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Spent fuel performance under repository conditions: A model for use in SR-Can

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Abstract

The SKB performance assessment study SR-Can will use a new model for estimating the release rate of radionuclides from the canister after water can enter the canister. This report describes the background to development of the model and the details of the release rate estimates. The fraction of radionuclide inventory that can be released without dissolution of the fuel matrix is called the rapid release fraction (RRF). The RRF for each radionuclide that can be released without matrix dissolution is given as a triangular distribution with a peak at the most likely value. The matrix dissolution rate is estimated from several sets of experimental data. The data show that there is no enhanced dissolution to be expected due to alpha radiolysis under the conditions that will pertain in the SKB repository. The rate of matrix dissolution in the model is given as a triangular distribution with a range from 10^{-6} to 10^{-8} per year with a peak at 10^{-7} per year.

Contents

1 Introduction

1.1 Canister design

The repository in Sweden is based on the Swedish KBS-3 design. This is described in detail in a number of SKB reports, see e.g. SKB's Safety Report /SR 97, 1999/. The basic concept for the disposal of spent fuel is based on its encapsulation and emplacement in crystalline rock at a depth of about 500 m. The spent nuclear fuel is planned to be encapsulated in spheroidal graphite cast iron canisters that have an outer 50 mm thick shield made of copper. Once filled and sealed, the copper-iron canisters will be emplaced individually in vertical boreholes in the floors of deposition tunnels feeding off central tunnels. The space between the canisters and the wall of the borehole will be filled with compacted bentonite. The tunnels and shafts will be backfilled with a mixture of crushed rock and bentonite, and sealing plugs will be emplaced to block specific transport pathways for groundwater.

The function of the canister is to isolate the spent fuel from the surrounding environment. The design is shown in Figure 1-1 for the BWR version of the canister and a cross section of both the BWR and PWR versions are shown in Figure 1-2. A summary of the fuel properties that were considered when designing the canisters is given in Table 1-1.

The spent BWR fuel will be encapsulated with fuel channels and the spent PWR fuel with control rods. The dimensions in Table 1-1 are the design-basis dimensions. There are several different fuel types in use with slightly different dimensions. The design and fabrication of the canisters are described in /Werme, 1998; Andersson, 1998; Andersson, 2002/.

Table 1-1. Fuel properties of importance for canister design.

Fuel type	BWR	PWR
Overall length	4,398 m	4,243 m
Cross-sectional area	140×140 mm^2	214×214 mm^2
Number of fuel rods	63–100	15×15 or 17×17
Enrichment (% U-235)	max 3.6% (with Gd 4.2%)	max 4.2%
Burnup (max)	60 MWd/kg U	60 MWd/kg U
Burnup (average)	38 MWd/kg U	38 MWd/kg U
Decay (min)	30 years	30 years
Decay heat per assembly	100–150 W	300–450 W

50 mm copper

Estimated weight (kg):

Copper canister	7,400
Insert	13,600
Fuel assemblies (BWR)	3,600
Total	24,600

Figure 1-1. *Dimensions and weight of the canister.*

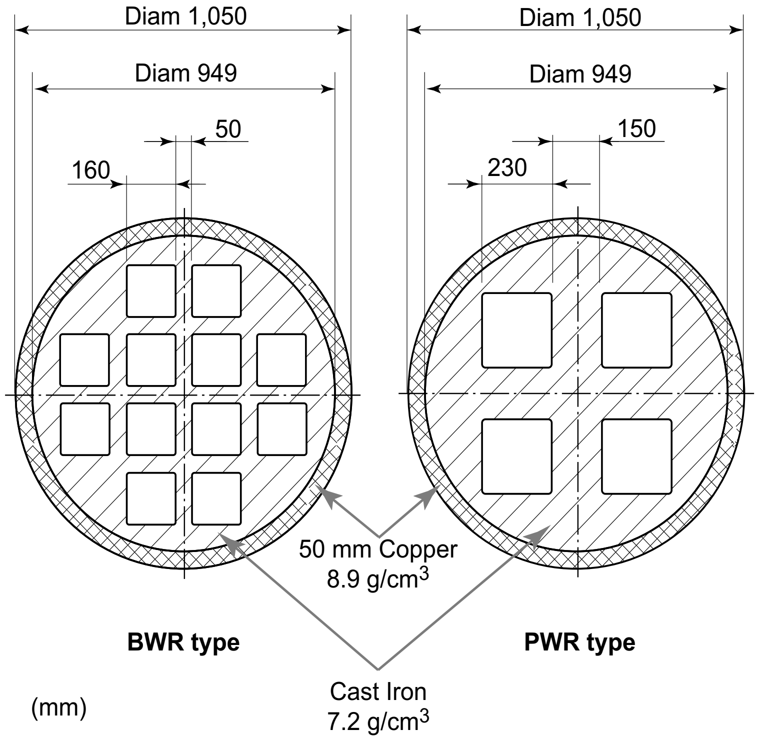

Figure 1-2. *Schematic design of inserts for 12 BWR and 4 PWR assemblies.*

1.2 Burnup distribution of the fuel

The present inventory of fuel at the CLAB facility, 19,400 elements (22 April 2003), has an average burnup of 33 MWd/kgU. This is an increase from the average 31 MWd/kgU for 15,247 elements at 30 June 1998. Despite the trend towards higher burnup, there are very few elements with a burnup exceeding 50 MWd/kgU. In the 1998 data there were 5 and on 22 April 2003, the count was 17. The burnup distribution is shown in Figure 1-3.

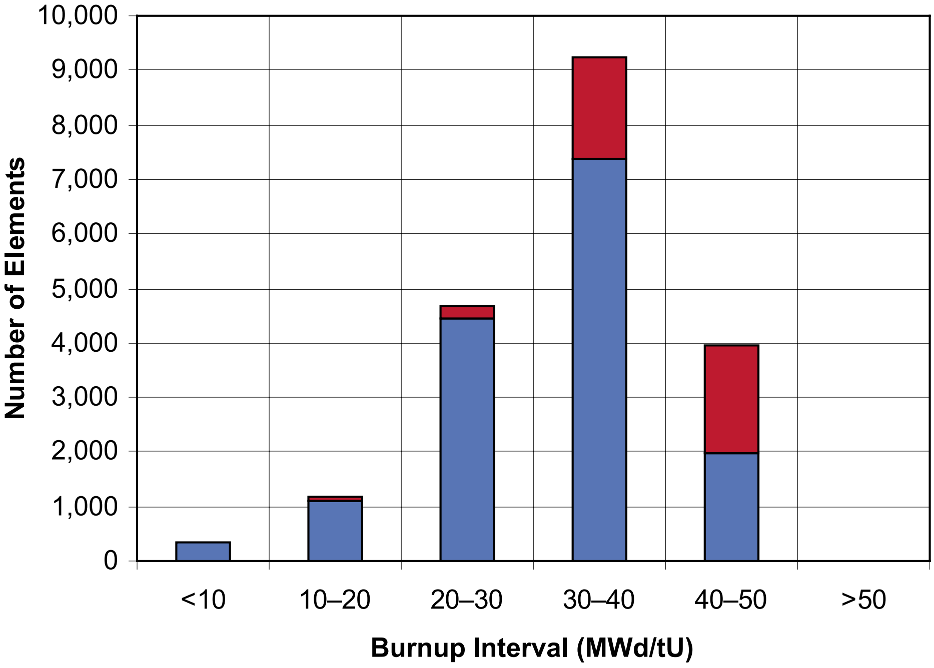

Figure 1-3. *Comparison between the burnup distributions at 30 June 1998 (blue) and 22 April 2003 (blue + red).*

1.3 Conditions inside the canister after closure

The atmosphere in the canisters after loading with fuel and sealing will be either air, or rare gas if the radiolytic production of nitric acid from water accidentally transferred into canister and nitrogen gas is deemed to be unacceptable. The oxygen and water that is initially present in the canister will be consumed through corrosion reactions with the cast iron insert. Once that has happened, there will be no more corrosion reactions occurring inside the canister until the copper and cast iron components have been penetrated.

1.4 Time for first water intrusion into the canister

The goal for canister production is that no more than 0.1% of all canisters will have flaws that exceed in size SKB's acceptance criterion that there must be at least 15 mm of intact copper ligament in the copper canister. In the Interim Main Report of the Safety Assessment /SR-Can, 2004/, a probabilistic calculation for the whole inventory of canisters is presented. This analysis shows that the expected time for penetration of the first canister will be somewhere between 400,000 and 1,000,000 years after disposal. No failures are expected during the initial 1,000 years when elevated temperatures will prevail in the repository and the most likely failures will occur considerably later in the canister's service-life.

The evolution of a failed canister is complex and depends on a number of uncertain factors. Water is likely to intrude into the canister, causing corrosion of the cast iron insert and leading to hydrogen gas generation. The build-up of gas pressure in the canister should be considerable and lead to gas release through the buffer. As corrosion proceeds, corrosion products, occupying a larger volume than the corresponding amount of metallic iron, will exert mechanical pressure on the copper canister, potentially leading to an expansion of the original defect in the copper shell. The corrosion also causes a weakening of the cast iron insert, making the canister more vulnerable to isostatic pressures. The evolution will also be influenced by external factors like the external mechanical load on the canister and by the thermal conditions. Possible evolution scenarios are discussed in the Interim Main Report of the Safety Assessment /SR-Can, 2004/ and will not be dealt with in this report.

2 Initial release

2.1 Background

During irradiation in the reactor, a certain percentage of the radionuclide inventory will have segregated to the gap between the fuel and the cladding and also to grain boundaries. Of these radionuclides, the behaviour of the fission gases is best known. A number of studies of fission gas releases have been published over the years. The behaviour of other potentially segregated radionuclides is far less well-known. This is of concern because these radionuclides will be released more rapidly than the radionuclides that are embedded in the fuel's UO_2 matrix. These fractions released to the fuel/cladding gap and to the grain boundaries are somewhat improperly collectively referred to as the "Instant Release Fraction". For a repository situation, the term "Rapid Release Fraction" would be more appropriate and would better describe this release since, although it may be considerably faster than the release of matrix-bound radionuclides, the release from the grain boundaries may well continue for an extended period of time. For safety analysis purposes, however, both these fractions are frequently treated as an instant release from the fuel. The contribution due to release from grain boundaries in the rim region is not relevant to the analysis, as the formation of a rim occurs only at burnup values above about 45 MWd/kgU /Johnson and McGinnes, 2002/.

The fraction of the radionuclides that is incompatible with the UO_2 matrix and is present in the fuel/cladding gap is generally considered to be comparable to the fission gas release to the fuel/cladding gap as measured in gas release testing of fuel rods /Johnson and Tait, 1997; Johnson and McGinnes, 2002/. Since there are far more data available on fission gas release than on the release from the matrix of other radionuclides, it can be of interest to discuss the fission gas release even though the fission gases are of little concern for the SR-Can safety analysis.

2.2 Fission gas release

Fission gas release is more strongly correlated to the linear heat rating than to the burnup of the fuel /Kamikura, 1992/. Operating conditions ensure that the linear heat rating is kept low and the fission gas release is minimized. Up to a burnup of about 40 MWd/kgU, the fission gas releases are typically <1% as is illustrated in Figures 2-1 and 2-2.

The studies of fission gas release have tended to focus on fuel rods with higher than average power ratings, such as corner rods in the fuel assemblies. This leads to an overestimation of the average fission gas release /Rönnberg, 2004/.

As can be seen in Figure 1-3, the major part (80%) of the Swedish fuel inventory has a burnup of less than 40 MWd/kgU. The number of fuel elements with an average burnup exceeding 50 MWd/kgU was 17 in April 2003. The average burnup, as stated in Table 1-1 is currently 38 MWd/kgU. The expected fission gas release for fuel with burnup less than 40 MWd/kgU is less than 1%. Based on the information in Figures 2-1 and 2-2, the average can be estimated to be about 0.5%. For the interval 40–50 MWd/kgU, the fission gas release is below 1.5% and the average is still close to 0.5% for PWR fuel. For BWR fuel, the fission gas release increases markedly after 40 MWd/kgU burnup with a maximum as high as 5% and with an average in the range of 2.5%. In view of the bias towards fuel rods with higher power ratings in the studied population, the data presented in Figures 2-1 and 2-2 can be regarded as realistic to moderately pessimistic estimates of the fission gas release from the current Swedish inventory of spent nuclear fuel.

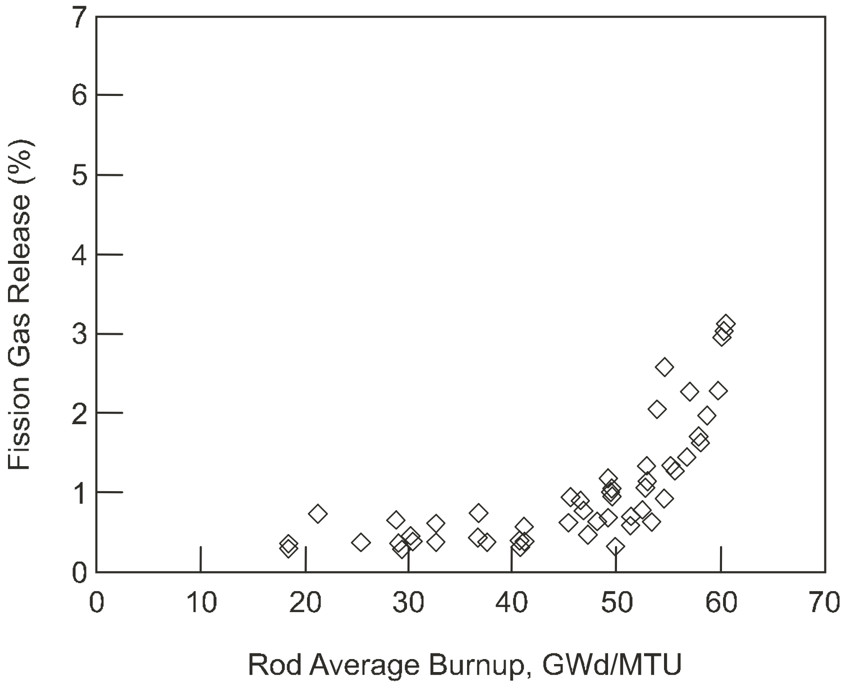

Figure 2-1. *Fission gas release from PWR fuel as a function of burnup /Vesterlund and Cosetti, 1994/.*

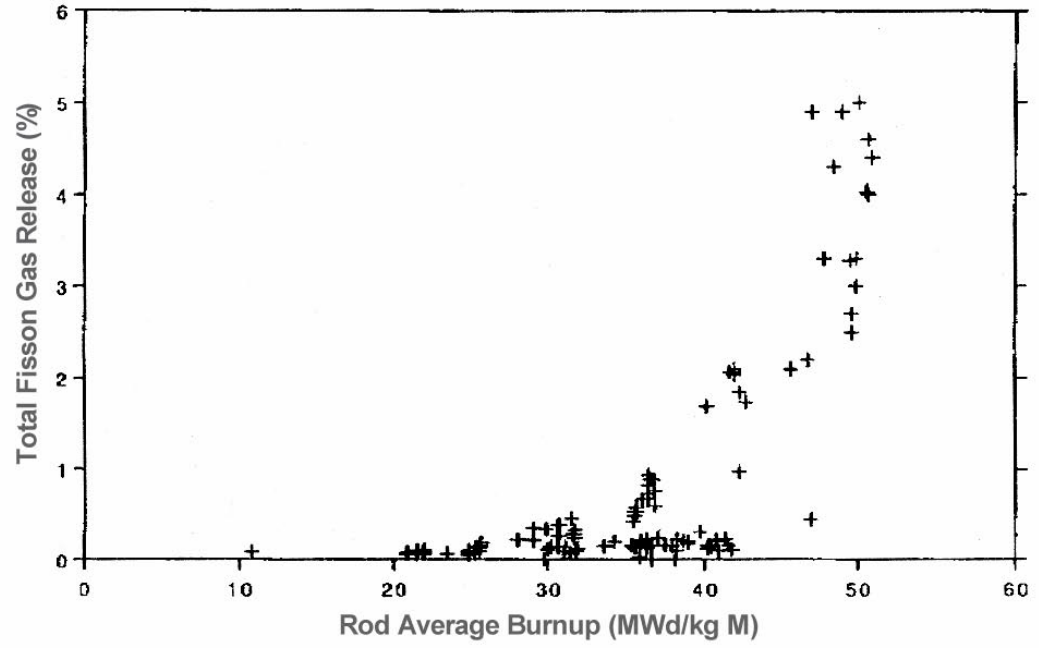

Figure 2-2. *Fission gas release from BWR fuel as a function of average rod burnup /Schrire et al., 1997/.*

2.3 Estimated initial release fractions

There are relatively few systematic studies of the release of segregated material other than fission gases in spent fuel. By far the most comprehensive study was published by /Stroes-Gascoyne, 1996/. In that publication, the rapid release of ^{137}Cs, ^{90}Sr, ^{99}Tc, ^{129}I and ^{14}C from CANDU fuel was reported. For LWR fuel, there is far less data available /see e.g. Forsyth and Werme; 1992; Gray et al., 1992; Gray, 1999/. It should be pointed out that some of the fuel used in Gray's studies had extremely high fission gas releases, up to 18%. This is very much outside the expected fission gas releases from fuel during normal operation (see Figures 2-1 and 2-2) and the release data from this fuel are, therefore, probably not relevant for safety analysis purposes.

It is generally assumed that the fission gas release and the rapid release of other segregated radionuclides are related. This seems to be a reasonable assumption for LWR fuel with gas releases in the range of a few percent /Johnson and McGinnes, 2002/. For some radionuclides, assuming a one-to-one relationship will be a reasonable assumption, while for others the relationship seems to be more complex. This will be discussed later.

As was mentioned before, no canisters are expected to fail during the first 1,000 years after disposal. After failure by penetration of the copper outer shell, there are several different possibilities for the internal evolution in a canister Interim Main Report of the Safety Assessmant /SR-Can, 2004/. The time at which water comes in contact with the fuel may be considerably longer than 1,000 years. In the present analysis, water contact is somewhat arbitrarily assumed to happen after 1,000 years, 10,000 and 50,000 years. As a consequence of this, the radionuclides that need to be considered are different at different points in time. Following /Johnson and McGinnes 2002; Johnson and Tait, 1997/, the following radionuclides need to be considered for rapid release after 1,000 years (Table 2-1).

Table 2-1. Key radionuclides for rapid release after 1,000 years.

Nuclide	^{14}C	^{36}Cl	^{79}Se	^{99}Tc	^{107}Pd	^{126}Sn	^{129}I	^{135}Cs
Half-life	5.73×10^{3}	3.0×10^{5}	1.13×10^{6}	2.1×10^{5}	6.5×10^{6}	2.3×10^{5}	1.57×10^{7}	2.3×10^{6}

The same set is important after 10,000 years, while after 50,000 years the ^{14}C inventory has dropped to insignificant levels.

The release fraction for ^{14}C

/Johnson and McGinnes, 2002/ point out that there are no new ^{14}C data reported since /Johnson and Tait, 1997/. /Johnson and Tait, 1997/ proposed a bounding value of 10% and best estimate of 5%. Leaching data from CANDU fuels show no correlation with power rating and burnup /Stroes-Gascoyne et al., 1994/. /Johnson and Tait, 1997/ point out that this might be expected since nitrogen impurity is the predominant source of ^{14}C and the levels of nitrogen impurity are not accurately known, but likely to be variable. The form of ^{14}C in the fuel may be as carbides, oxycarbides or elemental carbon /Van Konynenburg, 1994/. The ^{14}C release may, therefore, be in the form of organic hydrocarbons.

The fuel leach data for ^{14}C are very limited. Some data are available for LWR fuel from the NNWSI project /Wilson and Shaw, 1987; Wilson, 1990a and 1990b/. The NNWSI data ranged from 0.035% to 3.5% of the measured inventories. /Stroes-Gascoyne et al., 1994/ have reported leach data for CANDU fuel. In their study the gap and grain boundary releases ranged from 0.06% to 4.95% with an average of 2.6%.

The recommended distribution for the release fraction is triangular from 0.1% to 10% with a maximum at 5%.

The release fraction for ^{36}Cl

There are no leaching data for ^{36}Cl release from light water reactor fuel /Johnson and Tait, 1997; Johnson and McGinnes, 2002/. The estimates of the release fraction will have to be based on the CANDU fuel data of /Tait et al., 1997/. These data show that the ^{36}Cl release increases steeply with fission gas release and is three times the fission gas release for higher linear power ratings. CANDU fuel's linear power rating is much higher than that of light water reactor fuel. In the study of Tait et al the linear power ratings ranged from 33 to 50 kW/m, while for a light water reactor it is generally below 25 kW/m. It is likely that using the CANDU fuel data will result in an overestimate of the ^{36}Cl release. Lacking any data for light water reactor fuel, a best estimate for ^{36}Cl release would be that it is three times the fission gas release as suggested by /Johnson and Tait, 1997/ and is bounded by an upper value as suggested by /Johnson and McGinnes, 2002/ for the higher burnup range (48 MWd/kgU). This would lead to a best estimate of about 5% and a bounding value of 10%.

The recommended distribution for the release fraction is triangular from 1% to 10% with a peak at 5%.

The release fraction for ^{79}Se

/Wilson, 1990a and 1990b/ attempted to measure ^{79}Se in the fuel leaching experiments performed for NNWSI. All ^{79}Se data were below the detection limit, which was 4.5 pCi/ml. Based on this, a total ^{79}Se of less than 1.12 nCi can be calculated. Using the measured inventory (3.93 µCi) of the fuel used in the experiment /Guenther et al., 1991/, the released fraction of ^{79}Se can be calculated to be less than 0.03%. This is considerably lower than the 0.78% release of ^{137}Cs in the first leach cycle of Wilson's experiment and the fission gas release of 0.2%. This suggests that there is no real evidence for ^{79}Se segregation at low to moderate burnup. In view of this, it is reasonable to revise the release fraction for ^{79}Se and the data suggest that a best estimate would be 0.03%.

The recommended distribution for the release fraction is triangular from 0% to 0.1% with a maximum at 0.03%.

The release fraction for ^{126}Sn

/Wilson, 1990a and 1990b/ also reports “less than” values for ^{126}Sn. Following the same procedure used for ^{79}Se, a release fraction of <0.003% can be calculated. As for ^{79}Se, there is no real evidence for ^{126}Sn segregation at low to moderate burnup. In view of this, it is reasonable to revise the release fraction for ^{126}Sn and the data suggest that a best estimate would be 0.003%.

The recommended distribution for the release fraction is triangular from 0% to 0.01% with a maximum at 0.003%.

The release fraction for ^{99}Tc and ^{107}Pd

Technetium and palladium are present in spent fuel in metallic form as alloy inclusions. No new data have emerged since the evaluation by /Johnson and Tait, 1997/. The release fractions they suggested are, therefore, proposed. This means a best estimate of 0.2% and a bounding value of 1%.

The recommended distribution for the release fraction is triangular from 0% to 1% with a maximum at 0.2%.

The release fraction for ^{129}I

As pointed out by /Johnson and Tait, 1997/, the ^{129}I data for light water reactor fuel are very limited. In most cases the measured ^{129}I gap release is much less than the fission gas release. /Wilson, 1990a and 1990b/ reports ^{129}I release fraction data that are about 10% of the ^{137}Cs release fraction data. /Gray, 1999/ measures ^{129}I gap and grain boundary releases comparable to the fission gas release. /Gray, 1999/ used, however, a KI (20 mg/l) carrier in a borate buffer when extracting the iodine from the fuel samples. /Stroes-Gascoyne, 1996/ also used a KI carrier in a borate buffer to preclude loss of volatile I, in case this was present. The presence of free cesium and free iodine has recently been confirmed by /Desgrange et al., 2004/.

/Gray, 1999/ concludes that the combined gap and grain boundary inventories of iodine in a fuel rod approximately equal the fission gas release for the same fuel rod, although with a larger fraction at the grain boundaries than in the gap. /Stroes-Gascoyne, 1996/ conclude that for CANDU fuel there is a one-to-one correlation for fuel with low linear power rating (less than 42 kW/m).

Following these observations, the expected gap and grain boundary release of ^{129}I is <1% for fuel with burnup less that 40 MWd/kgU, and an average of 2.5% for BWR fuel with burnup approaching 50 MWd/kgU.

The recommended distribution for the release fraction is triangular from 0% to 2.5% with a maximum at 1%. A pessimistic estimate would be a distribution for the release fraction that is triangular from 0% to 5% with a maximum at 2%

The release fraction for ^{135}Cs

For fission gas releases from 0% to 1%, the Cs gap releases are similar to the fission gas releases /Johnson and Tait, 1997/. /Gray, 1999/ has measured both gap and grain boundary inventory values of ^{137}Cs. He confirmed that at fission gas releases less than 1%, ^{137}Cs releases are similar to the fission gas release, while at higher fission gas release (FGR), the correlation for ^{137}Cs: FGR was 1:3. For BWR fuel with an average fission gas release of 5%, the data suggest that the expected cesium release would be 3%.

In assessing the release fraction for ^{135}Cs we have assumed that this isotope behaves similarly to ^{137}Cs and, consequently, correlates with the fission gas release. The expected gap and grain boundary release of ^{135}Cs is 1% for fuel with burnup less that 40 MWd/kgU, and an average of 2.5% for BWR fuel with burnup approaching 50 MWd/kgU.

The recommended distribution for the release fraction is triangular from 0% to 2.5% with a maximum at 1%. A pessimistic distribution for the release fraction would be triangular from 0% to 5% with a maximum at 2%.

2.4 Long term stability of the release fraction

Over the four past years, /Poinssot et al., 2000, 2001 and 2002/ have published a number of papers where they analyze the possible consequences of long-term storage of spent fuel on its physical and chemical behaviour. The estimate is based on scaling the athermal diffusivity of fission gases due to fission-fragment irradiation to the value expected for alpha particles. /Olander, 2004/ was commissioned by SKB to investigate the possible consequences of such athermal diffusion on the long term stability of the instant release fractions of radionuclides.

/Olander, 2004/ analysed the thermal spike that is produced in the lattice as a result of alpha decay. It is this spike that would be responsible for “athermal” diffusion. The diffusion is actually thermally activated, but only on the local atomic scale in the vicinity of the alpha particle. The diffusion coefficient calculated for Xe as a result of the thermal spike integrated over all alpha decays was 1×10^{-26} cm^2/s, which is 5 orders of magnitude less than that estimated by /Poinssot et al., 2002/. It can be shown that the mechanism makes no significant contribution to release if the D value is 1×10^{-22} cm^2/s or less. Therefore, for spent nuclear fuel of the types and burnups that are currently in storage in Sweden and are foreseen for the near future, athermal diffusion will be not lead to an increase of the release fractions even after a million years.

2.5 Effects of helium accumulation

Helium builds up in spent fuel because of the decay of actinides by alpha decay. At 1,000 years after discharge from the reactor a fuel with burnup of 35 MWd/kgU would contain about 5×10^{18} atoms/g, while a fuel with burnup of 50 MWd/kgU would contain about 8×10^{18} atoms/g. At an age of 10^5 years, the concentration of He will have increased to 2.4×10^{19} atoms/g and 3.1×10^{19} atoms/g respectively.

/Desgranges et al., 2003/ implanted $^4He^+$ ions in a spent fuel sample, achieving a [He] of 2×10^{20} atoms/g, which is nearly an order of magnitude greater than the [He] present in spent fuel after 10^5 yr. They examined the distribution of fission product xenon and neodymium in the helium-irradiated samples and in comparable unirradiated samples and found that there was no major difference in distribution of these elements as a result of the irradiation.

/Roudil et al., 2004/ implanted 2.9 MeV ^3He ions in UO_2 at two different concentration levels – 0.2 and 2×10^{19} atoms/g. The as-implanted profiles appear to be symmetric. The samples were annealed at 850, 900 and 1000°C and then examined for He diffusion. The diffusion curves measured showed no peculiarities that might have arisen because of lattice damage caused by radiation.

/Guilbert et al., 2003/ implanted 1 MeV ^3He ions in UO_2 to give a concentration of about 3.6×10^{19} atoms/g. The as-implanted He profiles were asymmetric, with a broad tail towards the sample surface. This suggests damage due to the irradiation process. The samples were heated to 500 and 600°C. After annealing, the samples showed flaking at the surface with the largest effect seen in the 600°C sample. This was caused by gas bubbles coalescing and growing, initiating a crack in the UO_2, followed by flaking off of the material above the implantation depth. Since there was a dramatic difference in the behaviour of the samples heated to 500 and 600°C, it is by no means clear whether gas bubbles could coalesce at the much lower temperatures that will pertain in the repository. The concentration of He used in these tests was also far greater than that which will be present in spent fuel disposed of in the Swedish repository, even at very long times after disposal.

We conclude from the results of these He implantation studies that the mechanical stability of the spent fuel to be disposed of in Sweden will not be detrimentally affected by the accumulation of He in the fuel after disposal.

3 Model for matrix dissolution

3.1 Background

The time period for which we need to have a model for the dissolution of the spent fuel matrix begins after there is a hole in the canister that allows water to enter the canister and contact the fuel matrix. This time is thousands to millions of years after disposal of the canister in the geologic repository. At that time, the radiation from the fuel will have decayed to levels that are much lower than when the fuel was deposited in the repository. In addition, the nature of the dominant radiation will have changed from a predominance of β and γ radiation to a predominance of α radiation. The repository near-field environment will also have changed from the post-disposal conditions and will include the products of canister corrosion and H_2(g) generated during the anaerobic corrosion of iron.

In this section, we will begin by discussing the factors that affect the dissolution of UO_2, starting with solids that contain natural uranium and then progressing to experiments that contain solids with higher levels of radiation. As with any solid, the dissolution of UO_2 depends on the chemical composition of the liquid phase. The rate at which the solid approaches equilibrium or steady state conditions with the solution is influenced by the ratio of the surface area of the solid to the volume of the solution (SA/V). The SA/V ratio does not, however, affect the concentration of U in solution at equilibrium.

Pure, perfectly crystalline UO_2 is thermodynamically stable under the reducing conditions that will pertain in the repository after closure and consumption of the residual oxygen by minerals in the bentonite buffer, minerals and microbes in the repository host rock and the tunnel backfill, and by corrosion of the canister materials. The maximum concentration of oxygen for UO_2 to be stable that is calculated from thermodynamic properties data is 10^{-65} atm /Rai et al., 1990/. This is a level that, in practical terms, means there is no free oxygen present. It is extremely difficult to establish this condition during laboratory experiments. If oxygen is present at levels above 10^{-65} atm, the surface of the UO_2 solid oxidizes, producing UO_{2+x}, where x may be as high as 0.33 for solutions in contact with air /Shoesmith, 2000/. Even brief exposure to air at room temperature of a solid that has been prepared under reducing conditions (roasting in H_2 atmosphere at high temperature) can produce a surface layer that contains U in an oxidation state higher than (IV). When the surface layer is examined by XPS, the data from a broad peak are interpreted by spectral deconvolution to represent U(VI) and U(IV) in the UO_2 lattice. More recently, U(V) is also considered. See, for example, the characterization data in /Parks and Pohl, 1988/, who studied a sample of UO_2 covered by a surface layer several monolayers thick with a surface composition containing 17% U(VI).

Oxidation of UO_2 can occur in contact with normal air atmosphere and also in contact with the trace amounts of oxygen that are typically present in inert atmosphere glove boxes (on the order of 1 ppm oxygen or more). Bubbling of inert gases through solutions during experiments will also carry trace amounts of oxygen into the system and cause oxidation of the solid.

The “solubility” of UO_2 is also affected by the condition of the solid with respect to crystallinity. In the extreme case of a newly precipitated solid that displays no X-ray diffraction pattern the solid is amorphous and cannot be considered (sensu stricto) to have characterizable thermodynamic properties. As the solid matures and becomes microcrystalline, we would expect the properties of the solid to approach those of perfectly crystalline UO_2. In the real case, for sintered materials that are used for nuclear reactor fuels, the solids contain about 5% porosity. This will be accompanied by defects in the crystal lattice that will affect the behaviour of the solid in solution. The defect structures might affect both the rate of dissolution and the final level of [U] in solution. Healing of defects during exposure to water has been reported by /Stultz et al., 2004/. This suggests that sample behaviour may depend on the number of defects in the sample and on their nature. It also suggests that sample behaviour may change with time as defects heal.

Impurities in the UO_2 solid may be present in solid solution or as separated micro-phases. For those elements in solid solution, if the valence of the impurity is (IV) the effect on solubility of U should be minimal. In the more general case, where the valence is not (IV), the impurity will affect the electronic structure of the solid. UO_{2+x} is a semiconductor, whose properties change from n-type to p-type at the composition where $x = 0$. This means that oxidation of the solid produces a p-type semiconductor. Introduction of lower valence impurities into the lattice requires oxidation of U(IV) to U(V) or U(VI) if charge balance is to be preserved. This could be important for spent fuel since it contains about 4% by weight of fission products, many of which are trivalent rare earth elements.

Solid UO_2 made from U with present day natural isotopic composition or with U that is depleted in the 235 isotope contains very low levels of radioactivity. Spent fuel that is available for testing contains very high levels of activity that are dominated by β and γ activity. These radiation types diminish in significance with time and at times of interest to repository performance assessment, α activity is dominant. This is important because the yield of radiolysis products and even the nature of the radiolysis products is different for the different radiation types. In addition, the effects of alpha radiation are confined to a layer of about 25 μm in the solution above the solid. To estimate the effects of α activity on the dissolution of spent fuel in the long term, samples of UO_2 containing an isotope of U with a shorter half life than normal U isotopes have been studied. Experiments have also been done with UO_2 containing Pu isotopes; these carry the added complication of potential problems with sample homogeneity and with the effects of including a different cation into the UO_2 lattice.

Radiolysis reactions produce equal amounts of oxidants and reductants in the fluid phase. The principle reducing species formed is hydrogen, which is known to be an active reducing agent at elevated temperatures, but has been considered in previous performance assessments to be too slow in its reaction at repository-relevant temperatures to be effective in counteracting the effects of the oxidizing species. Hydrogen is also produced in large quantities in the anaerobic corrosion of iron, which is the material of the canister insert that is closest to the fuel in the disposal canister. The pressure of hydrogen inside the container is expected to be ≥5 MPa, the hydrostatic pressure at the repository horizon. Corrosion of iron will also produce Fe(II) ions in solution, which can act as a reducing agent.

To provide a reference frame for the discussion of experiments designed to evaluate the long-term performance of spent fuel we will begin with a review of the available data concerning the solubility of UO_2 solids. We will then proceed to discuss the potential effects of $H_2(g)$, Fe(II), and radiolysis reactions on the results of experiments with UO_2-based solids and the relevance of these experiments for prediction of the long-term performance of spent fuel in the repository. We will focus our discussions on solutions of low ionic strength since this is the medium for which most data is available and the one most relevant to the repository conditions.

3.2 Solubility of uranium dioxide

The solubility of uranium dioxide can be obtained in two different ways: (1) direct measurement of the solution concentration in an experiment that contains pure UO_2 followed by interpretation of the data using modelling that accounts for the solution reactions that affect the speciation of U in the solutions, or (2) calculation of the solubility using thermodynamic data generated by other reactions of U. These include oxidation of UO_2 to U_3O_8 and burning of U metal in air to produce U_3O_8 to provide enthalpy of formation data and heat capacity measurements to provide entropy data. These data can be combined to give the free energy of formation of UO_2(cr). Both data from solubility studies and thermodynamic properties measurements are available for UO_2.

The "solubility" of amorphous UO_2 will provide an upper limit to the [U] to be expected under repository conditions and also in experiments conducted under reducing conditions that successfully excluded oxygen. We will discuss only experiments that included active control of redox conditions in this section. The [U] found in solution from experiments that started with crystalline UO_2 has been found to be closely similar to that found when freshly precipitated amorphous material was used. This has been interpreted to indicate that the solubility in all of the experiments was controlled by an amorphous phase on the sample surface even though the predominant solid present was crystalline /Rai et al., 2003; Neck and Kim, 2001/.

/Rai et al., 2003/ attempted to measure the solubility of crystalline UO_2 produced by precipitation from solution at 90°C. The product they obtained at low pH (<2) was crystalline, but that found at pH 4.9 to 5.3 was amorphous. Thus, their data at pH 4.9 and 5.3 represent the solubility of amorphous UO_2. The value found for total U in solution was log $M_U = -9.2$, or $[U] = 6.3\times10^{-10}$ M.

/Rai et al., 1990/, in their early attempts to measure the U(IV) hydrolysis constants and the solubility product of $UO_2 \cdot xH_2O$(am), discussed the difficulties of obtaining conditions for experiments that eliminate oxygen to the extent that is necessary for dealing with U(IV). They obtained [U] of about 10^{-8} M in the pH range 7 to 10 for room temperature experiments. This [U] is about 20 times higher than that found by /Rai et al., 2003/ and may indicate that even with the use of Fe powder or $EuCl_2$, it is difficult to exclude the effects of minor oxidation of U(IV) to U(VI). Their data was consistent with that of other reported experiments in showing that there is no dependence of "solubility" of UO_2 on pH in the range of 5 to 10. This is interpreted to indicate that the dominant U species in solution is $U(OH)_4$.

/Parks and Pohl, 1988/ conducted experiments on the solubility of UO_2(cr) at temperatures between 100 and 300°C using gold bag autoclaves. The solid sample was provided by UKAEA (via P Tremaine) and consisted of 250 μm spheres with a density of about 94% theoretical, which is similar to the density of unirradiated nuclear fuel materials. The solid had a stoichiometry of $UO_{2.00}$ as determined by its x-ray unit cell parameters if the solid were pure UO_2. Chemical analysis showed that the sample contained 450 ppm Al. This corresponds to 0.45 mole % Al in the cation sites. It is not known what effect this chemical substitution would have on the lattice parameters of the UO_2, and therefore on the determination of its stoichiometry.

/Parks and Pohl, 1988/ treated their solid by reduction in hydrogen at 900°C for 12 hours to ensure that the solid was UO_2. After cooling to room temperature under hydrogen atmosphere the sample was transferred to a nitrogen glove bag for loading into the autoclaves. During this transfer, the sample was exposed to air atmosphere for as long as 10 minutes. XPS analysis of the surface of the sample showed the presence of U(VI) to the extent of 17% in the outer surface layers.

The experiments of /Parks and Pohl, 1988/ used an overpressure of 50 MPa of hydrogen gas to ensure that reducing conditions were maintained. The experiments were started by heating to 300°C, which is a high enough temperature for $H_2(g)$ to be an effective reducing agent. This was demonstrated by samples that contained Pt capsules with buffers in them. These showed reduction of NiO to Ni, CoO to Co, and Fe_2O_3 to Fe_3O_4 during the runs. The total [U] found at pH 10.4 was 2.2×10^{-10} M at 100°C. There was no obvious dependence of [U] on temperature found between 100 and 300°C and no dependence on pH for pH >4. This was interpreted to indicate that the soluble species of U was $U(OH)_4$.

/Rai et al., 2003/ offer the following interpretation of the results of /Parks and Pohl, 1988/. The U(VI) on the surface of the sample dissolved in the initial stages of the experiment. The presence of a strong reducing agent in the system should have been able to reduce the U(VI) in solution to U(IV), thereby creating supersaturation. The U(IV) in solution would then be equivalent to starting the experiments from oversaturation rather than undersaturation. Thus, the solubility might be controlled by freshly precipitated UO_2(am). This seems to be a credible explanation of the results. It should be noted, however, that the [U] measured by /Parks and Pohl, 1988/ is about 3 times lower than that found by /Rai et al., 2003/ in their experiments. This suggests that the results of /Parks and Pohl, 1988/ may provide a better estimate of the solubility of UO_2(am) than those of /Rai et al., 2003/. We are left, however, with the uncertainty of the effect, if any, that the presence of 0.45 mole% Al in the solid might have on the results.

In the discussions that follow, we will use the results of /Rai et al., 2003/ to indicate the expected value for the "solubility" of pure UO_2(am). Measurements that give concentrations higher than 6.3×10^{-10} M for total U will be interpreted as to be influenced by the presence of trace oxygen or radiolysis products. Measurements that are less that 6.3×10^{-10} M for total U will be interpreted to indicate lower amounts of U(VI) in the starting samples and/or less influence of tramp oxygen to produce U(VI) than is required to saturate the solution with UO_2(am). For comparison, the solubility based on thermodynamic data for UO_2(cr) found using the SKB database is $U = 10^{-15}$ M.

3.3 Experiments using unirradiated UO_2

In the In Can Processes Project samples of unirradiated fuel pellets were studied in dilute synthetic groundwater. Tests were conducted in closed plastic vessels in an inert atmosphere (N_2) glovebox. Reducing conditions were achieved by including a strip of Fe metal in the solutions. The groundwater used had been preconditioned with Fe metal to remove any traces of oxygen. Corrosion of the metal strip during the experiments would also produce $H_2(g)$. The presence of $H_2(g)$ was indicated by the erratic behaviour of the glovebox O_2 detector. Details of the tests are in /Ollila et al., 2003/.

Samples were pretreated with several stages of aqueous pretreatment to remove any U(VI) that might be present on the surface of the samples. The last two pretreatment stages included an Fe strip in the solution. The final concentration of U in the last step prior to start of the dissolution rate testing was <0.1 ppb U ($<4\times10^{-10}$ M). This is similar to or less than the "solubility" of pure UO_2(am) /Rai et al., 2003/. Samples were then changed in the glove box into new reaction vessels, groundwater was added and a dose of spike enriched in ^{235}U was added to follow the dissolution process. Samples taken after 1 day of exposure showed small amounts of U in solution – generally less than 0.1 ppb. After 7 days of testing all samples had levels less than the detection limit of the ICP-MS used for analysis (<0.02 ppb U, $\sim10^{-10}$ M). Some tests were conducted in solutions that had been pretreated with Fe strips but the tests did not contain an Fe strip. These tests had solution concentrations of U between 0.1 and 0.85 ppb. Thus, the presence of the Fe strip during the testing clearly affected the test results and lowered the concentrations of U in the solutions.

The final series of tests was conducted using a solution exchange procedure to try to minimize the effect of any oxidation of the fuel surface during changing of the reaction vessels. The amount of O_2 in the N_2 atmosphere was very low (0.1 ppm), but this would be sufficient to explain the 0.1 to 0.5 ppb [U] found in the day 1 samples during previous testing. Before the isotope dilution tests were started, the samples of UO_2 were covered with 50 ml of Fe-treated groundwater and allowed to stand for 2 hr. This step was intended to dissolve from the surface any oxidized material that might have formed during sample transfer. The subsequent steps were to dilute the dissolved material so that testing would begin from undersaturation. First, 30 ml was removed from the solutions and replaced by fresh groundwater, giving a dilution of the solution. After 30 minutes this dilution was repeated, and after 30 minutes more a final dilution was made. Then a spike containing a $^{235}U/^{238}U$ ratio of about 10 was added to the solution so that dissolution/precipitation could be followed by measuring the isotopic composition of the solutions.

Analyses of the solutions from the dissolution/dilution steps (initial sample after 2 hr and after each dilution step) showed that all samples had <0.02 ppb U. Based on the dilutions starting with <0.02 ppb U, the final solution at the start of testing would have <0.0013 ppb U if no further dissolution had occurred. The concentration of ^{238}U calculated to be in solution 1 day after adding the spike using the measured ^{235}U /^{238}U ratio indicated that the solution contained 0.009 ppb ^{238}U at the start of the tests. Thus, dissolution of U had been occurring during the dilution stages. This suggests that some tramp O_2 was gaining access to the sample by diffusion across the liquid/gas interface during the dilution steps. The solutions contained ample amounts of Fe(II) ions, but these do not seem to have been able to consume the oxygen. It appears that oxidation of the UO_2 surfaces to produce some U(VI) that could dissolve was faster than the reduction of molecular oxygen by Fe(II) ions. The amount of spike added at the start of the isotope dilution phase contained 0.365 ppb ^{235}U. After 7 days the [^{235}U] was <0.02 ppb. Of the precipitated 0.34 ppb of ^{235}U, very little was recovered in the vessel rinse and acid strip solutions, indicating that it had precipitated onto the solid UO_2 surfaces.

The tests reported in /Ollila et al., 2003/ may have had the redox conditions controlled by either or both of Fe(II) ions in solution and the H_2 gas generated by the corrosion of the Fe strip. The results of the dilution steps discussed above indicate that H_2 gas is a more effective reducing agent than Fe(II) ions in this system. When actively corroding Fe was present, the [U] was lower than the solubility of amorphous UO_2, but was still much higher than that for crystalline UO_2.

/King et al., 1999/ studied the oxidation of UO_2 by γ-radiolysis in deaerated 0.1 M NaCl over-pressured with 5 MPa of either Ar or H_2. They found that not only did hydrogen suppress oxidation due to radiolytic oxidants; it also reduced the extent of surface oxidation observed in either Ar or H_2 atmospheres in the absence of radiation. They also found a "memory" effect. The subsequent re-oxidation of the surface after the H_2 atmosphere had been replaced by Ar was retarded.

/King and Shoesmith, 2004/ reviewed the electrochemical studies related to the effect of H_2 on the dissolution of UO_2. They concluded that the mechanism of the effect is not certain, but that it appears to involve the catalysis of the H_2/H^+ redox couple on the UO_2 surface. The reaction occurs on the noble metal particles (ε-Ru phase) in SIMFUEL and spent fuel and possibly on non-stoichiometric grain boundaries in the case of UO_2 electrodes. They showed that the homogeneous reaction of H_2 with oxidants in solution could not explain the effect.

3.4 Experiments using UO_2 doped with ^{233}U

There are several reports of experiments using high levels of α-doping with activities that are at or above spent fuel activities at the time the fuel is removed from the reactor. Since we are only concerned with time periods greater than 1000 years after disposal in the model for use in performance assessment, we will only consider studies that used low levels of α-doping. These studies have used samples doped with ^{233}U.

Within the In Can Processes Project, Ollila performed experiments with ^{233}U-doped UO_2 with doping levels of 5% and 10%, corresponding to approximately 10,000 year and 3,000 year old fuel, respectively, in closed systems containing an iron strip /Ollila et al., 2003/. Control samples of unirradiated fuel pellet materials were tested in parallel. In the experiments, about 1 g of UO_2 fragments (1–4 mm size) placed on a silica saucer was leached in 50 ml of synthetic granitic groundwater. In the pre-treatment stage, no systematic difference in behaviour of the samples was seen. All samples initially indicated dissolution of solid during the first two cycles of testing, with some indication of more rapid dissolution of the material with the higher doping. After 3 weeks in the second cycle of testing, however, the samples all showed [U] <0.02 ppb and there was no evidence of enhanced dissolution due to alpha radiolysis. The actual solution [U] was determined to be 0.005 ppb using the change in isotope ratio when a new dose of spike was added. This is a [U] of 2×10^{-11} M, substantially less than the "solubility" of UO_2(am) but still much higher than the predicted solubility of UO_2(cr). This is interpreted to indicate that there is still some effect of trace levels of O_2 gaining access to the samples by diffusion through the plastic reaction vessel walls.

The higher amounts of dissolution in the first 4 weeks of testing under reducing conditions suggests that the behaviour of the samples is controlled by defect structures in the solids that are annealing through dissolution and reprecipitation reactions. If tests are started and show this type of behaviour, then it is probably impossible to achieve solution concentrations that are less than the solubility of UO_2(am) unless the leaching solution is changed one or more times to allow dissolution and removal of the amorphous material.

Testing of these samples has continued after the In Can Processes Project was finished and two sets of samplings have been carried out /see Ollila and Oversby, 2004, for details/. The first series covered 4 months and the solution concentrations of ^{238}U were in all cases below the detection limit of 0.02 ppb. The solid samples were transferred to new saucers and reaction vessels. The old reaction vessels were rinsed 3 times with water and then stripped with 1 M HNO_3. The old saucers were also rinsed and treated with 1 M HNO_3. The analyses of these solutions showed that most of the U that was recovered was found on the saucers. It is likely that some grains of UO_2 that had separated from the samples were included in this saucer rinse solution. The total amount of U recovered was used to calculate a dissolution rate for each sample. If the material recovered from the saucers is included in the calculation, the dissolution rate is 2.6×10^{-6}/year. This implies a sample lifetime under test conditions of 0.38 My. If the material from the saucers is excluded from the calculation, the dissolution rate would be 0.5×10^{-6}/year, giving a sample lifetime of 2 My. As before, there was no indication of enhanced dissolution due to alpha radiolysis.

In the next dissolution period, a test covering 52 days, even less uranium was mobilised. In the sampling at the end of this test the bulk leaching solution and the solution inside the saucers were analysed separately. The saucers were reused for the next testing period, so they were not acid stripped. If the solution from the saucers was filtered prior to analysis, the [U] was <0.02 ppb. If the solution was not filtered, the [U] was between 1.3 and 5.6 ppb. This indicates that particulate matter was present in the saucers, either as sample grains or colloids. The bulk solution samples were not filtered and all had [U] <0.02 ppb. The dissolution rate calculated for these tests including material recovered from the unfiltered saucer samples was 8.5×10^{-8}/year (average of 6 tests). The sample lifetime calculated from the dissolution rates is 13 ± 6 My. As in the previous tests, there was no indication of enhanced dissolution due to alpha radiolysis. A sample of the bulk leach solutions was split into three portions and each portion was spiked with either 0.25, 0.37 or 0.5 ppb of a ^{235}U solution. Subsequent determination of the $^{235}U/^{238}U$ ratio allows the calculation of the amount of U in solution before spike addition. The solution concentrations were determined to be 0.001 to 0.005 ppb (0.4×10^{-11} to 2×10^{-11} M). This shows that the solution concentrations are significantly lower than that expected for UO_2(am) but still much higher than the predicted solubility of UO_2(cr).

In the Spent Fuel Stability Project (SFS), the Institute for Transuranium Elements (ITU) has been leaching a 10% ^{233}U doped UO_2 pellet in10 mM NaCl at 16 bar H_2 pressure /SFS Second annual report, 2003/. The 10% doping level has an α-activity corresponding to spent nuclear fuel about 3,000 years after removal from the reactor. The ^{233}U concentrations were measured to be about 2×10^{-12} M, which means that the total uranium concentration would be 2×10^{-11} M. This is the same as the value found by Ollila /Ollila et al., 2003/. When the H_2 pressure was lowered successively down to 1.6 bar, 0.16 bar and finally to 0 bar (replaced by Ar gas), no changes in the ^{233}U concentrations could be found. This is similar to the memory effect that was observed by /King et al., 1999/.

Experiments at ITU where Ar/6% H_2 was bubbled through the leaching vessel during leaching of discs of UO_2 produced somewhat different results /SFS Second annual report, 2003/. The sample with 10% ^{233}U doping showed higher ^{238}U concentrations in solution than an undoped sample, about 2×10^{-9} M and about 5×10^{-10} M, respectively, after 8000 hours. The samples started at much higher solution concentrations (4×10^{-9} M and 2×10^{-9} M, respectively for [^{238}U]) and showed a general decrease of [U] throughout the test period. Although the final concentrations are much lower than what is expected under oxidising conditions, they are higher than what was found in the other set of ITU experiments. A possible explanation for this behaviour may lie in the detailed characteristics of the samples. Testing of similar samples (probably cut from the same pellets) under oxidizing conditions showed that the release of U from the 10%-doped sample was higher than the undoped sample, but release from a 1%-doped sample was the same as the undoped sample. There should be no increase in U dissolution or solution concentration due to radiolysis effects at the levels of doping used in these samples above that found from oxidation effects of an air atmosphere /Shoesmith, 2000/. The ^{233}U-doped materials used in the In Can Processes tests showed a similar effect, with greater releases for the 10%-doped samples in air atmosphere tests /Ollila et al., 2003/. Testing of these materials under reducing conditions showed an apparent elevated release from the 10% doped sample in early tests, but the “effect” disappeared after several weeks of testing with changes of solutions. We interpret the initial elevated releases in both cases to a higher level of defects in the sample crystalline structure. We further predict that the ITU samples should approach each other in behaviour if the solutions were changed and the tests restarted.

3.5 Tests using spent fuel

Testing of spent fuel is needed to understand how the presence of fission products and higher actinides affects the leaching behaviour of the UO_2-based material and to be able to distinguish between the release behaviour of U and other radionuclides. Unfortunately, testing of spent fuel is always accompanied by a high dose of β and γ radiation. Thus, results from testing of spent fuel must be considered to represent upper limits on the release rates of radionuclides to solution with respect to conditions appropriate to the long-term performance of the repository.

/Spahiu et al., 2000/ reported that for testing of crushed spent fuel in the presence of 5 MPa of hydrogen the solution concentrations of uranium were several orders of magnitude lower than when the atmosphere was argon. The concentrations of U were as low as $1–2\times10^{-10}$ M at 70°C, while at 25°C the concentration was 5×10^{-9} M. The presence of hydrogen obviously had a profound effect on the release of uranium to the solution. In these experiments, the Sr and Cs showed no increase in solution concentration within experimental errors. The experiments were performed in a stainless steel autoclave. In later experiments, a quartz-lined autoclave was used instead /Spahiu et al., 2003/. The reason for changing the autoclave material was concern that the presence of the steel could have affected the results by catalyzing the reduction of uranium by hydrogen. The second set of experiments produced similar uranium concentrations. The average over the samplings was about 5×10^{-10} M at 70°C, and no tendency to increase was shown during the experiment. In latter experiments, however, the samplings showed generally decreasing Sr release rates ranging from 0 to 10^{-4} of the inventory per year. These variations did not correlate with variations in the uranium concentrations.

/Röllin et al., 2001/ performed flow-through tests with spent fuel using an air atmosphere and an atmosphere of H_2/0.03% CO_2 and 10 mM $NaHCO_3$. The flow rate for oxidizing conditions was selected after testing at 4 different flow rates and showing that the relationship of [U] versus 1/(flow rate) was linear; i.e. that [U] decreased as flow rate increased. This shows that the solution concentrations were far from saturation since the rate of dissolution was independent of flow rate. The relationship of [U] versus 1/(flow rate) was checked at 3 flow rates under reducing conditions and also found to be linear. For a flow rate of 0.1 ml/min, the [U] under oxidizing conditions was about 1 ppm (3×10^{-6} M), while the [^{137}Cs] was 2 ppb (1.5×10^{-8} M). When the atmosphere was changed to H_2/0.03% CO_2, the concentrations in solution dropped dramatically, giving values of about 0.7 ppb (3×10^{-9} M) for [U] and 0.002 ppb (1.5×10^{-11} M) for [^{137}Cs] for a flow rate of 0.02 ml/min. The initial dissolution rates determined by this method were 3 to 4 orders of magnitude lower in the presence of hydrogen than the rates found under aerated conditions. If the concentrations measured in the flow through tests are converted into sample dissolution rates, one finds a dissolution rate under the test conditions of 0.1/year for both U and Cs under oxidizing conditions and 2×10^{-5}/year for Cs and 1.5×10^{-5}/year for U under reducing conditions. These rates are for powdered fuel and water flow rates much higher that those expected in the repository.

Flow-through tests give the initial rate of dissolution when the flow rate is high enough so that the results are not affected by approach to saturation in the solutions. For oxidizing conditions, the results in /Röllin et al., 2001/ fulfilled that condition and can be considered to represent an upper limit to the dissolution rate of spent fuel under oxidizing conditions. For comparison, /Forsyth and Werme, 1992/ measured long term Cs release rates of about 2×10^{-4} year^{-1} in static tests under oxidizing conditions. For Sr the corresponding values were 7×10^{-5} year^{-1}. In the static tests, there was no obvious increase in the U concentration, which stayed relatively constant, albeit with a large spread, at about 2×10^{-5} M (5 ppm). Assuming congruent dissolution of Cs, Sr and U in the static tests, the estimated oxidation/dissolution rate in the static test would be 10^{-4} year^{-1}. This is three orders of magnitude lower than what /Röllin et al., 2001/ measured in their flow through tests.

For the tests under reducing conditions, the [U] in the /Röllin et al., 2001/ flow through experiments was about an order of magnitude greater than the solubility of UO_2(am). Thus, the tests appear to be affected by oxidants, probably produced by radiolysis of the solution. The flow rate of H_2 seems to have been too slow to completely counter the effects of radiolysis. Under repository conditions, the ingress of water will be very slow and the abundance of H_2 will be very high. Thus, much lower dissolution rates should be expected under repository conditions.

At Forschungszentrum Karlsruhe (FzK) within the 4th framework EU programme, /Grambow et al., 2000/ carried out co-dissolution experiments in 5 M NaCl solutions with 7.5 g of fuel with 8.5 g metallic iron powder. The experiments ran for nearly 4.5 years. In parallel, experiments were also carried out without iron present. In the reference tests (no iron present) the Sr release rate was 4.6×10^{-7} day^{-1}. That corresponds to a lifetime of the sample of about 6,000 years. The sample lifetime based on total U release was also about 6,000 years. For the test with iron present, the Sr release rate was less than 1×10^{-9} day^{-1} (0.37×10^{-6} $year^{-1}$) at the end of the experiment, and the U release rates had dropped to less than 1×10^{-9} day^{-1}, i.e. to the same level as the Sr release rate /Loida et al., 2001/. The higher initial release rates may have been caused by dissolution of a pre-oxidised surface layer. Alternatively, a build-up of corrosion products to a certain level may be necessary in order to overcome the higher rate of production of radiolytic oxidant from fresh spent fuel as compared to the simulated old fuel using α-doped UO_2.

The experiments reported by /Grambow et al., 2000; Loida et al., 2001/ used a relatively high burn up fuel (50 MWd/kgU) that had a high average linear power rating (ca 30 kW/m) and had been ramped during its time in the reactor. Ramping and high linear power rating can cause segregation of fission products in the fuel. High burn up can also give dissolution properties that are worse than those for fuels with lower burn up (<40 MWd/kgU). Thus, the results of the FzK experiments should be interpreted to give an upper limit for the release rate to be expected from the fuel population that will be disposed of in Sweden.

3.6 Key results for development of the fuel dissolution model

In sections 3.2 through 3.5 we have summarised the experimental results that form the basis for the fuel dissolution model to be used in SR-Can. The most important points are listed here:

1. The solubility of amorphous UO_2 is 6.3×10^{-10} M (0.15 ppb U). Any experiments that have solution concentrations of U higher than this level must contain U(VI).

2. The presence of reducing agents such as Fe(II) and H_2 in the system is very important for limiting the dissolution of UO_2 and spent fuel. H_2 is more effective than Fe(II) in lowering the [U] in solution.

3. When experiments are conducted for long enough periods of time to eliminate artefacts due to sample preparation and to allow the high-energy surface sites to equilibrate with the bulk of the sample, no evidence for any increase in U concentrations in solution or dissolution rate due to alpha radioactivity can be found for samples that contain alpha levels appropriate to the long term disposal condition for spent fuel.

4. Since the solution concentrations for U under the test conditions that are most successful in eliminating oxygen are extremely low, it is not possible to measure the dissolution rate of the samples directly. The best estimate of dissolution rate that can be obtained is by measuring total release from the samples at the end of a long test period and assuming that the release rate is linear. This method will overestimate the long-term release rate since in all cases where testing with H_2 has been conducted, the dissolution rate decreases with exposure time.

3.7 A model for spent fuel dissolution in SR-CAN

The experimental results discussed in sections 3.3, 3.4, and 3.5 can be used to construct a model for the expected behaviour of spent fuel in the repository; however, we must consider the data as a whole and not just the results of one set of experiments. Tests that use currently available spent fuel will be affected by the high level of radiation and radiolysis product formation in solutions. Tests using α-doped UO_2 will have the correct level and type of radiation, but will not include the effects of fission products on dissolution properties. Even though the [U] in solution may be in equilibrium with the matrix solubility, the spent fuel may continue to slowly release fission products to solution since the solubility equilibrium of the matrix is a dynamic process. Uranium will dissolve from high-energy sites, such as grain boundaries or fracture surfaces and precipitate onto the fuel itself or onto other surfaces in the container. When the high-energy sites have been eliminated, the rate of processing of U through the solution at equilibrium can be expected to decrease.

Except for the materials that are included in the initial release fractions, the fission products and actinides will be distributed throughout the fuel matrix. They will be available for dissolution only as they become exposed to water through the dissolution of the matrix. The decay products from U and other actinides will be formed inside the matrix and will also only be available for solution as they are exposed to water through matrix dissolution.

The model for spent fuel behaviour in the long-term is, thus, the rate of processing of U through the solution phase under static conditions representative of the environment inside the disposal canister. These conditions are highly reducing, with an atmosphere of H_2 gas formed by the anaerobic corrosion of iron. There will be no stray oxygen remaining at the time of first contact of the fuel with water. The radiation due to alpha decay in the fuel will not influence the rate of dissolution to any significant extent (see section 3.4). To estimate this rate of processing, we will use the experimental results to calculate the lifetime of the experimental samples under the test conditions. This will give a lower limit to the lifetime of the fuel under repository conditions.

Note that we cannot use a model for fuel behaviour that simply multiplies U solubility times water flow rate because the matrix dissolves at equilibrium and U precipitates from solution at equilibrium at the same rate. This process releases fission products, actinides, and decay products to solution. The fate of the elements released will be determined by their solubility and transport properties.

There are two reasons that the experimental data give a lower limit to the fuel lifetime. First, the test samples contain fracture surfaces that will dissolve initially at a more rapid rate than that which will obtain for the bulk sample. Because of the low [U] under reducing conditions, the rate of processing of U through solution is very low, and these high-energy sites may influence experiments over many years. The lifetimes of test samples show a tendency to increase as the samples are tested so long as the experimental conditions remain constant /Ollila and Oversby, 2004/.

The second reason that experimental data will underestimate the lifetime of spent fuel in the repository is the influence of stray oxygen. Laboratory conditions cannot achieve the required exclusion of trace amounts of oxygen during experiments. Many experiments showed precipitation in the early stages under reducing conditions, which indicates that U(VI) was present in the starting materials. The U(VI) dissolved and when reducing conditions were achieved, it was reduced to U(IV) and the solutions were supersaturated. The material that precipitates is UO_2(am), which has a much higher solubility that crystalline UO_2. Estimates of sample lifetime from these tests can be obtained using total release, which overestimates the long-term release rate.

Published data show clearly that the corrosion products from the canister insert will be important in limiting the dissolution of spent fuel under long-term disposal conditions. Hydrogen gas seems to be more effective than Fe(II) ions, but both seem to have an effect. We will use the experimental data that can be converted into release rates (as opposed to just upper limits on solution concentrations) to obtain estimates of the expected lifetime for spent fuel in the repository after first contact with water.

The /Röllin et al., 2001/ flow-through data showed a drop in dissolution rate of four orders of magnitude in H_2-saturated solutions as compared to aerated solutions. The measured rate was 0.1 year^{-1} in aerated solutions and 2×10^{-5} year^{-1} in hydrogen saturated solutions. That is, the dissolution rate is about four orders of magnitude lower in hydrogen saturated solutions than in oxygenated solutions. As was mentioned above, the uranium concentrations in the tests with hydrogen saturated solutions are too high to represent dissolution of only U(IV). In static long-term tests in aerated solutions under conditions where there is a very small or no change in uranium concentration, the measured dissolution rate is about 2×10^{-4} year^{-1} based on the Sr release rate. That is, the flow tests measure a rate that is three orders of magnitude higher than the rate near uranium saturation. If one were to assume a similar relationship between the maximum dissolution rates and the dissolution rate near uranium saturation for the hydrogen saturated conditions, the rate would be about 2×10^{-8} year^{-1}. This comparison should only be considered as qualitative, since we have no theoretical basis for converting the flow-through rates to dissolution rates near equilibrium [U] under reducing conditions.

The experiments performed by FzK /Grambow et al., 2000, Loida et al., 2001/ give release rate data that can be translated into fuel lifetimes. The medium is 5 M NaCl. If the uranium had been present as U(IV), the ionic strength would have been of little importance. There is, however, reason to believe there are predominantly U(VI) species in the solution. Regardless of that, the release rate based on the long term Sr and U release rates of 4×10^{-7} year^{-1}, gives an estimated fuel lifetime of 2.7 million years.

Both the flow-through experiments of /Röllin et al., 2001/ and the experiments at FzK used real spent fuel. /Spahiu et al., 2000, 2003/ also used spent fuel in autoclave experiments. In the first experiment, both the uranium and the strontium levels were constant within the accuracy of the measurements. In the second experiment performed in a different autoclave, there was a slow increase in the Sr concentration over one year while the U concentration remained constant. Based on the total strontium release, the release rate would be in the range 10^{-4} to 10^{-5} year^{-1}. For the longest sampling interval (133 days) no release of strontium was detected. Although Sr release is often used as an indicator of matrix dissolution, it cannot be excluded that at these very low Sr levels and release rates, Sr segregated to (for example) grain boundaries may be the main contributor to release. At the first sampling, the fractional Sr release was more than an order of magnitude higher than the fractional U release, indicating that there is reason to suspect that segregated Sr is a large contributor to the total Sr release. Even though the effect of hydrogen on the uranium concentrations in solution can be clearly demonstrated in these experiments, at this time they cannot be used to obtain kinetic data although the Sr leach data from the second autoclave experiment can be used to set a pessimistic upper limit for the release rate.

The experiments with ^{233}U-doped UO_2 performed at ITU with 16 bars H_2 over-pressure and at VTT with corroding iron present produced the lowest reported U concentrations, 0.4×10^{-11} to 2×10^{-11} M in both experiments, indicating that those experiments were most successful in excluding oxygen from the reaction vessel. While the experiments at ITU do not give any kinetic data, the experiments at VTT /Ollila and Oversby, 2004/ can be used to estimate the lifetime of the sample from the total amount of recovered uranium in the test vessel.

The first set of experiments at VTT led to an estimated lifetime of the sample of 0.4 to 2 million years. This is to be compared to the 0.15 million years determined from the total recovered uranium in the FzK experiments /Grambow et al., 2000; Loida et al., 2001/. The second set gave an estimated lifetime of the sample of 13 ± 6 million years. The corresponding lifetime of the fuel based on the long-term Sr and U release rates in the FzK experiments was about 2.7 million years. These two estimates for spent fuel in NaCl and for α-doped UO_2 are similar enough to give confidence that these data can be used to estimate the lower limit to the lifetime of spent fuel under disposal conditions.

The hydrogen and the dissolved Fe(II) species will be present in the water contacting the fuel for as long as there is corroding iron present. The iron corrosion rate can be estimated to be 0.05 to 0.1 μm per year /Smart et al., 2002/. The wall thickness of the cast iron insert is on the average 50 mm. The time required to corrode away the cast iron would be 0.5 to 1 million years. During that time period, the radiolysis due to α-radiation will have dropped to insignificant levels and the dissolution rate is expected to be the same, or lower than, the dissolution rate with α-radiation and iron corrosion products.

Taken together the FzK and VTT data give a best estimate of the minimum time to dissolve the fuel of 2.7 million years to 19 million years. As discussed above, the actual lifetime of the fuel under repository conditions is expected to be much longer. /King and Shoesmith, 2004/ used an electrochemical model to predict the lifetime of spent fuel. They found that the maximum fractional dissolution rate in the presence of H_2 should be 10^{-7} to 10^{-8} per year.

The estimates for a minimum spent fuel lifetime based on three different experimental methods are summarised in Table 3-1.

The weight of the evidence from experimental studies suggests that the model for fuel dissolution in SR-Can should be a linear dissolution rate in the range of 10^{-6} to 10^{-8} per year. A triangular distribution with a peak at 10^{-7} per year would best represent the available data.

Table 3-1. Estimates of minimum lifetime for spent fuel in millions of years.

Source of data	Basis of estimate	Minimum lifetime, my
VTT experiments	UO_2 with and without ^{233}U	13 ± 6
FzK experiments	Spent fuel long-term rate	2.7
Electrochemistry	Model for dissolution	10 to 100

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