U and the other actinides⁶. The Np available in solution for transport away from the repository will thus be lowered, being controlled by a solid phase other than its hydroxide.

Most of the fission products have relatively short half-lives and the container over its lifetime will protect against releases. Furthermore once leached into the groundwater, the delay mechanisms in the geological barrier will substantially reduce the amounts of these nuclides reaching the biosphere. This has been discussed in further detail in the KBS-3 report.

CONCLUSIONS

- Uranium and actinide release from spent UO₂-fuel appears to be controlled by solubility constraints.
- Under oxidizing conditions, Sr-90 is continuously released from the fuel, although at a rate decreasing with time. After 400-500 days of contact the Sr-90 leach rate is about $3 \cdot 10^{-7}$ /d. The Sr release rate can be used as an upper limit from the matrix alteration rate.
- Experimental data coupled with safety analysis show that spent UO₂-fuel is an adequate waste-form for final disposal. However, many aspects of spent fuel dissolution in groundwaters are far from fully understood and require further studies.

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