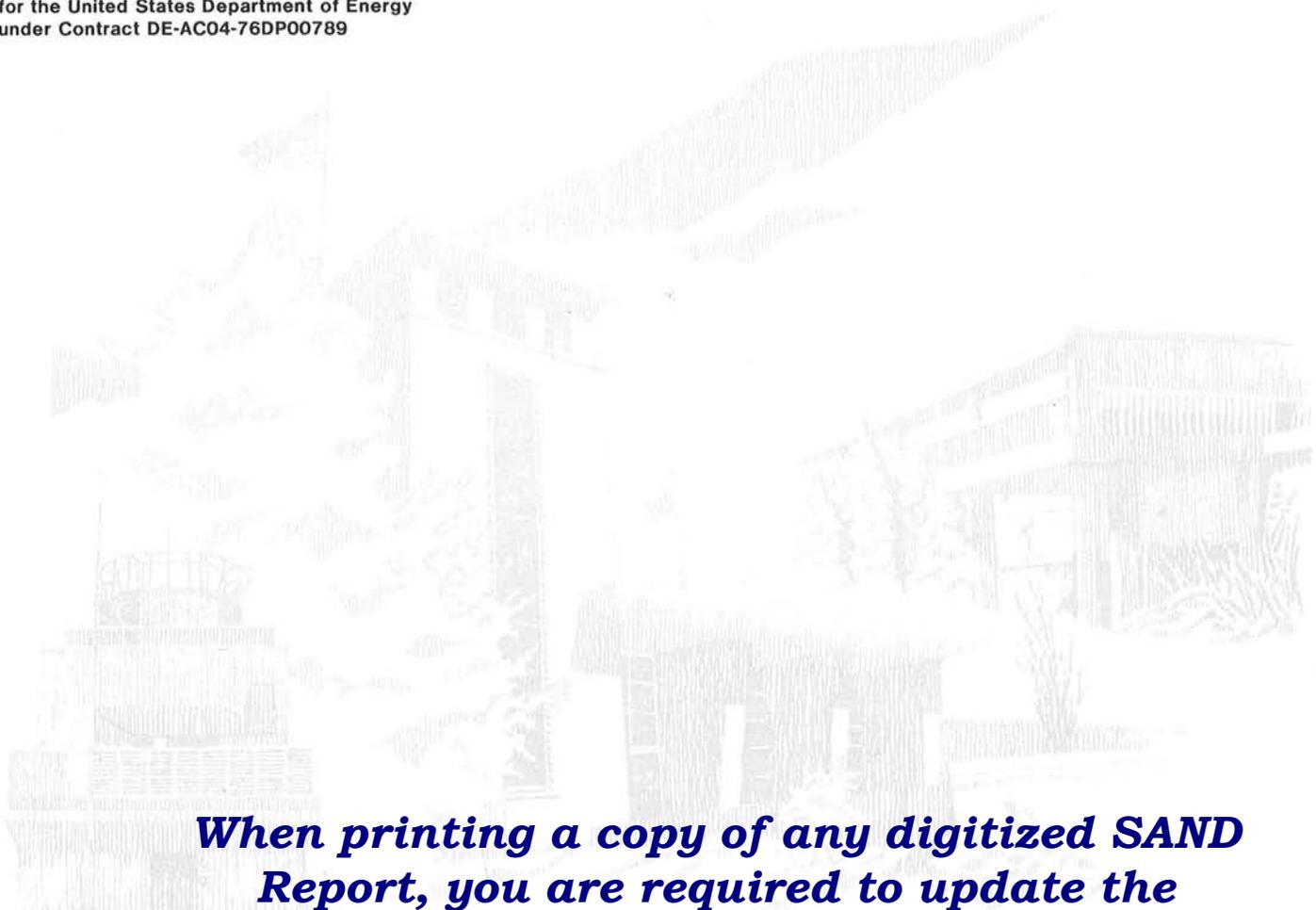


Proceedings of the Workshop on the Source Term for Radionuclide Migration From High-Level Waste or Spent Nuclear Fuel Under Realistic Repository Conditions

T. O. Hunter, A. B. Muller, Editors

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PROCEEDINGS OF THE WORKSHOP ON THE SOURCE TERM
FOR RADIONUCLIDE MIGRATION FROM HIGH-LEVEL WASTE OR
SPENT NUCLEAR FUEL UNDER REALISTIC REPOSITORY CONDITIONS

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INTRODUCTION

Inherent in the creation of energy from nuclear power is the generation of some nuclear wastes. The management and disposal of these wastes is a burden accepted along with the benefits derived from nuclear energy. Deep geologic disposal is preferred in most NEA countries as the disposal option for high-level nuclear waste or for spent nuclear fuel. It is current technical opinion within the NEA Member countries (NEA, 1985) that the safe disposal of such wastes deep in stable continental geologic formations appears to be feasible on the basis of existing technology.

The assessment of the performance of these disposal systems and the demonstration of their long-term safety relies heavily on modeling the behavior of the engineered repository and the surrounding host geological medium as an integrated waste isolation system (NEA, 1983). This involves a detailed description of the system of natural and engineered barriers to radionuclide migration into the biosphere and an evaluation of the performance of this system under a number of plausible scenarios. Essential to the modeling is the ability to predict the quantities, rates, and pathways in which radionuclides released from a repository may migrate in the geosphere. This in turn depends on a number of natural and engineering parameters. Among the parameters to which the modeling results are most sensitive is the "source term," which describes the rate at which the various radionuclides are mobilized from the waste.

At this point, there is no universally accepted view as to where in the system the "source term" refers. Although regulatory or conventional definitions exist, it is generally felt that from a technical modeling perspective, the source term refers to the specification of the flux of radionuclides across the interface between the engineered repository model and the geosphere transport model. One of the purposes of this workshop was to examine the role and appropriate definition of the source term for use in modeling.

Until recently, performance analyses usually involved making major assumptions about this term. These assumptions were based on the calculated radionuclide inventory in the repository at a given time, discharging at an estimated release rate. The rate was determined based on assumptions about canister lifetime and waste form stability. Since performance analysis results have been shown to be extremely dependent on this term, it has become necessary to assess the realism of the assumptions and to develop more detailed phenomenological models of the source term.

Such model development requires evolving a more fundamental understanding of the physical and chemical processes that influence the source term. Experiments under realistic in situ conditions are essential to this understanding. A number of the papers in these proceedings describe such experiments. Identifying and quantifying the effect of parameters that most

influence source term are also essential. This task appears throughout the papers in this volume. Finally, the role of source term modeling in the broader perspective of repository system performance assessment is discussed in several of the papers. Together they are an attempt to summarize the current state of understanding of the source term and of its modeling under realistic repository conditions.

SUMMARY OF SESSION I: ROLE AND USE OF SOURCE TERM

An issue underlying the assessment of the role and the use of radio-nuclide source terms in performance assessment modeling is the question of where the "release" takes place, i.e., at what point is the "source term" to be defined. Is it at the outside of the waste package, further out in the near field, or at the near-field/far-field boundary. The point at which the source term is defined may, in some cases, affect the type of model or model coupling to be used. The question is of practical, as well as regulatory, importance. Although the question was not resolved, it seems to have been generally felt that in practical, modeling terms, the source term should be defined at the interface where the waste package model is coupled to the next model (be it a near-field model for HLW or a far-field transport model for LLW or ILW) in the overall performance assessment scheme used.

A number of important specific points on the definition and role of the source term were made by speakers in this session. It was shown (Rickertson) that the physical relationship to and the influence on each other of the waste packages in a repository may considerably influence and reduce the release from an individual package. The geometry of the repository and the direction of water flow through it can considerably influence the release rate in cases where the release from individual canisters is of short duration. The spread in time of degradation of the waste packages can also give a considerable reduction of the release rate from the whole repository.

The presentation on releases from a salt repository (Stelte) showed that because of the present lack of rate data on corrosion and rate data on concrete interaction with the water, stacked conservative assumptions had to be used to assess release rates. The small amount of available water had to be assumed to fully participate in both reactions, whereas in reality, one mechanism would dominate and there would be less water available to the other reaction. The stacking of conservative assumptions was also observed (by Neretnieks) to give strongly exaggerated release rates in a granite repository. It was generally recognised that more realistic modeling will give a considerable reduction in projected release rates when better data become available. An example where many different mechanisms such as congruent release rate, solubility limits, decay in backfill, and changes of redox conditions due to alpha radiolysis, were integrated in a release model was demonstrated (Neretnieks). The redox front was projected to extend out into the rock outside the backfill. It was contaminated within a few tens of meters from the canisters. In rock with less ferrous iron minerals, the oxidized region might extend much farther and impact the far-field conditions.

The excavation of the repository was shown (Braithwaite) to have a beneficial effect on the flow rate of water to the waste package because of the high capillary suction pressures of the tuff in this case. The unsaturated tuff will not give off its water to an empty hole. In this situation,

a backfill with higher capillary suction will draw in more water than if the backfill were designed for a lower capillary suction than the rock. It was also projected that in an unsaturated medium, the low availability of water may only wet a very small fraction of the waste surface, thus decreasing the contact area and leach rate. As several others did, this presentation used sensitivity analysis as a tool to identify the sensitive mechanisms and parameters.

The need for site-specific data in any detailed source-term modeling was emphasized by all speakers. The question of gas production and escape, both from radiolysis and from generation during canister corrosion, was generally felt to be an area warranting additional work.

HOW RELIABLE DOES THE WASTE PACKAGE CONTAINMENT HAVE TO BE?

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ABSTRACT

The final rule (10 CFR Part 60) for Disposal of High-Level Radioactive Wastes in Geologic Repositories specifies that the engineered barrier system shall be designed so that, assuming anticipated processes and events, containment of high-level radioactive wastes (HLW) will be substantially complete during the period when radiation and thermal conditions in the engineered barrier system are dominated by fission product decay. This requirement leads to the Nuclear Regulatory Commission (NRC) being asked the following questions: What is meant by "substantially complete"? How reliable does waste package containment have to be? How many waste packages can fail? Although the NRC has not defined quantitatively the term "substantially complete", a numerical concept for acceptable release during the containment period is discussed. The number of containment failures that could be tolerated under the rule would depend upon the acceptable release, the time at which failure occurs and the rate of release from a failed package.

1.0 INTRODUCTION

Under the Energy Reorganization Act of 1974 the Nuclear Regulatory Commission (NRC) has responsibility to license the disposal of high-level nuclear waste (HLW) by the Department of Energy (DOE) [1]. In addition, the Nuclear Waste Policy Act of 1982 states that it is federal responsibility to provide for HLW and spent fuel requiring permanent disposal [2]. Thus, DOE has responsibility for disposal of HLW and spent fuel and NRC has responsibility to license the DOE repository or repositories.

The regulation for Disposal of High-Level Radioactive Wastes in Geologic Repositories, 10 CFR Part 60, specifies [3] that the engineered barrier system shall be designed so that, assuming anticipated processes and events, containment of HLW (within the waste packages) will be substantially complete during the period when radiation and thermal conditions in the engineered barrier system are dominated by fission product decay (300 to 1000 years).

The regulation also specifies [3] that the release rate of any radionuclide from the engineered barrier system following the containment period shall not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1000 years following permanent closure, or such other fraction of the inventory as may be approved or specified by the Commission.

The requirement for substantially complete containment within the waste packages leads to the NRC being asked the following questions:

1. What is "substantially complete"?
2. How reliable does the waste package containment have to be?

2.0 DISCUSSION

2.1 WHAT IS "SUBSTANTIALLY COMPLETE?"

NRC has not defined quantitatively the term "substantially complete containment". DOE, however, could consider the following or other appropriate approaches:

Limit the release of radionuclides from the waste packages during the containment period to the same number of curies that is permitted annually from the engineered barrier system following the containment period.

2.2 HOW RELIABLE DOES WASTE PACKAGE CONTAINMENT HAVE TO BE?

If the term "substantially complete" were interpreted quantitatively as described above, the level of reliability required for waste package containment could be defined as follows:

Waste package containment should be sufficiently reliable so that radionuclide releases during the containment period do not exceed 1×10^{-5} per year of the radionuclide inventory calculated to be present 1000 years after permanent closure.

The reliability of the waste package that would be required during the containment period would be such that the calculated cumulative number of failures during the containment period and the release calculated to result from them would not exceed the quantity stated above.

A basis for calculating the number of waste package failures that could be tolerated during the containment period is presented in Section 2.3.

2.3 HOW MANY WASTE PACKAGES CAN FAIL?

The number of waste packages that can fail during the containment period without exceeding the release criterion depends upon:

1. The estimated fractional rate of release from a failed package.
2. When failure occurs.

Although the number of curies that may be released annually during the containment period is constant ($1 \times 10^{-5} \times 1000$ year inventory), the acceptable fractional annual release will increase with time to failure. It may be calculated as follows:

$$\begin{aligned} \text{Acceptable Fractional Annual Release} = \\ 1 \times 10^{-5} \times \frac{1000 \text{ yr. inventory (curies)}}{\text{current inventory (curies)}} \end{aligned}$$

For example, the total activity in curies of inventory in one BWR spent fuel rod varies with time after discharge as shown below [4]:

$$\begin{array}{ccc} \frac{10 \text{ years}}{960} & \frac{300 \text{ years}}{11} & \frac{1000 \text{ years}}{4.6} \end{array}$$

This example is also true on a relative basis of the total inventory of spent fuel waste packages in the repository at 10, 300,

and 1000 years. Therefore, the permissible annual release at 10 years after emplacement (in this example, the time between discharge and permanent closure was taken as zero, although we know this will not be the case) may be calculated as a fraction of the total radionuclide inventory at that time, e.g.,

$$\frac{4.6 \text{ curies}}{960 \text{ curies}} \times 1 \times 10^{-5} \times \text{inventory 10 years after permanent closure}$$

$$= 4.8 \times 10^{-8} \text{ of current (10 yr.) inventory.}$$

Once the acceptable annual fractional release is known and the annual release from a failed waste package is estimated, an acceptable number of waste package failures may be calculated.

Assumptions:

1. The repository will contain 70,000 waste packages.
2. A failed waste package will release 1×10^{-5} per year of the inventory in the package.

Thus, the fractional annual rate of radionuclide release from one failed waste package would be:

$$\frac{1 \times 10^{-5} / \text{yr.}}{\text{number of curies}} \times \frac{\text{number of curies}}{\text{package}} \times 70,000 \text{ packages} = 1.43 \times 10^{-10} / \text{yr.}$$

Therefore, the number of waste package failures that could be tolerated 10 years after permanent closure in a repository containing 70,000 wastes packages is:

$$\frac{\text{acceptable fractional release } (4.8 \times 10^{-8} / \text{yr})}{\text{fractional release per package } (1.43 \times 10^{-10} / \text{yr})} = 335 \text{ packages}$$

Therefore, 335 package failures could be tolerated 10 years after permanent closure if annual fractional release of a failed package does not exceed 1×10^{-5} of the inventory in the package. The release rate from a failed package at 10 years, however, may be much higher than 1×10^{-5} per year because the temperature will be relatively high. For example, if the leak rate were a hundred times higher only three failed packages could be tolerated; if it were a thousand times higher, none could be tolerated.

3.0 CONCLUSIONS

1. NRC has not defined quantitatively the term "substantially complete containment." One of the approaches that is being considered, however, is to allow a radionuclide release rate

during the containment period that does not exceed the absolute quantities permitted in the post-containment period, i.e., 1×10^{-5} per year of the radionuclide inventory of the repository 1000 years after permanent closure. Since the radionuclide inventory is larger during the containment period, the fractional release at the time of containment failure must be correspondingly smaller.

2. If such an approach were allowed, the reliability of the waste package containment should be such that the calculated cumulative number of failures during the containment period and the releases calculated to result from them would not exceed the quantity stated above.
3. The cumulative number of waste package failures that could be tolerated during the containment period would depend upon when failure occurred and the rate of radionuclide release from a failed package.

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1. Public Law 93-438, Energy Reorganization Act of 1974, Sec. 202, 42 U.S.C. 5842.
2. Public Law 97-425, The Nuclear Waste Policy Act of 1982, 96 stat. 2207, Sec. 111(a).
3. 10 CFR 60, "Disposal of High-Level Radioactive Wastes in Geologic Repositories," Subpart E, Technical Criteria, paragraph 60.113.
4. NUREG/CR-2482, Vol. 7, "Review of DOE Waste Package Program, Subtask 1.1 - National Waste Package Program, Draft Biannual Report", Evelyn Gause, Peter Soo, September 1984, pp. 31 (adapted from ORIGEN-2 calculated values presented in ORNL/TM-6008, 1977).

INTEGRATION OF REPOSITORY AND WASTE PACKAGE PERFORMANCE
IN THE EVALUATION OF SOURCE TERMS

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ABSTRACT

A number of features of the near-field regime, in addition to the waste form and waste package release processes, may be important to determination of the source term. These aspects include waste package degradation rates and the spatial distribution of waste package sources through the repository. This paper considers the relative importance of these features in a simple but useful model. The sensitivity of the source term to these features is explored for representative geologic systems currently being evaluated in the U.S. program.

INTRODUCTION

Performance assessments of geologic repository systems that involve modelling of transport of radionuclides from the repository through the hydrogeologic system to the accessible environment generally do not rely upon detailed representations of the source term. For example, the repository release is approximated by a single block or point source with a release rate estimated based on waste package or waste form analyses. However, because there will be many waste packages in the repository and because these waste packages will be distributed throughout a large section of the host rock, dispersive effects can occur within the repository that may significantly affect the repository releases to the far field relative to the waste package release rates. Not all such effects can be evaluated without detailed site and repository data. However some of the effects can be estimated from relatively rudimentary considerations. It is the purpose of this paper to investigate the feasibility and advisability of incorporating some of these simple considerations into the current repository system performance assessment efforts.

GEOMETRIC EFFECT

The first feature of the repository that is considered is the distribution of waste packages throughout the repository. The contribution of different waste packages to the release from the repository will depend upon the relative position of the waste packages within the repository. A simple example of this geometric effect is shown in Figure 1. The large peak represents the fractional rate of release of the repository inventory at the repository boundary neglecting the spatial separation of the waste packages. This peak is simply the direct sum of the release rates from all packages independent of their location in the repository. In reality, however, the releases from the packages located near to this boundary would reach the boundary sooner than those farther away. Therefore, at a given time the contribution from each waste package to the source term depends upon the distance from the boundary and the time needed for radionuclides to reach that

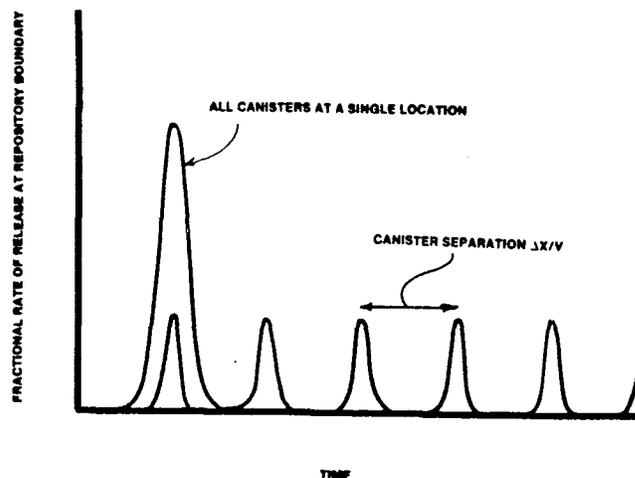


Figure 1. Effect of Spatial Distribution of Waste Packages.

boundary. In the simple picture in Figure 2, the large peak is decomposed into a series of smaller peaks, effectively reducing the peak release rate and spreading the release out in time. For a repository with as many as 30,000 waste packages, such modifications could be significant.

The impact of the geometry is a function of the boundary chosen for the evaluation of the repository release rate. The choice of this boundary depends upon the radionuclide pathways through the repository in the scenario being considered. Since the rate of release at this boundary is dependent upon the flux of radionuclides across the boundary, the geometric effect is also a function of the radionuclide velocity at this boundary.

The effect also depends upon any dispersion in the transport of the radionuclides through the repository before reaching the boundary. Figure 2 shows how the release rate at the boundary can be affected. In this case the source term is effectively averaged over the individual waste package release rates. One possible source of such an effect is hydrodynamic dispersion of the radionuclide concentration within the repository. In this case, the fractional release rate due to the distribution of waste throughout the repository can be approximated by

$$q(t) = \frac{V}{L} \frac{1}{2} \left[\operatorname{erf} \frac{(X_0 + L - Vt)}{\sqrt{4aVt}} - \operatorname{erf} \frac{(X_0 - Vt)}{\sqrt{4aVt}} \right]$$

where erf is the error function, V is the radionuclide velocity, L is the length of the repository, X_0 is the distance of the repository from the boundary, and a is the dispersivity. This expression is illustrated in Figure 3. Although this representation for the geometric effect has been derived from simplistic hydrodynamic dispersion considerations, it applies to any of the dispersive effects that may occur in the repository. In general, the effect of the geometry on the source term will be to provide a release duration L/V , corresponding to the (retarded) transit time of the radionuclide through the repository, and an average fractional release rate of V/L .

The integration of the waste package and repository performance requires some care. The release at the boundary at a specified time may have contributions from more than one waste package. For example, radionuclides which take a long time to travel to the boundary may arrive at the same time as those released later from waste packages nearer to the boundary. The total release rate is evaluated by integrating over all such contributions. Formally, this integration is the convolution over the waste package fractional release rate, q_p , and the geometric term, q_R :

$$q(t) = \int_0^t q_p(t') q_R(t - t') dt'$$

The integration is illustrated for a simple representation of the waste package release rate in Figure 4. The fractional release rate from the combined system has a behavior which differs significantly from the single-packaged behavior.

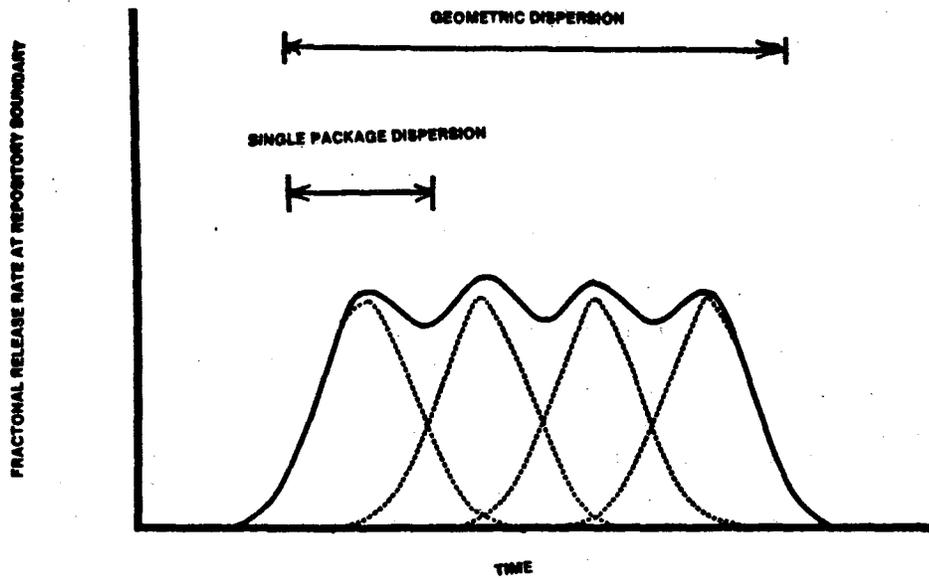


Figure 2. Effect of Dispersion on Geometric Release Rate.

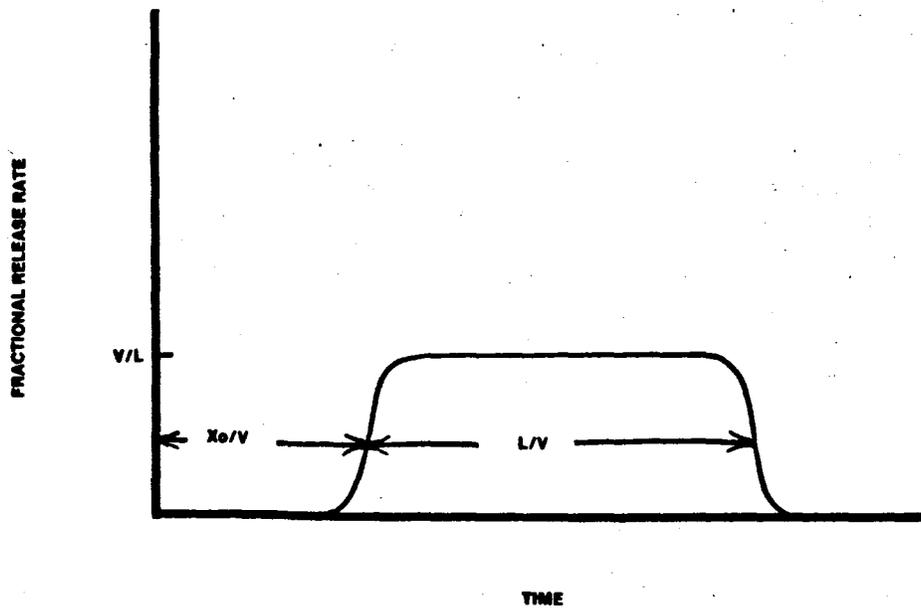


Figure 3. Analytic Solution for Geometric Effect.

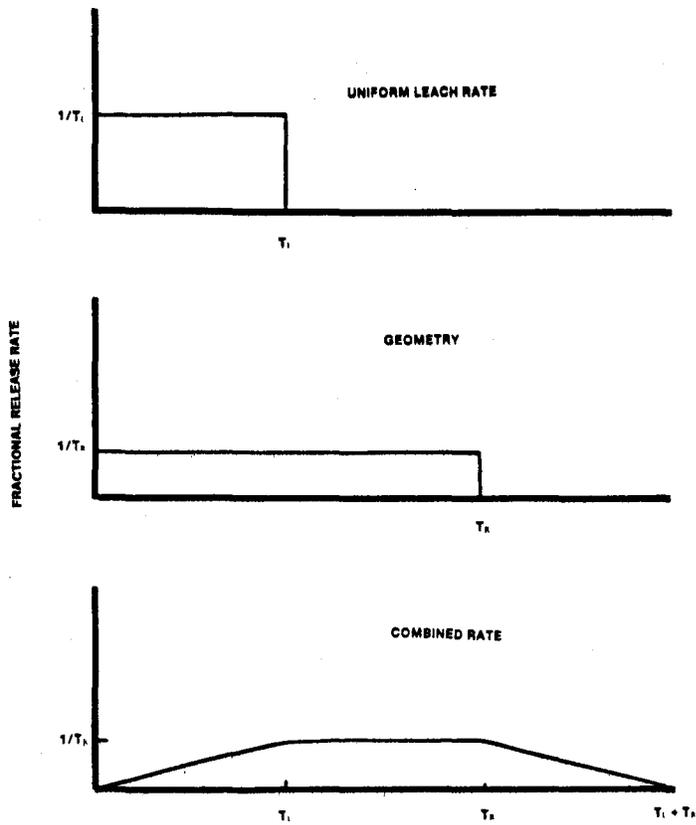


Figure 4. Integration of Leach Rate and Geometry.

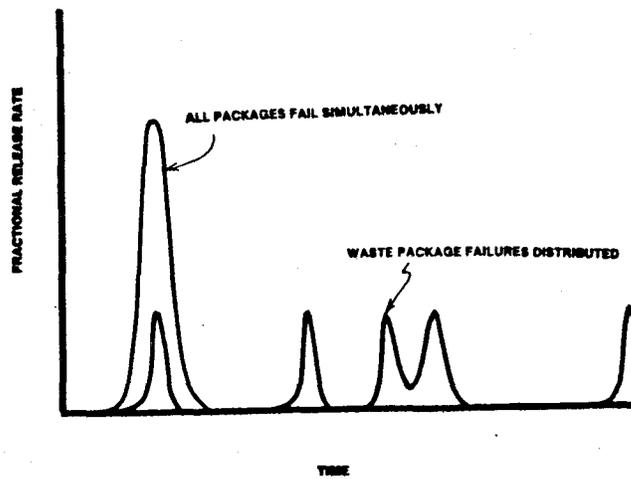


Figure 5. Effect of Waste Package Failure Rate.

The peak value of the integrated source term corresponds to the smaller of q_p and q_R . This result makes sense physically and, in fact, it can be shown from the properties of the convolution integral that the fractional rate of release from the combined system is always less than or equal to the smaller of the component fractional release rates. Therefore, it is possible that the source term that accounts for the repository geometry can be much smaller than that evaluated from the waste package analyses alone.

WASTE PACKAGE FAILURE RATE

A second feature of a repository that can influence the source term is the fact that waste package failure is a stochastic process in which the failures are distributed over time. Since no release is possible until the waste package fails, a distribution of the failure rates can affect the overall release rate. Figure 5 compares the fractional release assuming all packages fail at the same time to the rate in which the failures occur distributed over time. This figure does not take into account the geometric distribution of waste packages. For the case where the distribution of failure is taken into account, not only is the release rate spread over a longer time but, because the releases at a given time come from a subset of the total set of waste packages, the peak release rate is reduced. Therefore, the integration of the waste package failure rate into the waste package release rate may affect the determination of the source term.

Figure 6 shows the result when the waste package release rate is integrated over a probability distribution for the failure rate. A single-parameter, Poisson-type failure rate is assumed in this case and the result shows that a significant effect on the system release rate is possible.

INTEGRATION OF REPOSITORY AND WASTE PACKAGE PERFORMANCE

Figures 7 and 8 show the effect of taking into account both the geometric effect and the waste package failure rate in evaluating the source term. Figure 7 shows the impact of the geometric effect on a system in which the leach rate is one part in 10^5 per year and for which the Poisson failure frequency is 10^{-4} per year. For a repository transit time of 10,000 years (fractional release rate of 10^{-4} per year), the only detectable effect is in the first 20,000 years and in the tail of the distribution. For a repository transit time of 10,000 years, the effect is more pronounced. Finally, for a repository transit time of 1,000,000 years, the source term is dramatically reduced by the geometric effect.

The sensitivity of the calculated source term to the waste package failure rate is illustrated in Figure 8. In this case the repository transit time is set at 1,000 years and the waste package release rate is set to 10^{-4} yr^{-1} . For a failure frequency of 10^{-3} yr^{-1} there is some effect on the source term. This effect becomes much more important as the frequency is reduced below 10^{-4} yr^{-1} .

In these examples, the peak value of the source term is controlled by the most constraining of the three effects. For early times, the peak value can be much less than the peak value from any individual component due to synergistic effects.

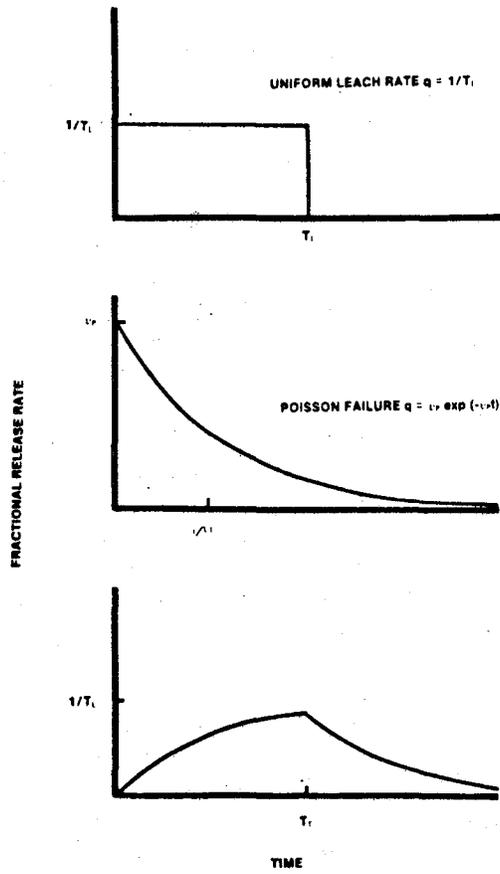


Figure 6. Integration of Leach Rate and Waste Package Failure Rate.

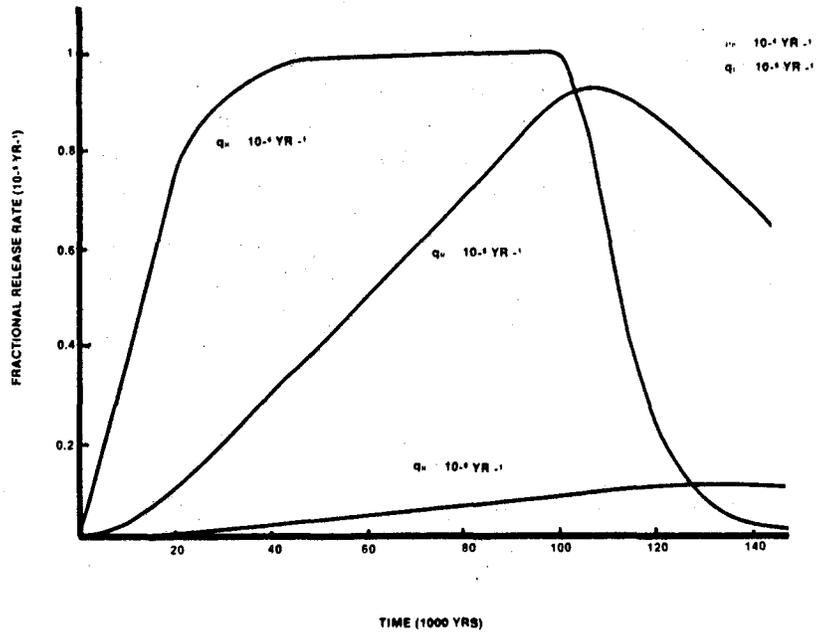


Figure 7. Dependence of Source Term on Geometric Effect.

APPLICATIONS TO SPECIFIC SITES

Although it is still too early to perform definitive analyses for any specific site, existing information can be used to investigate the relative importance of the effects being discussed. Figure 9 shows the results calculated for a repository constructed in a basalt flow. Such a formation is presently being investigated at the Hanford Site near Richland, Washington. Preliminary evaluations indicate that the expected time to failure for a waste package under these conditions may be as high as 6500 years with a variance of 2000 years based upon existing corrosion data. A Gaussian distribution that gives these values has been assumed for the failure rate. The waste package release rate is based upon leach rate data for spent fuel and a leach rate of $2 \times 10^{-5} \text{ yr}^{-1}$ is used here. Radionuclide solubility limits to the leaching are not considered here. The scenario envisioned is one in which the ground water moves up vertically through the repository, dissolving radionuclides leached from the waste form. The ground water rises to the flow top and the radionuclides are then carried horizontally along the flow top to the accessible environment. For a vertical velocity of $3 \times 10^{-4} \text{ m/yr}$ in the host rock and a repository thickness of one meter (based upon one meter diameter canisters emplaced horizontally), the geometric factor alone is $3.3 \times 10^{-5} \text{ yr}^{-1}$. No radionuclide retardation is taken into account in this simple example.

Figure 9 shows that the waste package failure rate has some effect and delays the release by several thousand years. The integration of the waste package release rate and the geometric effect produces a source term that peaks at about 50,000 years. While the peak release rate is not substantially different from the leach rate, the source term in the first 10,000 years is significantly reduced. Therefore, estimates of releases to the accessible environment in this period could depend upon repository features.

Figure 10 shows the source term for a simple simulation of the Yucca Mountain site in Nevada. A horizon in the unsaturated tuffs is being considered as a candidate for a repository at this site. Due to the unsaturated conditions and low ground-water flux rates for this site, extremely low release rates are expected. For example, the waste form dissolution rate is probably less than $5 \times 10^{-9} \text{ yr}^{-1}$ due to the low flow rates. A geometric term of 10^{-3} yr^{-1} has been assumed based on a flux rate of about $3 \times 10^{-4} \text{ m}^3/\text{yr}/\text{m}^2$ and a waste package length of about 3 meters. An exponential distribution function with a mean time to failure of 10,000 years and a variance of 7000 years has been assumed. The results in Figure 10 show that the geometric term is of little consequence for this case since the waste package release rate is at least 5 orders of magnitude smaller than this effect. However, the release rate in the first 10,000 years is significantly reduced by the low failure rate.

The possible impact on source term for scenarios involving a disruption to the expected repository performance is shown in Figure 11. In this case a spent fuel repository in a bedded salt site is investigated. It is assumed that an exploratory borehole connects aquifers that overlie and underlie the host salt bed. Water flowing through the borehole can then dissolve the host salt. As the salt dissolves, waste packages can be exposed to the water and

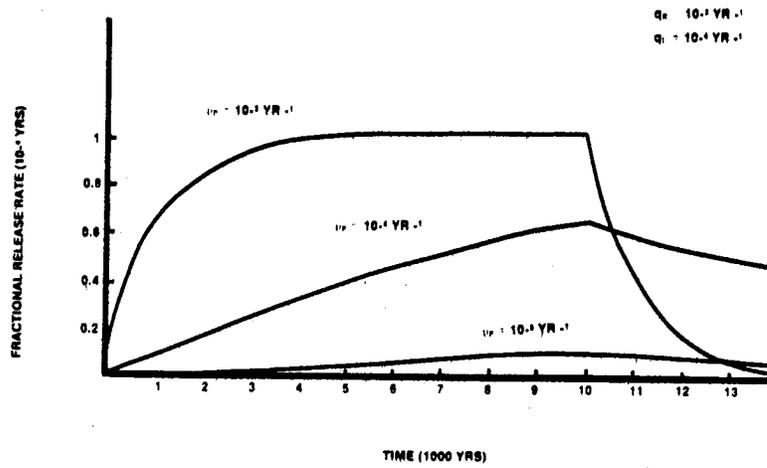


Figure 8. Dependence of Source Term on Failure Rate.

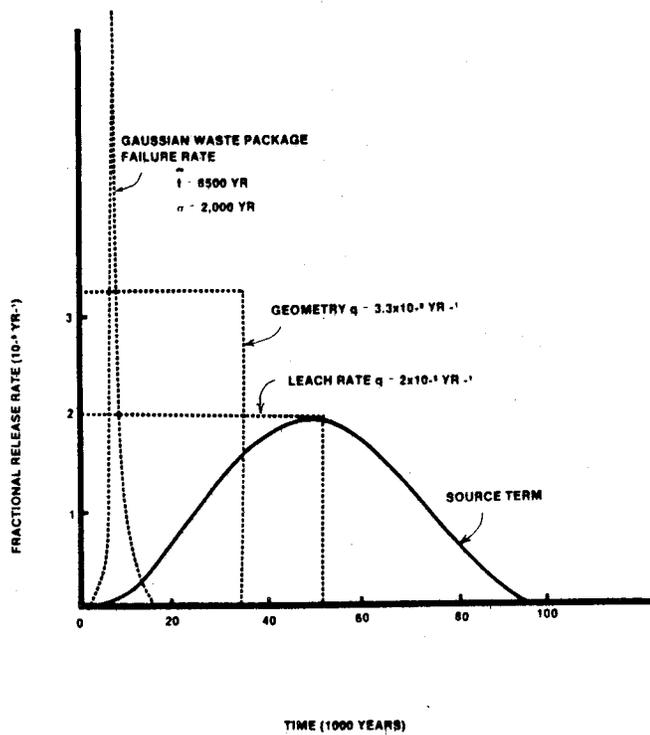


Figure 9. Integrated Source Term for Basalt Site.

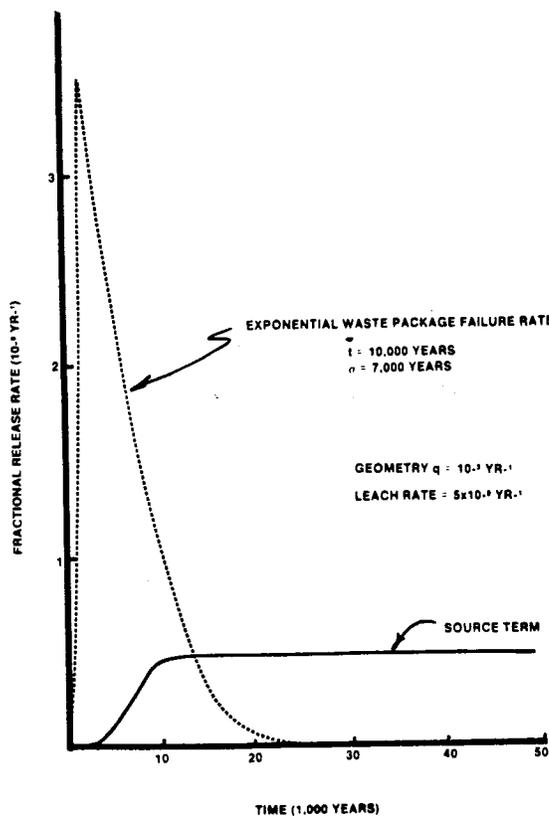


Figure 10. Integrated Source Term for Yucca Mountain.

waste package failure can permit the leaching and transport of radionuclides from the repository. The geometric term therefore depends upon the rate at which the dissolution front exposes the packages. This exposure rate has been evaluated in detailed assessments of this scenario [1] and the results are shown in the insert in Figure 11. The calculated waste package exposure rate continues for only 8 years until saturation of the brine limits further salt dissolution. A leach rate of 2.2×10^{-4} yr $^{-1}$ is assumed for the spent fuel and a Gaussian failure rate with a mean time to failure of 10,000 years and a variance of 2000 years have been assumed for the waste packages. The impacts of both the failure rate and the geometric term on the source term are dramatic. The peak release rate is reduced by more than an order of magnitude from the leach rate. The total calculated release from the repository system in the first 10,000 years would therefore be quite limited although specific system assessments using this source term would be needed to verify this conclusion.

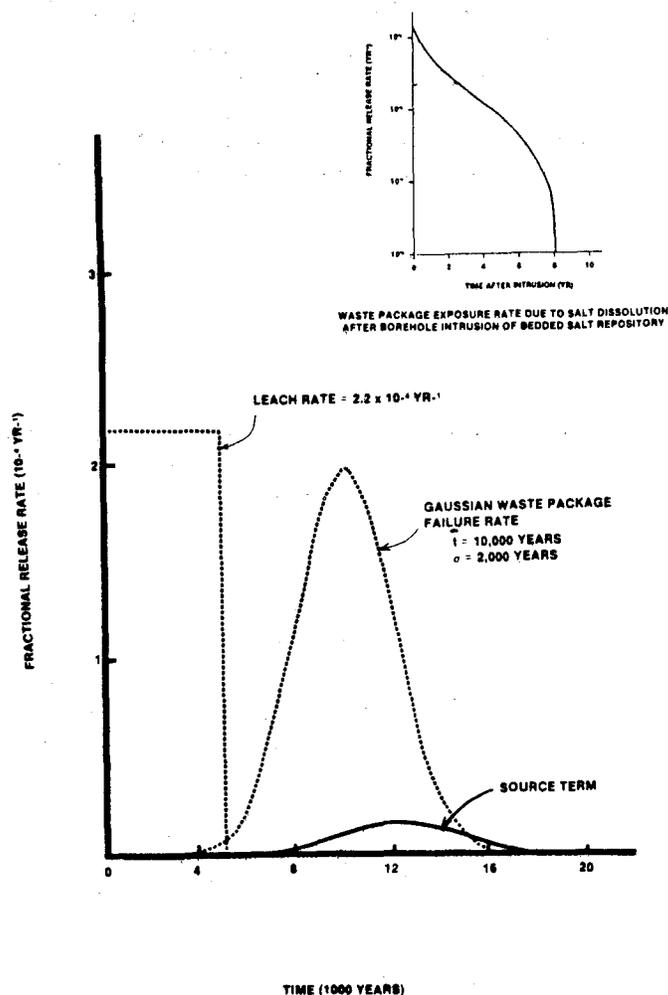


Figure 11. Integrated Source Term for Borehole Intrusion at Bedded Salt Site.

CONCLUSION

These applications demonstrate that there may be cases where the integration of repository and waste package performance may have profound impacts upon source terms. In some cases the geometric effect may be very important as in the case when the transit time through the host rock is very long. It also appears that waste package failure rates should be taken into account. The key parameters of the failure rate include the delay before release or the mean time to release and the peak frequency of waste package failures.

It should be noted that there are many other effects that could affect the source term. For example, very-near-field transport mechanisms and host rock/water interactions are likely to provide significant impacts on system performance. The simple model described here does not take into account these effects. Nor does it account for the dependence of the waste package release upon the location within the repository or the thermal and chemical conditions that may vary across the repository. These effects should be considered in future site-specific evaluations.

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THE IMPORTANCE OF THE SOURCE TERM FOR THE RELEASE OF RADIO-
NUCLIDES FROM A REPOSITORY IN A SALT DOME

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ABSTRACT

The release of radionuclides from a backfilled and brine saturated repository in a salt dome is analyzed as a function of canister lifetimes and solubility limits. The relationship between the waste package and the multi-barrier system of the repository is discussed.

Introduction

In the West German "Projekt Sicherheitsstudien Entsorgung" (PSE) a safety analysis for the isolation of radioactive wastes in a salt dome repository has been carried out [1]. Some of the results concerning the influence of the source term are discussed in the following.

During an operational period of the repository of 50 years mainly wastes from nuclear power plants, corresponding to a total electric energy of 2500 Gwa, will be deposited. Additional wastes come from research, medicine and other sources. Although two disposal options - reprocessed and spent fuel - , both of which require different repository designs, have been studied within the project, for the sake of clarity, we shall concentrate on the case of the reprocessed fuel repository only in the following.

The Repository Design

The site selected for the repository is the salt dome at Gorleben. The dome is covered with sediments of 300 m thickness. The drift system of the repository lies at about 800 m below surface. A brief sketch is given in Fig. 1. Here the repository is reduced to representatives for the different types of waste locations. On the left side of the repository, disposal chambers contain low- and medium level wastes without heat production, while on the right side heat producing medium and high level wastes are stored in boreholes of 300 m depth measured from the drift level.

The Scenario

A scenario which can lead to the transport of radionuclides into the biosphere has been selected to demonstrate the methodology developed so far. As the internal geological structure of the salt dome is yet unknown, it is assumed that a main anhydrite layer exists which forms a pathway for groundwater from the aquifer system of the overlying strata down to the repository level. It is conceivable that the shafts or nearby drifts at the center of the repository cross the anhydrite layer. After closure and sealing of the repository water may intrude into the repository from the main anhydrite. In contrast to possibly existing brine pockets in rock salt which might shed a limited amount of brine into the repository, water intrusion from the main anhydrite is limited by the void space of the repository only. It is assumed that unsaturated intruding water becomes saturated brine upon contact with the rock salt formation.

The inflow of brine driven by hydrostatic pressure of about 10 MPa is slowed down by several engineered barriers,

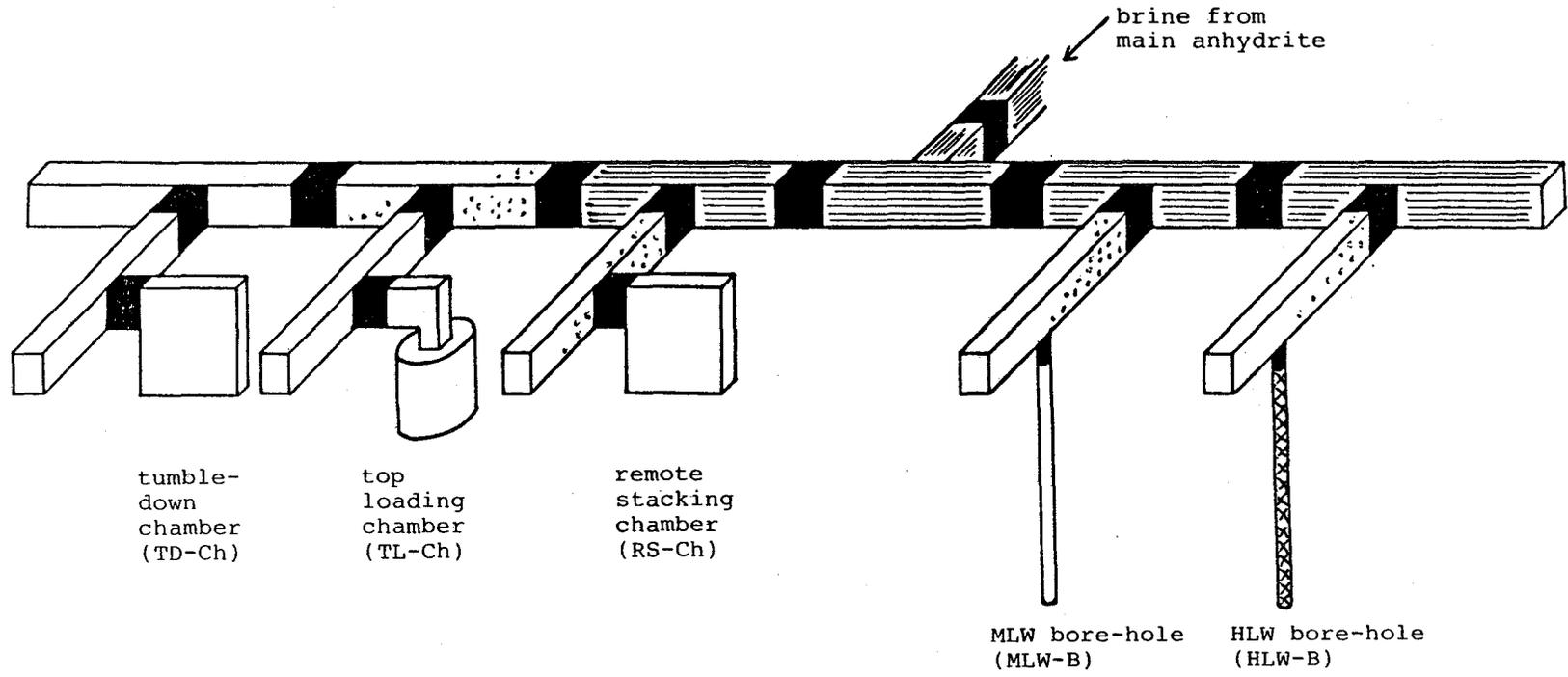


Figure 1

Reprocessed fuel repository 120 years after the onset of brine intrusion.

i.e. the backfill material (crushed salt) in drifts, dams (various materials) separating different parts of the repository, and sealings (salt concrete or condensed salt backfill) between drifts and chambers or boreholes. Dams and sealings are represented by black areas in Fig. 1. The flow resistance of the anhydrite is neglected because of its unknown properties. The void space of the repository which can be filled up by the intruding brine decreases with time. This is due to the creep of rock salt which leads to convergence of drifts, chambers and boreholes in the repository. This process results also in the compaction of the backfill materials in the drifts thus increasing the flow resistances and stretching the inflow of brine in time. In this way convergence works against brine intrusion. However, when a drift is flooded convergence loses the competition in this part. The hydraulic pressure rises in that area and the convergence rate drops significantly.

As a flashlight Fig. 1 also shows the distribution of brine in the repository 120 years after the beginning of brine intrusion (and closure of the repository). Although a part of the drifts is already flooded, no contact between wastes and brine has taken place as yet. On the contrary, an important change of the situation has occurred on the borehole wing of the repository. Here convergence overcame brine intrusion because of the higher temperatures in the borehole wing and particularly in the HLW field. The sealings of the boreholes have been compacted so strongly by the convergence process that their permeability has become comparable to that of rock salt. About 80 years after the onset of the scenario the boreholes are practically closed and subsequent contact between brine and wastes is impossible. The drifts above the boreholes are about to close at approximately 120 years where we put our flashlights. Although some brine could intrude, it is less than the water content of natural rock salt, so that no relevant migration of brine is expected. Reasonable variations of the model parameters did not change this situation.

The situation is different as regards the MLW boreholes. Some of the boreholes see enough brine for corrosion of canisters and leaching of radionuclides from the waste matrices. Although convergence is slowed down with the flooding of the boreholes, it still proceeds and squeezes contaminated brine into the overlying drift system and eventually into the central field where brine intrusion first started. Without the existence of the chamber field the contaminated brine would be pressed out of the repository the same way it came in. However, because of the lower temperature and the larger initial volume of the chamber field, the chamber field still remains in the phase of brine inflow so that contaminated brine from the MLW boreholes flows into the chamber field together with fresh brine from the main anhydrite until all drifts and chambers are filled with brine. A similar cyclic behaviour which reduces the radionuclide release from the repository also exists between the different chamber fields.

500 years after the beginning of brine intrusion all voids of the repository are filled with brine. In the final phase, starting from then onwards, MLW boreholes and chambers squeeze contaminated brine out of the repository through the main anhydrite to the aquifers of the overlying strata and from there radionuclides flow into the biosphere with the groundwater. The maximum concentration of radionuclides in the biosphere will show after about 10.000 years.

The coupled equations for brine flow, hydraulic pressure, and convergence for the drift network of the repository have been solved with the EMOS computer code at the Technical University of Berlin. Convective exchange of brine between neighbouring sections of the repository via temperature and density gradients and gas flow are also included. Mobilization of radionuclides is described by models for corrosion of canisters and waste matrices. The transport of radionuclides is controlled by the motion of the brine as well as by diffusion, precipitation and dissolution of the radionuclides themselves.

The convective brine exchange mechanisms - including diffusion - turned out to be rather unimportant for the radionuclide release from the repository when compared with the flow forced by convergence. The influence of the primary source term, i.e. the mobilization of radionuclides from the wastes, is discussed in detail in the following.

Mobilization of Radionuclides

Corrosion of the waste containing canisters can start with the small amount of brine migrating from the surrounding rock salt into the deposit locations as soon as the canisters have been emplaced. Later inflow of brine from the drifts sets up a continuous fluid phase able to transport radionuclides. Functions describing the failure of canisters and mobilization of radionuclides are defined from this point onwards.

The maximum canister lifetime depends on the type of canister used for a particular kind of wastes. It takes on the following values:

10 a	wastes without fixation and HLW canisters
40 a	concreted wastes
200/300 a	concreted wastes with lost concrete shielding
500 a	cast iron canisters

The maximum canister lifetime is diminished by the time between deposition of the waste and the first contact with brine flowing in from the drifts. However, by definition it does not become less than 10 % of the original value. A constant relative rate of canister failure, which is the inverse of the reduced maximum canister lifetime, is assumed.

As soon as a canister has failed, waste matrix corrosion starts. A constant rate of matrix corrosion, except for vitrified HLW, is assumed. The matrix lifetime depends on the waste form with the following values used:

10 a	wastes without fixation
50 a	homogeneous concreted wastes
100 a	heterogeneous concreted wastes
500 a	organic matrix

The relation for the HLW corrosion rate per unit surface reads:

$$j(T) = j(T=473K) \exp(-Q/R(1/T-1/473K))$$

$$j(T=473K) = 1 \text{ g m}^{-2} \text{ d}^{-1}$$

$$Q = 50 \text{ kJ mol}^{-1}$$

$$R = 8.31 \cdot 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Q is the activation energy and R is the universal gas constant. A canister contains 150 l of glass. The geometrical surface of 1.7 m² is increased by a factor of 10 because of fractures in the glass matrix. Via the temperature dependence a time dependence also enters into the corrosion rate. At a constant temperature of T = 473 K, which is the peak temperature the glass matrix reaches, corrosion would be completed after about 80 years. On the other hand, starting with a peak temperature of T = 363 K the time span would be 40.000 years, primarily because of the fact that the later temperature drop (after about 100 years) further decreases the corrosion rate.

As there is a possibility of varying the peak temperature either by interim storage of HLW before final disposal in the repository or by dilution it is interesting to note that a minimal mobilization of HLW can be achieved both at very low temperatures (363 K) and at very high temperatures (473 K). At low temperatures the slow corrosion of the glass matrix is the limiting factor while at high temperatures it is the large convergence rate which leads to a closure of the boreholes before brine can enter. From this we could learn that the optimization of the primary source term is not necessarily an optimization at the same time for the source term of the repository as a whole.

Variation of Canister Lifetimes

Canister and matrix corrosion functions are generally conservative estimates based on the assumption that sufficient brine is available for complete alteration of canisters and waste matrices. Table I shows the maximum brine contents for the different types of boreholes and chambers.

Table I

	brine volume V/m ³	metall mass M/Mg	cement/glass mass M/Mg
HLW-B	0	19	36
MLW-B	3	92	242
RS-Ch	206	3700	30000
TL-Ch	34	94	664
TD-Ch	116	1200	9400

Quantities given are per borehole (B) or chamber (Ch)

On the average approximately 1 l of brine is available per 100 kg of concrete. Corrosion of the metal present will further reduce the available amount of brine; therefore, the lifetimes given above seem to be extremely conservative. A variation of the canister lifetimes, representative also for the matrix lifetimes, has been performed in order to estimate the importance of the primary source term within the scenario. A useful quantity hereby is the cumulative relative release from the repository, which is an integrated release of a radionuclide relative to the initial inventory of the repository. In Table II the cumulative relative release after 100.000 years (release rates are negligible above this time scale) is given for a selection of important radionuclides among which Tc99 and Np237 are responsible for the main radiation exposure in the biosphere. Besides the reference case variations of the calculation with canister lifetimes increased by factors 10 and 100 are shown. IAl29 symbolizes iodine in the form of AgI, while I129 stands for iodine in more easily solvable form. It can be seen that the cumulative release is not very sensitive to the canister lifetime. This is mainly due to the very slow decrease of the brine contents of the repository in the "squeeze out" phase. Thus it may be concluded that the direction of further investigations should not be towards the reduction of the corrosion rate but towards a limit to the absolute amount of corrosion.

That this is possible seems to be guaranteed by the very small ratio of brine to concrete plus metal at the waste locations.

TABLE II

Cumulative relative release from repository after 1×10^5 a

Nuclide	canister lifetime*1	canister lifetime*10	canister lifetime*100	inventory M/kg
C14	2.14×10^{-3}	1.99×10^{-3}	1.22×10^{-3}	13.3
Se79	2.89×10^{-2}	2.67×10^{-2}	1.84×10^{-2}	444
Tc99	1.96×10^{-2}	1.83×10^{-2}	1.38×10^{-2}	65290
J129	2.93×10^{-1}	2.59×10^{-1}	1.49×10^{-1}	260
JA129	1.92×10^{-4}	1.90×10^{-4}	1.88×10^{-4}	15460
Np237	4.45×10^{-4}	4.36×10^{-4}	3.72×10^{-4}	38210

Solubility Limits

A limitation to the absolute amount of mobilization is already set by the solubility limit for a couple of radionuclides. Table III gives the solubility limits used for different radionuclides while Table IV shows the inventories of radionuclides at different waste locations.

Table III

Solubility limits

nuclide	Ch + MLW-B mol/l	HLW-B mol/l
C14	1×10^{-3}	1×10^{-1}
Se79	1×10^{-1}	1×10^{-1}
Tc99	1×10^{-1}	1×10^{-1}
J129	1×10^{-1}	1×10^{-1}
JA129	5×10^{-6}	
Np237	1×10^{-5}	1×10^{-4}

It is indicated from which location the maximum release of radionuclides originates and where the solubility limit is attained. In boreholes the canisters are more densely stacked than in chambers. Therefore, the relative brine contents of boreholes in smaller and solubility limits are more easily met.

MLW-boreholes have the highest inventory of Cl4 and its solubility limit is attained. In TD chambers no precipitation of Cl4 takes place and the main release stems from this location.

Table IV

Radionuclide inventories in kg

nuclide	total	TD-Ch	TL-Ch	RS-Ch	MLW-B	HLW-B
Cl4	13.3	0.96 ^r	0.0	0.08	12.2 ^s	0.0
Se79	444	1.18	0.0	7.22	43.7 ^r	391.4
Tc99	65290	22.1	0.0	64.2	4270 ^r	60930
I129	260	0.49	0.0	181 ^r	78.5	0.16
IA129	15460	0.0	0.0	15460 ^{sr}	0.0	0.0
Np237	38210	29.2 ^s	0.0	365 ^{sr}	189 ^s	37630

s - meets solubility limit

r - main release

Se79 and Tc99 do not meet their solubility limits. The main release comes from the MLW-boreholes which have the highest inventories.

The main release of I129 originates from the RS chambers. The mobilization of iodine in the form of AgI (IA129) is strongly suppressed by its low solubility limit.

Np237 attains its solubility limit in boreholes and chambers. The main release comes from the chambers because of their higher brine contents.

Present solubility limits are regarded in some cases as very conservative estimates which might be decreased with the increase of understanding of the chemical environments. For radionuclides which attain their solubility limits at all locations, a reduction of the solubility limit reduces the release from each of the locations by about the same factor. Radionuclides which are presently not controlled by solubility need a strong reduction of the solubility limit in some cases in order to affect the source terms appreciably.

In Fig. 2 for example the ratio of cumulative release of Tc99 at a given solubility limit to the release at the reference solubility limit (0.1 mol/l) is plotted for different locations.

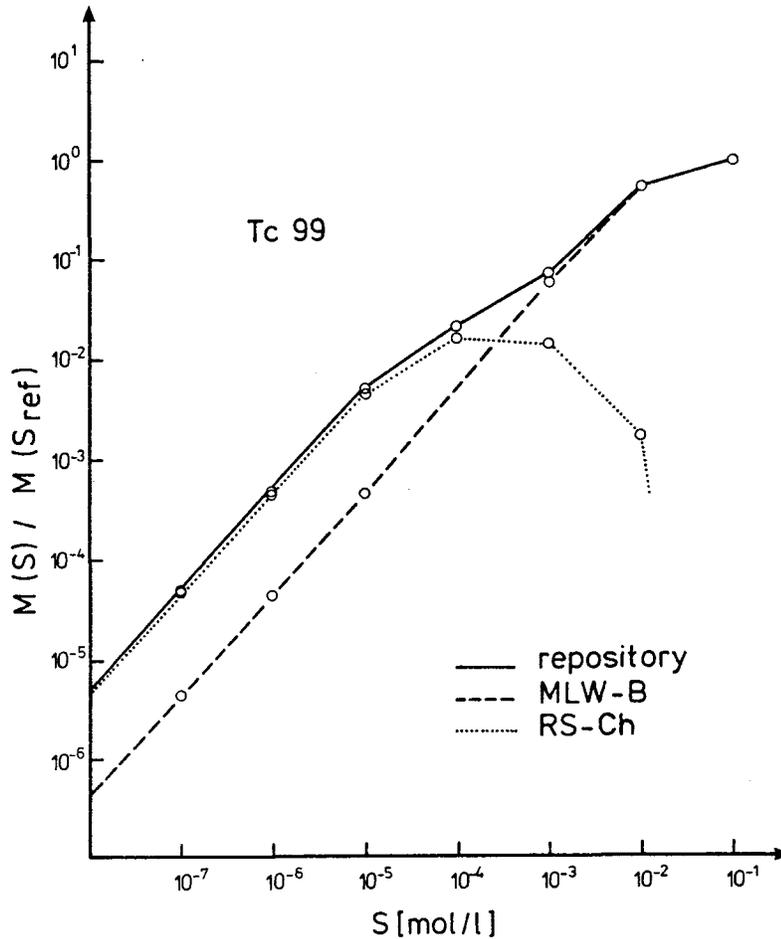


Figure 2: Release of mass M of Tc99 normalized to the reference case as a function of the solubility limit S

Dots symbolize data points while lines interpolate the data points. At the solubility limit 0.1 mol/l the ratio is 1 by definition. Tc99 is controlled nowhere by solubility. MLW boreholes are responsible for the total release of Tc99 from the repository. As discussed above, a part of the contaminated brine flows from the boreholes into the RS chambers. The net release from there is negative. For solubility limits between 10⁻² and 10⁻¹ mol/l Tc99 is controlled by solubility in the boreholes so that the release is proportional to the solubility limit (straight line).

With a smaller inflow of contaminated brine into the RS chambers the release from there recovers and makes up the main contribution to the total release from the repository at the solubility limit 10^{-4} mol/l. For solubility limits smaller than 10^{-5} mol/l, the releases from both of the locations and therefore also the total release from the repository, are proportional to the solubility limit. The contribution from the boreholes is an order of magnitude smaller than that from the chambers thus reflecting the ratio of brine flow from the two locations.

We have seen that although Tc99 is not far from being controlled by solubility in the reference case, a reduction of 4 additional orders of magnitude is needed until the proportionality of release and solubility limit is reached.

Finally, it should be mentioned that many of the results discussed above are also obtained in the case of the repository containing spent fuel. Particularly the closure of fields bearing the heat producing spent fuel canisters prior to brine intrusion shall be emphasized.

Conclusions

In the scenario discussed above, which is considered to be the most important of the possible scenarios, high level wastes in the case of reprocessed fuel, and spent fuel on the other hand, are prevented from coming into contact with inflowing brine by the rapid convergence of heated rock salt. Canister and matrix properties of these wastes are therefore irrelevant within this scenario.

It can be concluded that optimization procedures should not be restricted to the primary source term but be applied to the source term of the multibarrier system of the repository as a whole. For the rest of the wastes the release of radionuclides from the repository also does not depend sensitively on the properties of the primary source unless the total amount of corrosion of the waste matrices can be limited which is especially relevant for radionuclides which do not attain their solubility limits. The hope to limit corrosion in the forthcoming calculations is based on the fact that only a small amount of brine is available (1 l brine for 100 kg concrete). A better understanding of the chemical conditions in saturated brine in contact with wastes and under the influence of radiolysis may also lead to a reduction of solubility limits which is mainly important for radionuclides (e.g. Cl4 and Np237) which are already solubility controlled in the present study.

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SOURCE TERM MODELLING IN THE SWEDISH KBS - 3 STUDY

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ABSTRACT

The release rate of the individual nuclides from spent fuel in a deep geologic repository in crystalline rock is modelled. After canister breakdown when the fuel is wetted and starts to dissolve, the released nuclides migrate out into and through the backfill. The backfill which consists of a compacted bentonite clay has low permeability and effectively permits transport by diffusion only. The clay has strong sorptive capacity for most nuclides and retards their movement through the barrier. Many of the shorter lived nuclides Am^{241} , Cs^{137} , Sr^{90} , Pu^{240} decay considerably during their passage of the buffer. The longer lived nuclides will eventually be released to the outside of the buffer without significant decay.

During the ensuing semi-stationary phase the release rate will be determined by the dissolution rate of the uranium oxide matrix and the congruent release of the other nuclides. There are some exceptions notably Cs and I which are known to have migrated out of the fuel crystals during the reactor operation.

The dissolution rate of the uranium oxide is determined by its solubility and the various diffusion barriers between the fuel and the flowing water. These consist of clay backfill, possibly the clay which has intruded into the fissures and the slowly moving water in the fissures. The transport in the various barriers has been modelled. The dominating resistance in the cases studied was located in the slowly moving water in the narrow fissures.

The situation is somewhat complicated by radiolysis which may give rise to an oxidizing environment nearest to the fuel. This increases the solubility of many important species (U, Np, Tc..) and increases the release rates. The escaping oxidized species and the oxidizing agents (H_2O_2 , O_2) themselves will move out into the rock where they will react with divalent iron minerals in the rock. At the sharp redox front which develops within a few meters (to maximum a few tens of meters) downstream from the canisters, the redox sensitive elements (U, Np, Tc..) precipitate. They will be released to the flowing water outside the redox front in much smaller quantities than that by which they were released from the fuel.

INTRODUCTION

The present study is based on the conditions which will prevail in a repository for radioactive waste in crystalline rock at large depth as in the Swedish Nuclear Fuel Safety Project (KBS) concept.

The canisters with spent fuel are emplaced in holes in the floor of tunnels at 500m depth. The bedrock is crystalline e.g. granite or gneiss and has a low hydraulic conductivity $K_p < 10^{-10}$ m/s. The backfill consists of either compacted bentonite in the holes or a mixture of bentonite and quartz sand. The tunnels are backfilled with the latter mixture. See figure 1.

The bentonite, when wet, has a strong swelling pressure and very low hydraulic conductivity $K_p < 10^{-12}$ m/s. In the KBS concept the maximum temperature rise will be to less than 80°C on the canister surface. The copper canisters are designed not to corrode for very long times, they will not be penetrated in less than 100 000 years. If and when a breach occurs, the near field temperature is very near the ambient temperature in the bedrock, 25° C.

The present paper is concerned with the transport of species to and from the degraded canister when all the spent fuel or high level waste is exposed to the groundwater in the bedrock. The paper concentrates on the rate of release of radionuclides to the flowing water. It describes a method whereby input data to a far field migration model may be obtained.

CONCEPTUAL MODEL AND MAIN MECHANISMS

The basic approach to the problem has been to determine how much of the water which flows past the repository will exchange species with the canisters. The exchange is limited by the diffusional resistance in the nearly stagnant water in the backfill as well as the diffusional resistance in the slowly moving water in the bedrock. As the canisters are spaced fairly far apart it may be assumed that they do not influence each other.

The basic scenario is the following. At some time the canister material has degraded. The surface of the waste is wetted and the waste reacts "instantaneously" with the water, dissolving some constituents of the waste up to the solubility limit of that constituent in the chemical environment near the surface of the fuel. Some constituents like iodide and cesium will dissolve entirely in the water, others like silica of the glass, uranium of the spent fuel or nuclides like thorium will attain their equilibrium concentration in the water in contact with the waste.

There will be an instationary phase when the species diffuse out into the backfill and into the moving water. This is relatively short in relation to the total leach times of interest for the majority of the important nuclides, but some of the shorter lived nuclides decay considerably. During the ensuing stationary period the species are transported away from the fuel at a rate permitted by the rate of diffusion through the backfill and by the rate at which the flowing water can carry them away. The concentrations of the species in water in contact with the surface of the waste is at the solubility limit of the species or determined by the release rate from the matrix.

It is conceivable that all nuclides will not be released to the water at a rate large enough to keep the concentration at the solubility limit. This may occur if the release is dominated by the dissolution rate of the matrix of the spent fuel (congruent dissolution) where most of the waste (95 %) consists of UO_2 . The nuclides in the crystals of the fuel may only be released at the rate at which uranium is dissolved and transported away. Both the congruent dissolution case and the case limited by individual solubilities is treated.

The paper is structured as follows

- o Instationary period
- o Flowrate of water in the near field of the canister
- o Diffusion into the water flowing outside the backfill
- o Diffusion in the backfill
- o The influence of redox processes
- o Release rates to the far field

TRANSPORT OF DECAYING RADIONUCLIDES FROM SPENT FUEL THROUGH THE BACKFILL - INSTATIONARY PERIOD.

The migration of the radionuclides in the backfill takes place in a fairly complex geometry. The nuclides will migrate from the spot where they are dissolved, out into the backfill and then from the backfill into those sections of the rock which are intersected by fissures carrying water. A three dimensional treatment of the transport in the backfill by numerical methods has been done by Andersson et al. (1982) [1] assuming that all the canister surface has the same reactivity and that fissures intersect the repository hole in a regular fashion. The main emphasis of this treatment was on the steady state part of the transport.

Here we want to study that part of the leaching when the concentration profile is building up in the backfill. The main matrix constituent i.e. the uranium from spent fuel, is assumed to have reached a steady state earlier than the sorbing nuclides which are retarded during their transport. This is a fair approximation as the uranium under oxidizing conditions will not sorb strongly and thus will not be much retarded in the clay.

The sorbing nuclides will be considerably retarded during the instationary phase and if the time for first arrival at the outer boundary of the backfill is very large compared to the halflife of the nuclide, the nuclide may decay to insignificance before it reaches the outer boundary of the backfill.

A simplified treatment to assess the importance of the retardation is done below. The geometry of the backfill is modelled as a very thick (semi-infinite) slab of backfill. Nuclides are released into one side of the slab by congruent dissolution, and the transport rate of the nuclide past a plane at distance z_0 is calculated. As long as the transport rate past z_0 is very small, the thick slab is a fair approximation of a slab with thickness z_0 with many of the boundary conditions applicable to the subsequent transport in the bedrock.

When the radionuclides are leached from the spent fuel they will start to migrate into the backfill. Some of them like Cs and I will, except for a short initial phase, be released by congruent dissolution. This means that they will be released in proportion to their concentration in the fuel at any given moment. For all practical purposes the decay of the main matrix constituent U^{238} may be neglected in comparison to all other nuclides. The mass of the shorter lived nuclides will decrease in the fuel due to decay according to $m = m_0 e^{-\lambda t}$ if they have no precursor. m_0 is the mass of nuclide i at the time of burial. When the matrix dissolves it will attain a uranium equilibrium concentration at the surface of the fuel equal to the solubility $c_{U,sol}$ of uranium in the ground water. The matrix dissolves away as components diffuse out through the backfill. The dissolution rate can be determined. This has been discussed by Neretnieks (1982) [2] and will be treated later in this paper. The rate for the U^{238} release from the matrix is N_U . Other nuclides are released in proportion to their abundance in the fuel. Nuclide "i" is released with rate N_i

$$N_i = N_U m_i / m_U \quad (1)$$

First those nuclides which have no solubility limitation are treated. In this case all released nuclides are assumed to move into the backfill.

No solubility limitation.

For brevity we omit the index for nuclide "i". The transport through the backfill is described by equation (2) for the case of a flat backfill barrier. (We neglect the curvature in this analysis.)

$$\frac{dc}{dt} = D \frac{\partial^2 c}{\partial z^2} - \lambda c \quad (2)$$

for a decaying species.

The initial condition is $c = 0, z > 0, t = 0$
 The boundary condition for $t > 0$ at $z = 0$ is

$$N = N_U m_o / m_U e^{-\lambda t} = D_p \varepsilon_p A \frac{dc}{dz} \Big|_{z=0} \quad (3)$$

which indicates that all released nuclide is transported into the backfill. The uranium dissolution rate N_U is assumed to have become stationary and is thus constant. The boundary condition 3 implies that the congruent dissolution goes on forever. Although this obviously is not true, the dissolution time for the matrix is so large (many millions of years) in low permeability crystalline rock (Neretnieks and Rasmuson 1983) [3] that those nuclides which survive so long also will have attained a constant concentration in the backfill for distances larger than the envisaged backfill thickness.

$$c = b e^{-\lambda t} z \left\{ \frac{2}{\sqrt{\pi}} \frac{\sqrt{D_a t}}{z} e^{-\frac{z^2}{4D_a t}} - \operatorname{erfc} \left(\frac{z}{2\sqrt{D_a t}} \right) \right\}$$

where $b = N_U m_o / (m_U A D_p \varepsilon_p)$ (4)

and for the gradient we obtain $\frac{dc}{dz}$ to be

$$\frac{dc}{dz} = -N_U m_o / (m_U A D_p \varepsilon_p) e^{-\lambda t} \operatorname{erfc} \frac{z}{2\sqrt{D_a t}} \quad (5)$$

and thus

$$N /_{z=z_o} = N_U m_o / m_U e^{-\lambda t} \operatorname{erfc} \frac{z_o}{2\sqrt{D_a t}} \quad (6)$$

The rate of transport of radionuclide "i" past z_o as a fraction of that entering the backfill at $z = 0$, and $t = 0$ is

$$N_{z_o} / N_o = e^{-\lambda t} \operatorname{erfc} \frac{z_o}{2\sqrt{D_a t}} \quad (7)$$

Equations (4) and (7) consists of two parts. The first part accounts for the radioactive decay. The second part describes the change of concentration and flux of a stable species with time and distance. The convenient separability of the solution is due to the presence of the same decay term in equation (7) as well as in the boundary condition at the inlet, equation (3). If the importance of the outlet boundary condition is deemphasized, i.e. mainly the early times are considered, we can study the nondecaying part of the solution independently of the decaying part.

The treatment above has considered an infinitely thick backfill barrier and linear transport of the diffusing species. The backfill in a repository will have finite length and cylindrical shape more than slab shape. It has been shown (Neretnieks 1982) [4] that for "short times" and a reasonable ratio of the outer to inner radius $r_{out}/r_{in} < 2$ the approximations above give small errors and the simple solutions above for the infinite plane case give good results.

For screening purposes and for first estimates it is deemed to be sufficient to use the solutions for any of the geometries and boundary conditions. For $c_z/c_0 < 0.05$ the results differ very little.

Solubility limitation

In some circumstances some nuclides e.g. plutonium and thorium may have so low solubility that they precipitate at the fuel surface as the matrix dissolves away. The boundary condition at $z=0$ then becomes

$$c = c_0 \text{ for } t > 0 \text{ at } z = 0 \quad (8)$$

The following solution is obtained by Laplace transformation (Neretnieks 1984) [5]

$$c = \frac{c_0}{2} \left\{ e^{-z\sqrt{\frac{\lambda}{D_a}}} \operatorname{erfc}\left(\frac{z}{2\sqrt{D_a t}} - \sqrt{\lambda t}\right) + e^{z\sqrt{\frac{\lambda}{D_a}}} \operatorname{erfc}\left(\frac{z}{2\sqrt{D_a t}} + \sqrt{\lambda t}\right) \right\} \quad (9)$$

Equation 9 may also be used to obtain the flux past a plane at distance z_0 . As this flux cannot as easily be related to the release rate as for the case with no solubility limitations another approach is chosen. The concentration c_{z_0} at distance z_0 is related to the solubility concentration c_0 instead.

A generalized approach

For the case with no solubility limitation Equation 7 can be transformed to

$$N_{z_0}/N_0 = e^{-\tau} \operatorname{erfc} \frac{H}{2\sqrt{\tau}} \quad (10)$$

Equation 10 has only one parameter H

$$\text{where } H = z_0 \sqrt{\frac{\lambda}{D_a}} \quad (11)$$

The maximum of equation 10 is then a unique function of H . Figure 3 shows this function. The figure also shows at which times the maximum occurs.

This type of curve can be used to get an indication of which nuclides will strongly and which will be weakly affected by the presence of the buffer.

For the case where there is solubility limitation equation 9 can be written

$$c/c_0 = \frac{1}{2} \left\{ e^{-H} \operatorname{erfc}\left(\frac{H}{2\sqrt{\tau}} - \sqrt{\tau}\right) + e^H \operatorname{erfc}\left(\frac{H}{2\sqrt{\tau}} + \sqrt{\tau}\right) \right\} \quad (12)$$

if the same variable transformation is used as previously.

As in the previous case equation (12) is a unique function of H. It has no maximum but has an asymptotic value.

$$\begin{aligned} c/c_0 &= e^{-H} \\ \lim_{\tau \rightarrow \infty} & \end{aligned} \quad (13)$$

Figure 3 shows this curve also. It is seen that for H-values larger than about 30, c/c_0 becomes very small $< 10^{-15}$ in the same way as the maximum release N declines.

Some calculated results

Figure 2 shows the release N/N_0 for Pu^{239} for a case when there are no solubility limitations. The buffer thickness is taken to be 0.375 m. The apparent diffusivities in table 1 are used for the calculations. The figure also shows the release in a case where there is no retardation in the buffer. The peak release (5.4. % of original maximum leach rate) takes place after 40'000 years. At this time decay accounts for a decrease by a factor of 5.3. and the retardation effect contributes with another factor 3.5. The latter is somewhat on the low side to assure the applicability of equation (10). It somewhat underestimates the peak height and the portion on the downhill side.

Table 2 shows values of H for some nuclides of interest. For all nuclides the maximum release N/N_0 as well as the maximum (asymptotic) concentration c/c_0 are given in the table.

The only nuclide of those considered which decays to insignificance is Am^{241} . The nuclides Am^{243} , Pu^{239} , and Pu^{240} will be noticeably retarded. Sr^{90} and Cs^{137} will be somewhat retarded. Th^{229} comes predominantly from the Np^{237} chain which passes the backfill barrier and will thus not be influenced by the backfill.

STATIONARY PERIOD

Water flow around the canister

The water flow in the vicinity of the canister will be somewhat larger than in the undisturbed rock far from the caverns where the rock is not influenced by mining activities. Assuming that the bedrock can be treated as a porous medium and that the rock is much more permeable near the canister than far away, it can be shown that the flux through an infinitely long cylindrical hole is twice that in the undisturbed rock (Tietjens 1960) [6]. The same applies to flow in a fissure intersecting a hole perpendicular to its axis. The presence of more fissured rock near the backfilled holes acts as an empty hole in the above description. The presence of an impermeable area - the backfill - inside the permeable area does not influence the flow pattern in the rock. There are no detailed data on the size and orientation of the fissures in the rock. In the following the flowrate in the rock surrounding the backfill is taken to be twice that in the far field rock.

The flowrate of water in the bedrock in the far field can be determined if the hydraulic gradient and conductivity is known, the flowrate is $u_0 = K_p i$ and the velocity of the water is $u_p = 2u_0/\epsilon_R$ in the near field.

Mass transfer to the water flowing past the backfill

Two cases are treated. In the first case we assume that the bedrock around the backfill can be treated as a porous medium surrounding an infinitely long impermeable medium (the backfill). The assumption of an impermeable backfill is a good approximation for the bentonite clay which has a very low hydraulic conductivity compared to the bedrock.

The transport by diffusion of dissolved species is much faster than by flow (Neretnieks 1977) [7]. Transport by flow in the backfill is therefore neglected.

In the second case we assume that the bedrock consists of individual fissures intersecting an infinitely long clay cylinder at regular intervals. All water flow takes place in the fissures. The mass transfer to the flowing water is treated as follows: The water which approaches the backfill has a known concentration c_∞ of the species of interest. As the water approaches and flows past the backfill it picks up (or is depleted of) the species which diffuse in the water from (or to) the outer surface of the backfill. See Figure 4. In the following only outward transport will be described. Inward transport may be described in the same way. During its passage past the backfill the flowing water will pick up more and more of the diffusing species. When the water leaves the vicinity of the backfill, it has taken up an amount of species which is mainly dependent on the residence time of the water at the surface of the backfill and the diffusivity of the species. A rigorous treatment of this case is given by Andersson et al (1982) [1]. A simplified approach was taken by Neretnieks (1978, 1980) [8,9].

Assuming that the penetration depth of the diffusing species is short compared to flow length, the mass N transferred during this time can be obtained by solving the diffusion equation for the appropriate initial and boundary conditions. The solution is given in detail by Bird et al (1960 p. 537) [10]. The results can be written

$$N = 2\pi L r_3 \epsilon_R (c_\infty - c_3) \sqrt{\frac{4D_w}{\pi t_{res}}} = \frac{1}{R_3} (c_\infty - c_3) \quad (14)$$

Chambré and Pigford (1983) [11] arrive at the same result but a constant $2/\sqrt{\pi}$ higher (i.e. 13% higher release rate) by a slightly different method. They also give a range of validity to the use of equation (14). It is valid for

$$u_p r_3 / D_w < 4 \quad (15)$$

Mass transfer in the backfill

The distinction between the case where the rock is a "porous" medium and the case where it is a sparsely fissured rock becomes important when the migration in the backfill is to be treated. In the first case the diffusing species can enter the water in the rock everywhere along the backfill/rock interface, whereas in the second case the species must find the widely spaced individual fissures.

Rock is a porous medium

The diffusional transport through a cylindrical barrier can be written (Bird et al 1960, p. 287) [10].

$$N = D_1 2\pi L (c_1 - c_2) / \ln(r_2/r_1) = \frac{1}{R_1} (c_1 - c_2) \quad (16)$$

If backfill material can be injected into the porous bedrock to some distance r_3 (or into the individual fissures) there will be an additional transport resistance. This can be written analogous to equation 16.

$$N = D_2 \epsilon_R 2\pi L (c_2 - c_3) / \ln(r_3/r_2) = \frac{1}{R_2} (c_2 - c_3) \quad (17)$$

D_2 is the effective diffusivity in the backfill injected into the pores of the bedrock.

As it is implicitly assumed (not quite true) that c_1 , c_2 and c_3 are constant around the cylindrical circumferences, c_2 and c_3 can be eliminated from equations 19, 20 and 21 give

$$N = 2\pi L \frac{(c_1 - c_\infty)}{\frac{\ln(r_2/r_1)}{D_1 R_1} + \frac{s}{\delta} + \frac{\ln(r_3/r_2)}{D_2 \epsilon_R R_2} + \frac{1}{r_3 \epsilon_R \sqrt{\frac{4D_w}{\pi t_{res}}} R_3}} \quad (18)$$

δ/s is the equivalent fraction of the clay that is effectively utilized by the diffusing species. It is explained below.

The three terms in the denominator are proportional to the resistance to mass transfer in each section R_1 , R_2 and R_3 respectively. They can be used to compare the importance of the various diffusional barriers.

Rock is a fissured medium

A case where the rock is fissured with equally spaced horizontal fissures is also modelled.

The diffusing species from the degraded canister will have an effectively decreasing cross-sectional area to migrate in until it reaches the fissures. See figure 5. Assuming that all transport takes place between a circle segment $2b$ wide and an outer segment S wide at a radial distance $S - 2b$, an approximate average width for mass transport is obtained from the expression for diffusion between two concentric cylinders.

$$\frac{S - 2b}{\ln \frac{S}{2b}} = 2b \ll S \quad \frac{S}{\ln \frac{S}{2b}} \quad (19)$$

This expression can only be expected to be reasonably valid when the half distance between the fissures $S/2$ and the thickness of the buffer are nearly equal. As will be shown below the resistance in the buffer is small compared to other resistances and the inaccuracies introduced by the approximations will have negligible influence on the final results. Rigorous methods are available however and have been tested (Andersson et al 1982) [1].

Thus in the case of fissured rock only a part of the backfill length $= \delta/S$ is effectively utilized for mass transport.

The resistance in the backfill R_1 then increases by a factor S/δ as compared to the case where the rock is a "porous" material. For a porous medium $\delta = S$. Andersson et al (1982) [1] have shown that the approximations leading to equation 19 do not introduce grave errors.

The transport rate N of a species may also be expressed as an equivalent water flow rate Q_{eq} which would increase in concentration from c_1 to c_∞ .

$$Q_{eq} = N/(c_1 - c_\infty) \quad (20)$$

Equation (18) can be used to determine the release rate of a species when the concentration at the fuel surface (c_1) and in the waters far away (c_∞) is known.

Since the diffusivities of the nuclides in water do not differ appreciably from each other and are of the same order of magnitude as for other small dissolved ions, they will be transported equally fast with the same driving force (concentration difference). This is the difference between the concentration at the fuel surface c_0 and the concentration in the water far away, where it is 0. The nuclide transport can therefore be written:

$$N_i = \frac{1}{R} (c_{oi} - 0) \quad (21)$$

where N_i is the quantity of nuclide "i" that is transported at a concentration difference of $c_{oi} - 0$. The parameter R is equal to the sum of the transport resistances in clay and in fractures. R is determined with the aid of the model described above and is little dependent on nuclide type.

Equation (21) can also be interpreted in the following manner: Q_{eq} is the equivalent water flow, that arrives at the canister with the concentration 0 and leaves it with the concentration c_{i0} .

$$N_i = Q_{eq} c_{oi} \quad (22)$$

Q_{eq} has been calculated for the 5 m long canister. Table 3 gives values of Q_{eq} at different water flowrates u_0 in the rock. Table 4 shows that the resistance in the flowing water in the fissure is 10 times larger than that in the backfill and thus totally dominates the release rate.

The outward transport of uranium will determine the dissolution rate for the uranium dioxide matrix. The concentration of uranium at the surface of the pellets is determined in part by its solubility in the waters in question and in part by whether the dissolution rate is large enough to supply the water at the surface of the pellet with new uranium at the same rate as it diffuses away. Since no reliable data are available on the dissolution rate of spent fuel, it is assumed to be rapid, i.e. it is not limiting. The concentration at the surface will then be equal to the solubility of the uranium. This is determined primarily by the water's carbonate content and pH and by the water's redox potential Eh. The redox potential in surrounding water in the rock is negative, but can be positive at the surface of the pellet due to radiolysis. At positive Eh, the solubility of the uranium is determined by the concentration of carbonate ions. At the highest carbonate contents $HCO_3 = 275$ mg/l in Swedish groundwaters in crystalline rock, the solubility of the uranium = 360 mg/l. With $Q_{eq} = 0.57$ l/canister and year, and with $C_{0U} = 360$ mg/l, equation (22) gives

$$N_U^{out} = 0.57 * 360 = 205 \text{ mg U/year and canister.}$$

Each canister contains 1.4 tonnes of uranium, which means that it takes about 7 million years to dissolve the canister's uranium content. This also presumes that the production of oxidizing species via radiolysis is sufficient to oxidize the uranium at at least the same rate as it is carried away.

The nuclides contained in the uranium dioxide crystals are liberated as the crystals dissolve. They will have a concentration on the surface of the pellets that is proportional to their concentration in the pellets. Thus, nuclide "i" will have the concentration:

$$c_{oi} = c_{\text{uranium, sol}} X_i \quad (23)$$

where X_i = the fraction of nuclide "i" in the pellet and c is the solubility of uranium. The nuclide "i" is transported out to the water in the same manner as the uranium. The flow is as before $N_i = Q_{eq} c_{oi}$. If the nuclide "i" can dissolve in the water in the concentration c_{i0} , it will be transported out at the same relative rate as the uranium.

Some nuclides, e.g. Th and Pu, have solubilities that are lower than c_{i0} . They therefore precipitate on the surface of the pellets and are only transported away to a small extent. This is determined by the solubility of the individual nuclide. Thus, if the solubility $c_{i,sol}$ is smaller than c_{i0} according to (23), the outward transport of nuclide "i" will be determined by:

$$N_i = c_{i,sol} Q_{eq} \quad (24)$$

The outward transport of plutonium and thorium is greatly restricted by their low solubility.

Some cesium and iodine has been enriched at the surface of the pellets during reactor operation. This fraction of the cesium and iodine is assumed to be immediately available for leaching. Cs^{137} will decay during the life of the canister. Cs^{135} and I^{129} reach the water outside virtually unaffected by the buffer. However, since the canisters are penetrated at varying times and spread out over a very long time span, the accessible portion of these nuclides will, on the average for the repository on the whole, be released at a rate that is determined by the rate of canister penetrations. The majority of these nuclides as well will be released when the uranium dioxide dissolves. Since the dispersion in time of the disintegration of the canisters is comparable to the leach time for the uranium, the releases of these nuclides do not differ appreciably from those of the others.

Radiolysis and its consequences

The ionizing radiation can split the water into hydrogen and oxidizing compounds such as oxygen and hydrogen peroxide. The radiation can penetrate the canister wall and other solid materials and act at a distance of several decimetres from the canister. It is however, greatly attenuated on its passage through the solid materials, and its intensity on the outside of the canister is very weak (Christensen and Bjergbakke 1982) [12]. The α and β radiation has a very short range in solid materials and cannot have any effect until the water has come into direct contact with the uranium dioxide matrix. The effective range of the α radiation in water is about 0.03 mm. When the canister has been penetrated and water has got in to the surface of the pellets, α radiolysis can take place. Calculations have been carried out by Christensen and Bjergbakke (1982) [13]. They have assumed that the entire surface of the uranium dioxide pellets is covered by a layer, 0.03 mm thick, in which the energy from the α radiation is spent. In each canister, approx 4.2 l of free water could then be subjected to α radiolysis. This is greatly exaggerated, since the corrosion products from the canister material and the uranium dioxide occupy a larger volume than the original materials, so that even if this volume exists in the gap between the uranium dioxide pellets and the zircaloy cladding when the canister is intact, it is greatly reduced after a corrosion attack. Table 5 shows the radiolysis at different points in time expressed as equivalent generated quantity of hydrogen peroxide and hydrogen. These quantities of radiolysis products are probably greatly exaggerated. Radiolysis on this scale has not been observed at Oklo (Curtis and Gancarz 1983) [14], where a natural reactor has been active for

some 300 000 years. Radiolysis there has been 100-500 times lower, figured for a comparable quantity of fuel and burnup, than the theoretically maximum figures. Even low levels of iron dissolved in water catalyze the reverse reaction between hydrogen peroxide and hydrogen. This can reduce the net production of hydrogen and hydrogen peroxide by a factor of several hundred (Christensen and Bjerbakke 1982) [13]. The consequences of maximum radiolysis are explored below. However, the radiolysis is expected to be no more than 1/100th of the reported maximum values due to limitations in water supply caused by expansion of the corrosion products, hydrogen outflow and catalyzed reverse reaction.

The hydrogen peroxide produced by radiolysis is a powerful oxidant which can attack both the copper canister material and the lead and zircaloy that surround the uranium oxide pellets as well as the uranium oxide itself. In the presence of certain substances, hydrogen peroxide can spontaneously decompose to oxygen and water. The oxygen will thereby act as an oxidant in the same manner as the hydrogen peroxide. The fuel's metal oxides can also be oxidized to higher valence states. The uranium, which is tetravalent in the fuel, can be oxidized to hexavalent. Other nuclides can also be oxidized, the most important being plutonium, neptunium and technetium. Uranium, neptunium and technetium become many times more soluble in the groundwater at the higher oxidation state. When the uranium dioxide in which the other nuclides are contained is oxidized, these nuclides can be released. They can then be transported out from the repository.

Calculations have been carried out on the effect of the radiolysis (Grenthe et al. 1983) [15], where the simultaneous outward transport of radionuclides to the mobile water outside the canister has also been taken into account. The calculations are based on the assumption that chemical equilibrium always exists in a given volume of water, which is determined by the water content of the clay. The hydrogen peroxide formed according to table 5 and water with its content of carbonate and other dissolved species enters this volume. The same water flow carries away the reaction products. The water flow Q_{eq} is determined as before by the geometry of the near field.

The outward transport is determined in part by how much of the radionuclides have had time to be oxidized to the more easily soluble forms and in part by the supply of carbonates in the groundwater. The latter constitute complexing agents for uranium and neptunium. Calculations show that the copper in the canister - if it is accessible - will be preferably oxidized and prevent the fuel from being affected almost completely. Since the growth of the corrosion products makes it improbable that the copper will always be accessible for oxidation, the calculations were also carried out under the assumption that the copper does not react at all. In this case, the uranium dioxide is oxidized first. Table 6 illustrates this process and how much uranium, plutonium, neptunium and thorium has been transported out at different points in time. The total carbonate content has been set at 122 mg/l (2mmol/l) in the calculations. The large change in the quantity of Np and Pu dissolved in the time interval 960-9 960 years stems from the fact that the strongest reductant $UO_2(s)$ has been consumed after approximately 2 500 years. These

calculations show what happens for the case of initial canister damage. A canister that has been penetrated after 100 000 years and where no hydrogen peroxide leaves the system either, will have all its uranium dioxide oxidized to hexavalent after an additional 250 000 years, if the maximum possible radiolysis is assumed to prevail. If the radiolysis is limited to 1/100th of this, only about 50 kg of uranium will be oxidized in one million years. That will also be the amount of fuel dissolved in this period. The oxidation times calculated above are exaggeratedly short due to the fact that no lead, zirconium or copper is assumed to react and that the surface of the pellets is assumed to be covered with a uniform layer of water. The canister materials will be oxidized to a not insignificant extent. The oxidation of uranium dioxide will then be reduced accordingly. The corrosion products from both the fuel and the canister materials have all larger volume than the original materials. They will therefore fill the original volume that had been available for water. The porosity of the corrosion products must be small, since the canister and the surrounding clay and rock exert a powerful restraint on expansion. These effects should limit the effects of radiolysis greatly, which is supported by the conditions in the Oklo reactor where, after 1.8 billion years, only a very small fraction of the uranium dioxide has been dissolved (Curtis and Gancarz 1983) [14].

Only a very small portion of the oxidized hexavalent uranium leaves the canister, see table 6. By far most of important of the released nuclides are cesium, strontium, iodine and technetium. These have high solubility and can be transported away at the rate at which they are released from the fuel.

The radiolysis products can at most oxidize the uranium at approximately the same rate as that at which the water flow in the rock is able to transport it away from the canister. This outward transport in the equivalent flowrate Q_{eq} is about 200 kg/10⁶ years, provided that enough uranium exists in the hexavalent form, while the generation of hexavalent uranium is about 50 kg during the first million years. The release of the aforementioned nuclides is assumed in the further calculations to take place at the rate at which the uranium can be transported out.

Of the actinides, thorium and plutonium have such low solubility under the conditions that prevail in the vicinity of the fuel that they precipitate in the form of solid phases and are only transported away from the canister to a very small extent.

Some of the hydrogen peroxide and other oxidation products, such as hexavalent uranium, may leave the canister and reach the clay and the rock outside the clay. Both the clay and the rock contain bivalent iron compounds, which are readily oxidized to trivalent iron (Torstenfelt et al. 1983) [16]. When all available divalent iron in a zone has been oxidized, conditions in the water become oxidizing and many actinides become more soluble than under the reducing conditions that normally prevail in rock where there is still divalent iron. Thus, an oxidizing zone can be formed nearest the canister, which slowly expands as more oxidizing substances are transported out.

Calculations of the propagation of this so-called "redox front" have been carried out (Neretnieks 1983 [17], Neretnieks and Åslund 1983 a,b [18,19]). In these calculations, it is assumed that all produced hydrogen peroxide or an equivalent quantity of other oxidizing species penetrate out to the clay and rock. When all iron in the clay has been consumed, the hydrogen peroxide diffuses into the rock and reacts with the iron there. In fractured rock, the hydrogen peroxide is also carried away with the flowing water in the fractures, but diffuses from there out into the microfissures in the rock and oxidizes a rock volume downstream of the canister. Figure 6 illustrates this propagation.

The propagation of the front downstream of a canister can reach a maximum of some 50 metres in one million years in relatively iron poor rock (0.2% Fe (II)) (Neretnieks and Åslund 1983 a) [18] if the greatest possible radiolysis is assumed to take place and all hydrogen peroxide goes out into the rock. Swedish crystalline rock contains 1-10% divalent iron (Torstenfelt et al 1983) [16]

In practice, the front only moves a few metres. The transverse propagation of the front by diffusion has one negative consequence. Radionuclides that are readily soluble under oxidizing conditions spread out in the oxidized region. When these radionuclides come to the redox front and precipitate, the water in a much larger cross-sectional area of the rock will be saturated with the radionuclide than the very limited cross-sectional area in the vicinity of the canister. If the redox fronts from many canisters reach each other, most of the water that passes the total cross-sectional area of the repository will be saturated with the nuclides to the concentration to which they can dissolve under reducing conditions. Figure 7 illustrates the propagation of the radiolysis front sideways in a fracture and how a radionuclide that is highly soluble under oxidizing conditions precipitates to the lower solubility at the redox front and is transported further at the maximum concentration c_{sol} . Under unfavourable circumstances, all water downstream of the repository can become saturated to this concentration. Since, on the average, 150 m^2 of the repository's cross-sectional area can be ascribed to each canister, the water flow per canister can be

$$Q_{eq}^{red} = 150 U_o [m^2] [1/(m^2 \text{ year})] (= 15 \text{ l/year in central case)} \quad (25)$$

Since the radiolysis will in practice be much less than the maximum possible, the transverse propagation of the radiolysis front is far less. Calculations show that only a small portion of the water downstream of the repository will become saturated in the manner previously described. In the further calculations, however, it is assumed that all water will be saturated.

RELEASE OF NUCLIDES TO THE FAR FIELD

A radionuclide with high solubility under oxidizing conditions precipitates at the redox front. The water downstream of the redox front has a low concentration c_{sol} , but the front has been broadened and a larger water flow is transporting the nuclide.

In the case of those nuclides that are not affected by the redox front, leaching takes place with a flow of:

$$N_i = Q_{eq} c_{oi} \quad (26)$$

and

$$N_i = Q_{eq} c_{i,sol} \quad (27)$$

and the two expressions distinguish the case where the outward transport is not limited (26) from the case where the outward flow is limited by the solubility of the nuclide (27).

In the case of those nuclides that precipitate at the redox front, the flow beyond the redox front is:

$$N_i = Q_{eq}^{red} c_{i,sol}^{red} \quad (28)$$

Thus, the release to the far field can be determined by:

- 1) The outward transport rate of the uranium oxide; equation (26) (or possibly the oxidation rate),
- 2) The fact that some nuclides have low solubility and do not dissolve when the fuel (UO_2) is transported away or altered; equation (27); the release of these nuclides may be less than by mechanism 1),
- 3) Those nuclides that precipitate at the redox front - equation (28) - will be released at a lower rate than that due to mechanisms 1) or 2). For species e.g. uranium with more than one isotope the different isotopes are released in relation to their concentration in the precipitate. The sum of them making up the solubility concentration.

Trivalent and tetravalent actinides at low concentrations will probably be coprecipitated together with uranium when uranium precipitates at the redox front. This has been shown experimentally for plutonium (Grenthe et al 1983) [15]. An equally large fraction of the actinide precipitates as of the main component, uranium. The following actinides can be expected to be coprecipitated: Pu, Np, Th, Am. They will be transported to the far field in quantities reported in the righthand column (7) in table 7.

With this precipitation mechanism, the plutonium isotopes, neptunium and thorium would deliver a nuclide flow to the far field that is 30-1000 times lower than their own solubility permits.

Since this mechanism has as yet only been shown experimentally to apply for plutonium, it is not used in the safety analysis.

The release of the various nuclides is shown in figure 8 for a case where the canister has degraded after 10^5 years.

DISCUSSION AND CONCLUSION

The models discussed here are based on some rather straightforward concepts: diffusion and retardation by linear reversible sorption in the backfill, diffusion in slowly moving water in fissures and reactions of oxidizing species with reducing minerals in the rock.

Various simplifying assumptions have been used to make the mathematical modelling so simple that reasonably simple analytical and approximate solutions have been possible to derive. Most of the simplified descriptions have been compared to more rigorous calculations using numerical techniques to handle the complex geometries involved e.g. 3D modelling of the migration in the backfill, 2D advection dispersion + 1D matrix diffusion and reaction to describe the redox front migration etc. It was found that the simple analytical solutions perform surprisingly well in most cases. Even in the considerably more complex numerical solutions many important simplifying assumptions have had to be made. Furthermore the data presently available on fissure geometry, width, spacing etc. are far from exact. In many cases the poor data and the inaccuracies introduced by various assumptions seem to introduce more variability than even rather strong simplifications in the models. The simple models helped to understand many of the involved processes better than the "rigorous" solutions. The latter were however necessary to use also in order to understand the limitations and errors introduced by the various simplifications. At present parts of these models are being further developed.

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Notation

A	Cross section area	m ²
b	half fissure width	m
c	concentration	mol/m ³
c ₀	initial or boundary concentration	mol/m ³
c ₁	concentration at fuel or canister surface	mol/m ³
c ₂	concentration at clay/rock interface	mol/m ³
c ₃	concentration clay/water interface	mol/m ³
c _∞	concentration in water far away	mol/m ³
D _a	apparent diffusivity includes sorption effects	m ² /s
D _{pε_p}	effective diffusivity	m ² /s
D _w	diffusivity in water	m ² /s
D ₁	effective diffusivity of backfill clay surrounding the canister	m ² /s
D ₂	effective diffusivity of clay injected into fissures	m ² /s
H	equation 11 z ₀ (λ /D _a) ^{1/2}	--
K _p	hydraulic conductivity	m/s
L	canister length	m
m	amount of nuclide	mol
m _U	amount of uranium	mol
m ₀	amount initially (at start of leaching)	mol
N	flowrate of nuclide	mol/s
N _U	flowrate of uranium	mol/s
Q _{eq}	equivalent flowrate to carry dissolved species in a concentration equal to that at the fuel surface	m ³ /s(1/year)
r	radial distance	m
r ₁	radius of canister (or fuel)	m
r ₂	" repository hole	m
r ₃	" clay (in fissures) interface	m
R	mass transfer resistance total	s/m ³
R ₁	" of clay backfill	s/m ³
R ₂	" of clay in fissure	s/m ³
R ₃	" of flowing water in fissure or in porous rock	s/m ³
S	fissure spacing	m
t	time	s
t _{res}	residence time of water as it flows around (past) canister	s
T _{1/2}	halflife of nuclide	s
z	distance	m
z ₀	thickness of barrier	m

Greek letters

δ	equivalent width for diffusion in clay backfill	m
ϵ_p	porosity of clay backfill	-
ϵ_R	flow porosity of rock $\epsilon_R = 2b/S$	-
λ	decay constant	s^{-1}
τ	λt dimensionless time	-

Subscripts

i	nuclide "i"
sol	at solubility

Compound	$D_a \cdot 10^{12}$ m^2/s
I^-	9
TcO_4^-	53
Cs^+	8
Sr^{2+}	25
Ra^{2+}	25
Pa	1
Th ¹⁾	10^{-2}
U ¹⁾	1
Np ¹⁾	0.4
Pu ¹⁾	$3 \cdot 10^{-2}$
Am ¹⁾	$1.5 \cdot 10^{-2}$

1) The dissolved species are probably carbonate, hydroxyl and mixed complexes, see Allard (Asilomar Sept 10-15, 1981) [21].

Table 1. Upper limits of apparent diffusivity values of some nuclides for breakthrough calculations.

Nuclide	$T_{1/2}$	$D_a \cdot 10^{12}$	H	N/N_0 max	c/c_{sol} max
I-129	$2 \cdot 10^7$	9	$4.15 \cdot 10^3$	0.97	1
Tc-99	$2 \cdot 10^5$	53	$1.70 \cdot 10^{-2}$	0.92	0.99
Cs-137	30	8	3.59	0.010	0.027
Sr-90	28	25	2.10	0.053	0.12
Ra-226	$1.6 \cdot 10^3$	25	0.278	0.54	0.75
Th-229	$7.3 \cdot 10^3$	10^{-2}	6.50	$2.9 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$
Pa-231	$3.6 \cdot 10^4$	1	0.293	0.53	0.75
U-234	$2.5 \cdot 10^5$	1	0.111	0.73	0.89
U-235	$7.1 \cdot 10^8$	1	$2.09 \cdot 10^{-3}$	0.98	1
U-238	$4.4 \cdot 10^9$	1	$8.38 \cdot 10^{-4}$	1	1
Np-237	$2 \cdot 10^6$	0.4	$6.22 \cdot 10^{-2}$	0.81	0.94
Pu-239	$2.4 \cdot 10^4$	$3 \cdot 10^{-2}$	2.07	0.054	0.13
Pu-240	$6.6 \cdot 10^3$	$3 \cdot 10^{-2}$	3.95	$6.6 \cdot 10^{-3}$	0.019
Am-241	458	$1.5 \cdot 10^{-2}$	21.2	$< 10^{-9}$	$< 10^{-9}$
Am-243	$7.4 \cdot 10^3$	$1.5 \cdot 10^{-2}$	5.28	$1.6 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$

Table 2. Half life $T_{1/2}$, Apparent diffusivity and parameter H in a buffer of thickness is 0.375 m. Maximum N/N_0 for soluble species and maximum $c/c_{solubility}$ for solubility limited species.

U_0 1/(m ² year)	Q_{eq} 1/year	
0.01	0.19	
0.03	0.32	
0.1	0.57	central case
0.3	0.94	
1	1.57	
3	2.41	

Table 3. Q_{eq} at different water flows u_0 in the rock for a 5 m long canister.

u_0 1/m ² y	2b mm	S m	R1/R1 -	R2/R1 -	R3/R1 -	Q_{eq} 1/y
0.1	0.1	1	1	0	10	0.57

Table 4. Determined equivalent water flowrate Q_{eq} for leaching of spent fuel and relative resistances to mass transfer of the various barriers. R_1/R_1 , R_2/R_1 and R_3/R_1 are relative resistances in backfill around the canister.

Time after discharge from reactor (years)	H ₂ O ₂ and H ₂ production (mol/y)	H ₂ O ₂ and H ₂ produced in the time interval (mol)
100	4.6	
300	3.2	780
600	1.8	750
1 000	1.31	620
10 ⁴	0.34	7 400
10 ⁵	0.025	16 200
10 ⁶	0.009	15 800
Total produced during 10 ⁶ years		41 550

Table 5. Theoretical maximum hydrogen and hydrogen peroxide production from radiolysis in 1.4 tonnes of uranium. The radiation is spent in 4.2 l of water spread out in a 0.03 mm layer on the uranium dioxide surface.

Years after deposition	Dissolved quantity, g, in the time interval		
	U	Np	Pu
0-1	0.12	$2.4 \cdot 10^{-11}$	10^{-12}
1-260	24	$7.5 \cdot 10^{-9}$	$2.4 \cdot 10^{-10}$
260-960	95	$2.1 \cdot 10^{-8}$	$7.2 \cdot 10^{-10}$
960-9 960	286	2 000	10^{-3}
9 960- 10^5	10^4	2 500	0.012
10^5 - 10^6	$1.1 \cdot 10^5$	-	0.024

Table 6. Dissolution of nuclides from a canister under the influence of radiolysis as per table 5, $Q_{eq} = 1$ l/year and the canister materials are inert. The total carbonate content is 2 mM.

Column 1 2	3	4	5	6	7	
Nuclide	Quantity per canister 10^5 -year-old fuel	Congruent dissolution (6.8×10^6 years dissolution (time))	Solubility limit under oxidizing conditions	Solubility limit at redox front	To far field. Min. of col. 3, 4, 5 as activity	To far field. co-precipitation with uranium
	g Bq	g/y	g/y	g/y	Bq/y	Bq/y
^{238}U	1.4×10^6 1.66×10^{10}	0.21	0.21	<u>1.5×10^{-4}</u>	1.8	=
^{234}U	a) 9.8×10^{10}				10.5	=
^{235}U	a) 1.24×10^9				0.13	=
^{236}U	a) 1.92×10^{10}				2.1	=
^{239}Pu	386 8.81×10^{11}	5.7×10^{-5}	<u>1.41×10^{-6}</u> b)		3 200	94
^{242}Pu	862 1.24×10^{11}	1.3×10^{-4}	<u>3.15×10^{-6}</u> b)		460	4.9
^{237}Np	2 960 7.77×10^{10}	4.3×10^{-4}		1.2×10^{-4}	3 100	3.3
^{230}Th	86 6.22×10^{10}	1.3×10^{-5}	<u>2.3×10^{-7}</u>		170	1.8
^{241}Am	4.19×10^{-5} 5.18×10^6	<u>6.2×10^{-12}</u>			0.76	5.6×10^{-4}
^{243}Am	1.91×10^{-2} 1.45×10^8	<u>2.9×10^{-9}</u>			21	0.016
^{99}Tc	895 5.70×10^{11}	1.3×10^{-4}		3×10^{-6}	1 900	=
^{129}I	c) 1.86×10^9				270	=
^{135}Cs	c) 1.97×10^{10}				2 900	=

Table 7. Releases of certain radionuclides to the far field. Based on 1.4 tonnes uranium, $Q_{eq} = 0.57$ l/y, $Q_{eq}^{red} = 15$ l/y. Underlined values are limiting.

- a) Follows uranium-238
b) Sum of Pu-239 and Pu-242 is $4.56 \cdot 10^{-6}$ g/y
c) No solubility limit
= Same as in column 6

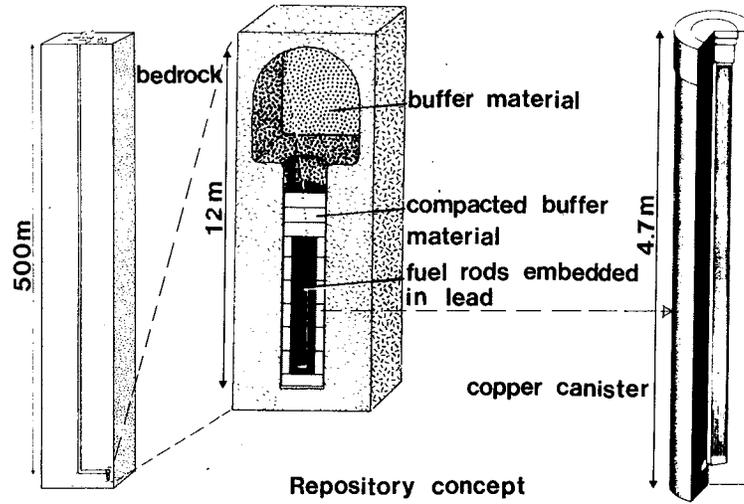


Figure 1 Repository as proposed in the Swedish Nuclear Fuel Safety study (KBS 1983). /20/

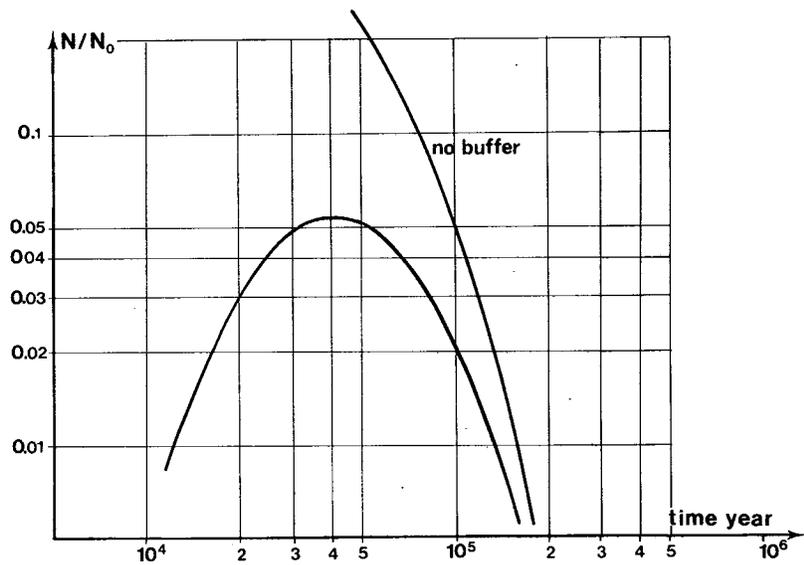


Figure 2 Breakthrough curve for Pu²³⁹. $D_a = 3 \cdot 10^{-14} \text{ m}^2/\text{s}$, $z_0 = 0.375 \text{ m}$.

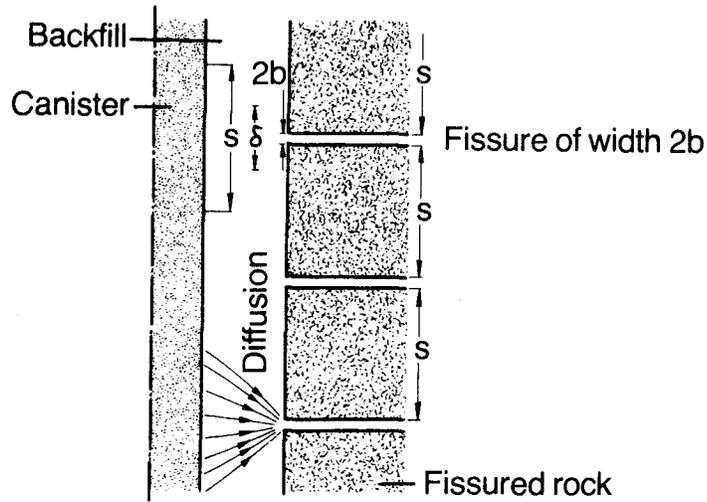


Figure 5 Shows a crosssection of the hole with a canister.

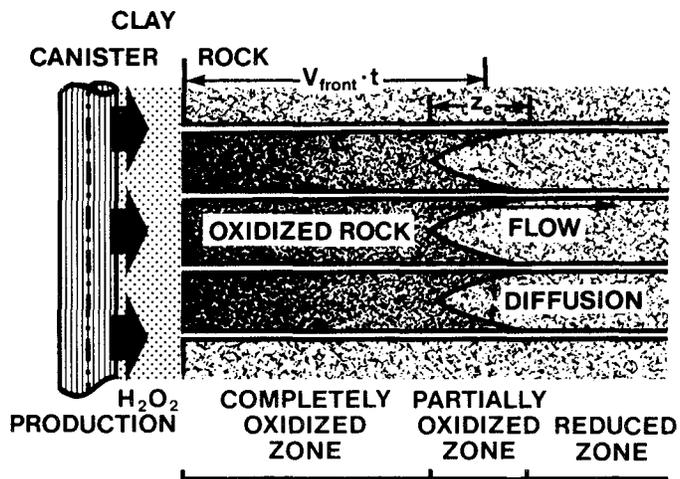


Figure 6 Propagation of the radiolysis front downstream of a canister. The hydrogen peroxide and other oxidizing substances move with the water in the fractures, but also diffuse from the fractures into the rock, where the bivalent iron is oxidized to trivalent iron.

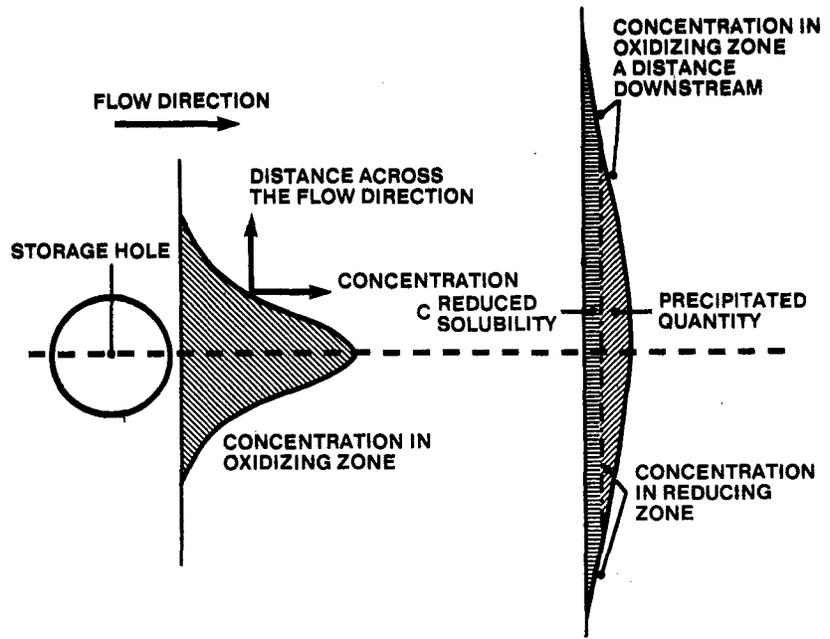


Figure 7 The concentration of a nuclide in the water in a fracture plane. A radionuclide with high solubility under oxidizing conditions precipitates at the redox front. The water downstream of the redox front has a low concentration c_{sol}^{red} , but the front has broadened and a larger water flow transports the nuclide.

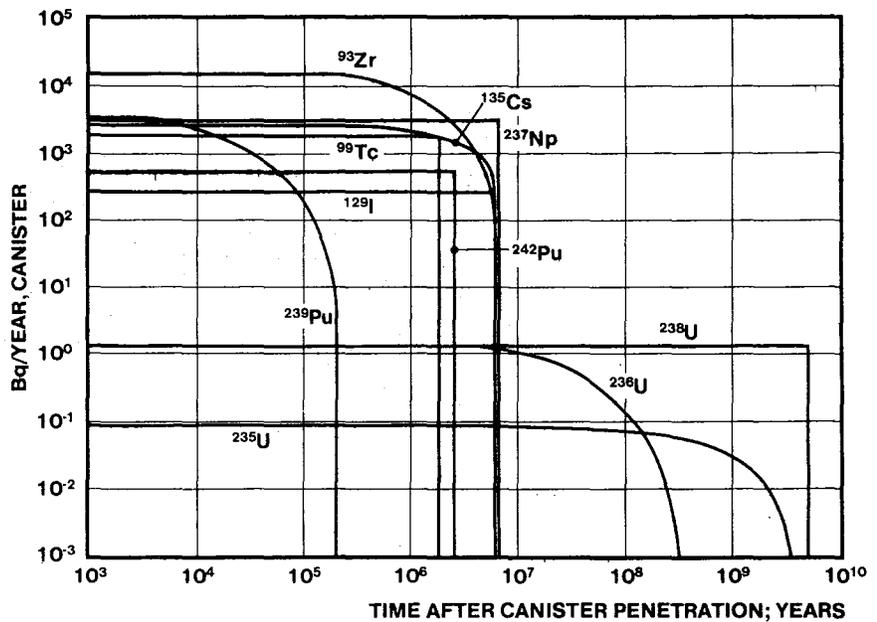


Figure 8 Release of radionuclides from the near field to the flowing water in the far field.

SOURCE-TERM CONSIDERATIONS FOR A POTENTIAL RADIOACTIVE-WASTE
REPOSITORY LOCATED IN UNSATURATED TUFF

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ABSTRACT

The Nevada Nuclear Waste Storage Investigations project is studying the feasibility of locating a repository for high level radioactive waste in the unsaturated tuffs at Yucca Mountain near the southwest part of the Nevada Test Site. An important part of these studies is the formulation of physically appropriate source terms for use in mathematical models used to assess the performance of the potential repository. Performance assessments conducted to date have used a preliminary source term based on simple assumptions and currently available data; this source term is described, along with the results of a sensitivity study that show the important parameters affecting the time-dependent radionuclide release rates.

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INTRODUCTION

The Nevada Nuclear Waste Storage Investigations (NNWSI) project is studying the feasibility of locating a repository for high-level radioactive waste on or near the Nevada Test Site (NTS) in southern Nevada. Currently, the project is evaluating a site at Yucca Mountain near the southwest part of the NTS. The host rock in which the waste materials would be placed is a densely welded, fractured tuff located entirely in the unsaturated zone. Recent hydrological modeling studies (Sinnock et al., 1984) suggest that the flux of water in the host rock is very low and is confined to the rock matrix. Water flux values ranging from 0.001 to 0.1 mm/yr are expected and are consistent with laboratory measurements of unsaturated permeabilities (Peters et al., 1984). The unsaturated, low-water flow condition is a distinguishing characteristic of this particular site.

Sandia National Laboratories (SNL) is assessing the postclosure performance of the waste-isolation system at Yucca Mountain. In order to determine compliance with the various isolation and containment regulations that will be imposed on any geologic waste-disposal system by the U.S. Nuclear Regulatory Commission (NRC), the capability must exist to analyze the performance of the various system components at several different levels of detail. For example, an analysis of the time to failure of a waste container must be performed using space and time scales that are smaller than the ones used in the determination of groundwater travel time to the accessible environment. To develop the needed capability, the performance assessment task at SNL is divided into two efforts: 1) an assessment of water flow and radionuclide transport through the site; and 2) an assessment of radionuclide release from the total system. The former involves two- and possibly three-dimensional analyses of the hydrologic and transport characteristics of the near- and far-field geologic and geochemical settings. The latter involves simpler, largely one-dimensional studies of the total system; this less-detailed capability is required because of the expected large number of statistical sensitivity/uncertainty studies that must be performed to demonstrate system performance against long-term isolation standards.

In order to include radionuclide transport in either the site or the total-system assessments, descriptions of the rate of release of radionuclides as a function of time to the near-field geologic setting are required. These descriptions, or source terms, may be either phenomenological or empirical and will not, in general, be the same for both assessments. The radionuclide release from the waste package and the transport characteristics of the host rock surrounding the waste package must be determined to identify the quantity of rock (and thus the boundary) that must be accounted for in each source-term expression. For example, if the physical model in the total-system assessments includes only isothermal, single-phase flow, its source term must account for the transport processes occurring in the thermally and mechanically disturbed host rock surrounding the waste package. On the other hand, the multidimensional site assessments may include non-isothermal effects, and the source term in this case could then be the time-dependent release from the waste package.

A description of radionuclide release from the waste package is a crucial ingredient of any source term because, as mentioned in the preceding paragraph, this description must be included in the source terms used in

both the site and total-system assessments and is necessary for determining regulatory compliance with releases at the boundary of the engineered-barrier system. The Lawrence Livermore National Laboratory (LLNL) is designing the waste package and determining its detailed preclosure and postclosure performance, but it will be several years before the laboratory has collected sufficient data to allow these detailed analyses to be completed (Oversby, 1983; McCright et al., 1983). Because several current NNWSI activities require system performance assessments, (e.g., environmental assessments, data priority studies, site-characterization plans), an effort was undertaken at SNL to develop a source term that uses available data. A brief description of the analysis used in the development of this preliminary source term is included in the next section. A more detailed description of this procedure is contained in Braithwaite (1985). The third section gives the results of a sensitivity study that shows the effect the independent parameters included in this term have on the time-dependent release of radionuclides.

CURRENT NNWSI SOURCE TERM

APPROACH AND ASSUMPTIONS

In this section, the approach and assumptions employed in developing the preliminary source-term model currently used in the total-system-assessment codes are given. Principally, the development involved the identification of three items: the appropriate waste form(s), the definition of the waste-form environment, and the appropriate description of the process controlling radionuclide release rates. A brief justification for each of these items is given separately below. It is very important to note that the source term described in this paper was developed for use in the system codes from information available in the spring of 1984. The level of detail is considered to be consistent with the detail of the system transport code (Sinnock et al., 1984) and, as such, does not represent the current state of knowledge. For a current status of waste package studies, see the paper by V. Oversby and D. McCright (1984) in these proceedings.

Waste form

According to current plans, the first commercial radioactive-waste repository will receive spent fuel; it may also receive a small quantity of either reprocessed defense waste or commercial waste (or both). The source term described in this paper considers only spent fuel.

Radionuclide transport and water availability

The hydrological information currently available provides estimates of the quantity and qualitative path of water flowing into and out of the repository horizon, but does not specify the water movement through the waste package or through the thermally and mechanically disturbed host rock surrounding the emplacement borehole. The characterization of the latter hydrological processes is the objective of several ongoing studies at SNL and LLNL.

Without detailed near-field hydrological information, there can be no analysis of the release-rate-reducing effect of the transport of radionuclides in solution from the waste form to the edge of the borehole

wall and then through the host rock to the appropriate boundary of the source term. Therefore, it was assumed in this source term that the transport of dissolved species in solution from the waste form to the borehole wall is fast and that the transport characteristics of the disturbed rock surrounding the waste package are equivalent to those for undisturbed rock.

To bound the possible saturation states of water within the waste package, both saturated (inundated) and partially saturated conditions were considered. Because the conductivity of the formation would be high under saturated conditions and because the natural state of the formation is unsaturated, conditions that would allow the waste package to become inundated would not be expected. However, before the waste canister fails in general, it is conceivable that a hole could develop in the top of it that would allow the inside of the canister to fill with water. Another reason for including the saturated environment was to make possible an assumption that the entire spent-fuel surface had become wetted. Since dissolution rates can be dependent on the quantity of wetted surface area, this latter assumption allows any surface-area effect to be bounded.

The rate of water influx to the waste package was calculated by assuming that all downward-percolating water intersecting the horizontal cross-section of the emplacement borehole would enter the borehole. Results of studies of the effects of backfilling drifts on water-flow patterns support the conclusion that this calculational procedure leads to conservatively high rates of water influx (Fernandez and Freshley, 1984). Further, all water flowing into the borehole was assumed to contact bare spent fuel. Thus, the inhibiting influence of air gaps (up to 70% void volume can exist within the borehole), claddings, or other waste-package components on water contact with the spent fuel was not included (except, as will be noted below, to delay the onset of dissolution until lower temperatures exist).

Environment

The groundwater composition used in the solubility limit and applicable leach-rate calculations was taken from water produced by a well (denoted J-13) located on Jackass Flats near Yucca Mountain. This composition is given by Kerrisk (1984) and is currently used to represent the vadose water within Yucca Mountain. Additionally, the groundwater was assumed to maintain equilibration with air at a partial pressure of 0.2 atm of oxygen; this condition produces an oxidizing electrochemical potential in the pH = 7 groundwater of approximately 700 mV.

The temperature of the spent fuel was always 25°C. This is a reasonable assumption because water should not contact the spent fuel until significant cooling has occurred and the activation energy for the spent-fuel leach rate is small (Braithwaite, 1985; Thomas, 1983; Johnson et al., 1981).

Radionuclide Release Mechanism

Congruent dissolution of the uranium-dioxide matrix is the mechanism used in this model to control the availability of radionuclides to the leaching groundwater. With the assumed uniform distribution of radionuclides throughout the spent fuel, this mechanism restricts their fractional rate of dissolution to that for the uranium-dioxide matrix.

Because of this restriction, this model is not capable of describing releases for species that are not contained within the matrix, such as portions of cesium and iodine, which can migrate to the spent-fuel gap, or carbon, which can exist outside the spent fuel. A few reasons why this approach was deemed reasonable are given by Braithwaite (1985).

IDENTIFICATION OF A DESCRIPTION OF THE RATE-CONTROLLING PROCESS

The dissolution or leach rate of the uranium-dioxide matrix is, in general, a function of time, the aqueous environment, and the chemical and physical properties of the spent fuel. Leach rates are typically determined experimentally in aqueous solution replenished often enough to ensure that any rate-retarding effects of soluble product buildup do not occur. However, if the leach rate is fast and little water is available, the concentration of the solubilized product can actually increase to the solubility limit. At this point, no further net dissolution will occur. Thus, saturation of the available water yields an upper bound on the dissolution rate.

The low-water-flux, unsaturated conditions expected at Yucca Mountain appear suitable to allow either solubility limits or leach rates to control the dissolution rate. That is, if water contacts the waste for relatively long times (e.g., in a water-filled container with breached areas only in the top), solubility limits coupled with water availability could control the rate. On the other hand, if the water-contact time is small (e.g., if a thin film or droplets flow over individual spent-fuel rods under partially saturated conditions), leach rates may control the dissolution. A separate analysis of potential water-flow patterns and associated contact times under both the expected partially saturated conditions and the unexpected short-term saturated conditions was performed. A description of this analysis is given by Braithwaite (1985). Part of this analysis showed that, for partially saturated conditions, water flow over vertically emplaced spent fuel should occur in discrete droplets with the surface-area coverage at any time being given by the following equation:

$$SA = C \cdot F \cdot A , \quad (1)$$

where

SA = surface area covered per waste package (m^2/pkg),

F = flux of percolating water ($m^3/m^2/yr$),

A = effective horizontal intercept area of groundwater by the package (m^2/pkg).

C = factor accounting for the residence time of the droplets and their ratio of contact area to volume ratio ($2 \times 10^{-4} yr \cdot m^2/m^3$).

The congruent leaching mechanism allows the analysis of the rate-controlling description process to focus on the dissolution rate of the uranium dioxide matrix. Because the half life of uranium is 4.5×10^9 years, radioactive decay will not significantly affect the quantity of uranium available for leaching over reasonable time periods. Therefore, the time before dissolution can commence (containment time) is not an important rate-determining effect. For convenience in this analysis, the rate of dissolution of the uranium matrix is defined as the mass fraction of uranium dissolved per year. This definition is related to the curie release-rate

expression used by the NRC when the total available mass is taken to be the inventory in the waste package 1000 years after closure. The mass-fraction-based release rate for the uranium matrix is given by equations (2) through (4) below.

For the dissolution rate controlled by the solubility limit and water availability:

$$R_m = F \cdot A \cdot S_m / M_m(1000) , \quad (2)$$

where

- R_m = fractional release rate of the uranium-dioxide matrix based on the 1000-year inventory (1/year),
- S_m = solubility limit of the uranium-dioxide matrix (kg/m^3)
- $M_m(1000)$ = mass of uranium remaining in the waste package at 1000 years after closure (kg).

Equation (2) is applicable to both saturated and partially saturated conditions.

For the dissolution rate controlled by the leach rate:

$$R_m = LR \cdot SA / M_m(1000) , \quad (3)$$

where

- LR = leach rate of the uranium matrix ($\text{kg}/\text{m}^2/\text{yr}$).

Equation (3) is directly applicable to the constant wetted surface area or saturated conditions under which the leach-rate measurements are made; however, equation (1) can be substituted into equation (3) to give an expression defining release rate under the partially saturated conditions in which exposed surface area may not be constant:

$$R_m = C \cdot LR \cdot A \cdot F / M_m(1000) . \quad (4)$$

To determine which of these two descriptions limits the rate of dissolution under the assumed environments, site-specific information is required concerning the leach rate and solubility limit of uranium dioxide. An initial uranium leach rate of $0.4 \text{ kg}/\text{m}^2/\text{yr}$ and a steady-state, long-term rate of $7 \times 10^{-4} \text{ kg}/\text{m}^2/\text{yr}$ were selected as being the most representative results of those available in the literature for the expected environment (Braithwaite, 1985). Solubility limits for most of the radionuclides were calculated by Kerrisk (1984) using the geochemical code EQ3/6. For congruent leaching, only the total solubility limit for uranium is important ($0.05 \text{ kg}/\text{m}^3$).

Using equations (2), (3) and (4), one can determine the uranium dissolution rate for the two controlling processes as a function of the water flux. The results are plotted in Figure 1 for the saturated condition and in Figure 2 for the partially saturated condition. The two figures can be used to identify the process controlling the dissolution rate for both conditions. It is important to remember that an average water flux greater than $1 \text{ mm}/\text{yr}$ is unlikely at the Yucca Mountain repository horizon; dissolution rates at a water flux up to $1000 \text{ mm}/\text{yr}$ were included in this study to allow the dissolution rate to be shown under partially saturated conditions and steady-state kinetic control. The justification for the

selection of each of the rate-controlling descriptions is given in the following paragraphs.

Saturated conditions: As shown in Figure 1, dissolution based on the solubility limit is lower than, and therefore constrains the fractional rates until unrealistically high water fluxes are reached. At this point, the steady-state leach rate, which is not a function of the flux under these inundated conditions, begins to dominate. Therefore, if the canister interior or emplacement borehole becomes inundated, the water availability, coupled with the uranium solubility limit, should control the dissolution rate of spent fuel.

Partially saturated conditions: As shown in Figure 2, leach kinetics should control the rate under partially saturated conditions. This is probably the case because of the short contact times between water droplets and spent fuel. While one expects the steady-state leach rates to dominate over the long term, the initial leach rate was initially selected as a conservative approach (by over two orders of magnitude) because the travel time for the droplets flowing over a spent-fuel rod (less than 10 seconds) probably represents the minimum possible value. Surface contamination, rod-to-rod contact, and the presence of discrete joints between individual pellets could increase droplet contact time and therefore the rate of dissolution.

If the actual leach rate were another 2.5 orders of magnitude higher than the assumed controlling initial leach rate, then solubility limits and water availability would constrain the dissolution process even under partially saturated conditions. With the uncertainty in the leach-rate data, water flow patterns within the waste package and water contact time, the choice of the solubility limit as a rate-controlling process is currently justified. Because the quantity of water flowing through the waste package does not depend on whether the local environment is fully or partially saturated, the dissolution rate based on solubility limits are identical for both saturated and unsaturated conditions.

SOURCE-TERM MODEL

The assumptions and analyses detailed above lead to a formulation of a preliminary source-term model. Three principal assumptions are inherent in this model: 1) the fractional rate of release of radionuclides from spent fuel is equivalent to the fractional rate of leaching of the uranium dioxide matrix; 2) the rate of dissolution of the uranium matrix is controlled by the solubility limit of the uranium coupled with the availability of water; and 3) the transport of dissolved species to the borehole wall rock is instantaneous, and the transport characteristics of the thermally and mechanically disturbed rock around the waste package are similar to undisturbed rock. It must be remembered that the congruent leaching assumption (#1) is not applicable to the entire inventory of several radionuclides, including cesium, iodine, and carbon (Oversby and McCright, 1984).

The preliminary source-term model can be described by Equation (5):

$$R_i(t) = F \cdot A \cdot \Pr\{T_c \leq t\} \cdot (\text{minimum of } S_m/M_m, S_i/M_i) \quad (5)$$

where

- $R_i(t)$ = The expected fractional rate (1/year) of release of the i^{th} species based, in general, on the mass inventory at the time of release (i.e., M_m or M_i could be time-dependent). For determining regulatory compliance, M_m or M_i is replaced with the mass inventory at 1000 years after closure.
 F = Specific discharge of groundwater (percolation flux) in the vicinity of the waste package ($\text{m}^3/\text{m}^2/\text{yr}$).
 A = Effective area of intercept of groundwater by package (m^2).
 S_m = Solubility limit of the uranium-dioxide matrix (kg/m^3).
 S_i = Solubility limit of the i^{th} waste element (kg/m^3).
 T_C = Time of container breach by water; i.e., the earliest time at which water can freely enter and leave the interior of the container (years); a random variable.
 M_m = Inventory (mass) of the uranium-dioxide matrix contained in the waste package at the time of dissolution, or at 1000 years if the NRC criterion is being determined (kg).
 M_i = Inventory (mass) of the i^{th} waste element contained in the waste package at the time of dissolution, or at 1000 years if the NRC criterion is being determined (kg).
 $\text{Pr}\{T_C \leq t\}$ = The cumulative probability distribution function of T_C .
 t = Time (yr) after closure of repository,

The minimum of the ratio of solubility limit to mass for either the matrix or the individual radionuclide is used in equation (5) to account for the precipitation of any species whose solubility limit would be exceeded under the assumption of congruent leaching.

SENSITIVITY OF RELEASE RATE TO SOURCE-TERM PARAMETERS

For purposes of comparing the release rate to the NRC regulatory criterion, the mass inventory, M , must be set at its 1000-year value in equation 6. By ignoring mass loss by dissolution up to 1000 years and assuming that the i^{th} waste element is a single-member decay chain, the following equation is obtained:

$$M_i(1000) = M_i(0) \exp [-693/T_{1/2}(i)] \quad (6)$$

where,

- $T_{1/2}(i)$ = the half life of the i^{th} species (years),
 $M_i(0)$ = the mass inventory at closure of the i^{th} species (kg).

The combination of equations (6) and (7) will be called the "regulatory release rate."

The cumulative probability distribution of container breach times is unknown; we assume it can be fit with a two-parameter distribution with arbitrary variance, σ^2 , and mean $T_C = a/r$, where a is the container wall thickness (m), and r is the mean corrosion rate (m/yr). By defining the distribution of breach times in this way, the effects of spent-fuel cladding on delaying or limiting the dissolution are explicitly ignored. Therefore, T_C is not a measure of the containment time specified in the NRC regulatory criterion.

The relative importance of the eight parameters appearing in the expressions for the release rate, equations (5) and (6), can be assessed by calculating and comparing the "normalized sensitivity coefficients" of the parameters relative to the release rate. The meaning of a normalized sensitivity coefficient is as follows: if a quantity R is a function of N parameters p_1, p_2, \dots, p_n , the normalized sensitivity coefficient, C_i , of R with respect to the i^{th} parameter p_i is defined by

$$C_i = (p_i/R)(\partial R/\partial p_i). \quad (7)$$

Evidently, C_i is a measure of the effect of a small, relative change in parameter p_i on relative changes induced in the dependent quantity, R. For example, a $C_i = -1$ means that a 10% increase in p_i would cause a 10% decrease in R if all other parameters remained constant.

The normalized sensitivity coefficients of the eight parameters appearing in equations (5) and (6) have been calculated or estimated and are listed in Table I. The C_i 's for all parameters except container-wall thickness, mean corrosion rate, and variance in container-breach time are exact and apply for arbitrary values of time and the eight parameters. The C_i 's for the three parameters, a , r , and σ , that appear in the cumulative probability distribution of container-breach time are order-of-magnitude estimates and apply at times near the mean character breach time, T_c ; these last three sensitivity coefficients were calculated using a piecewise-linear approximation to a general two-parameter distribution that was devised to simplify the calculations. Because all cumulative probability distributions are similar, differing only in their shape parameters, it is likely that sensitivity coefficients derived from a physically motivated, continuous distribution (such as the inverse Gaussian distribution) would differ from the results shown in Table I only in the magnitude of the numerical constants (1/2 and 3 in the present case) that multiply the mean and variance; in most cases, these numerical constants are numbers between 1/2 and 10, and the qualitative features of the results in Table I would not change.

The sensitivity coefficients listed in Table I show that water flux, intercept area, solubility, and the square root of the variance (or standard deviation) in container-breach time are equally important in determining the release rate; the magnitudes of the sensitivity coefficients for these parameters are all 1, a value that can be taken as establishing a reference level for "importance." Thus, radionuclide half life is relatively important only for those radionuclide species with half-lives less than 693 years: in practical terms, variations in magnitude among the regulatory release rates for short-lived species, such as Cesium-137, are likely to be caused as much by differences among species half-lives as by differences among the species solubilities. On the other hand, variations in magnitude among the regulatory release rates for long-lived species such as uranium-235 are almost certainly caused by differences among the species solubilities if other parameters remain unchanged.

Table I
Normalized Sensitivity Coefficients of Parameters in the
Regulatory Release Rate Expression

Parameter Name	Sensitivity Coefficient	Effect of 10% Change on release rate
Water flux Intercept area Solubility limit	1	10%
Initial mass Standard deviation for T	-1	-10%
Radionuclide half-life	$-693/T_{1/2}(i)$	-230% (cesium) -1% (americium) ~0% (uranium)
Container-wall thickness	$\sim -\bar{T}_c/2(3\sigma^2)^{1/2}$	-9% ($\bar{T}_c/\sigma = 3$) -87% ($\bar{T}_c/\sigma = 30$)
Mean corrosion rate	negative of wall thickness term	negative of wall thickness term

Container wall thickness and the mean corrosion rate are equal in importance. However, these two quantities are important relative to water flux, intercept area, and solubility only if the ratio \bar{T}_c/σ exceeds a number of the order of 10. If σ is taken as a measure of uncertainty in the rate at which uniform corrosion attacks the material of the waste canister, existing knowledge of that rate suggests that \bar{T}_c/σ is a number of the order of unity. For example, the lifetime against uniform corrosion of 1 cm of 304L stainless steel in the environment of the Yucca Mountain repository is estimated to lie between 3000 and 30,000 years with an expected value of about 10,000 years (McCright et al., 1983). Assuming that the 27,000-year spread represents 4 standard deviations, the value of \bar{T}_c/σ would equal 1.5, and the sensitivity coefficients for container-wall thickness and mean corrosion rate would be of the order of 1 or less. This example, which is based on the limited information available, suggests that container-wall thickness and mean corrosion rate may be slightly less important in determining the time-dependent release rate than water flux, intercept area, and solubilities. Reduction of the uncertainty in the types and rates of mechanisms that degrade waste-canister materials would be necessary before a different conclusion could be drawn.

SUMMARY

1. Source terms, or descriptions of the rate of radionuclide release to appropriate geologic settings, are required in total-system performance assessments, detailed site-performance assessments, and the determination of compliance with the criterion governing the release rate from the engineered barrier system.
2. A source term was formulated for use in the current total-system performance-assessment code that was based on information available as of the beginning of 1984. This term assumes that radionuclide release is controlled by congruent leaching and that the rate of uranium-dioxide dissolution is constrained by the uranium solubility limit coupled with the availability of water.
3. A study of the sensitivity of the regulatory release rate to parameters in the preliminary source term was performed. Results of the study suggest that water flux, intercept area, waste-element solubility, and the standard deviation in container-breach time have equal normalized sensitivity coefficients. Sensitivity coefficients for the mean corrosion rate and container wall thickness are equal, but are likely to be smaller in magnitude than the coefficients for water flux, etc.; this conclusion is based on limited current information.

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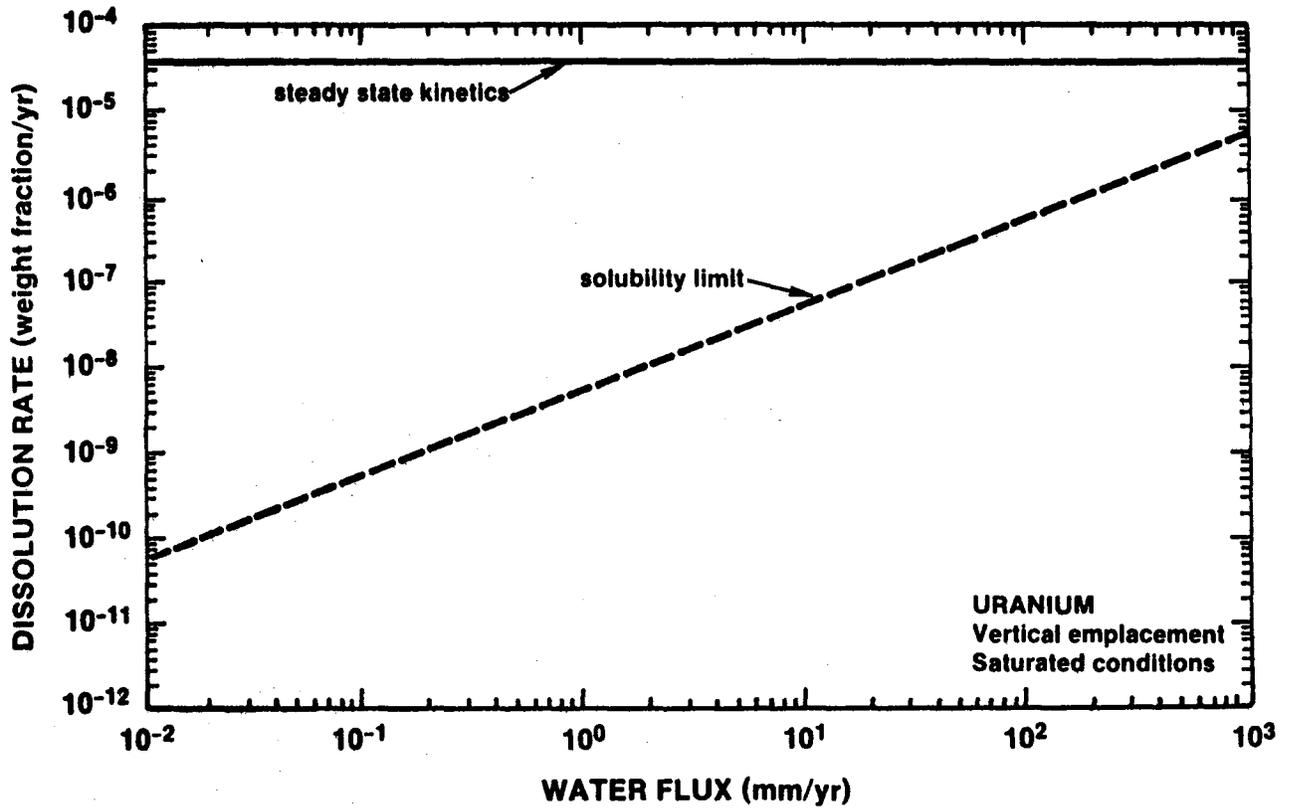


Figure 1. The effect of water flux on the dissolution rate of uranium dioxide under saturated conditions.

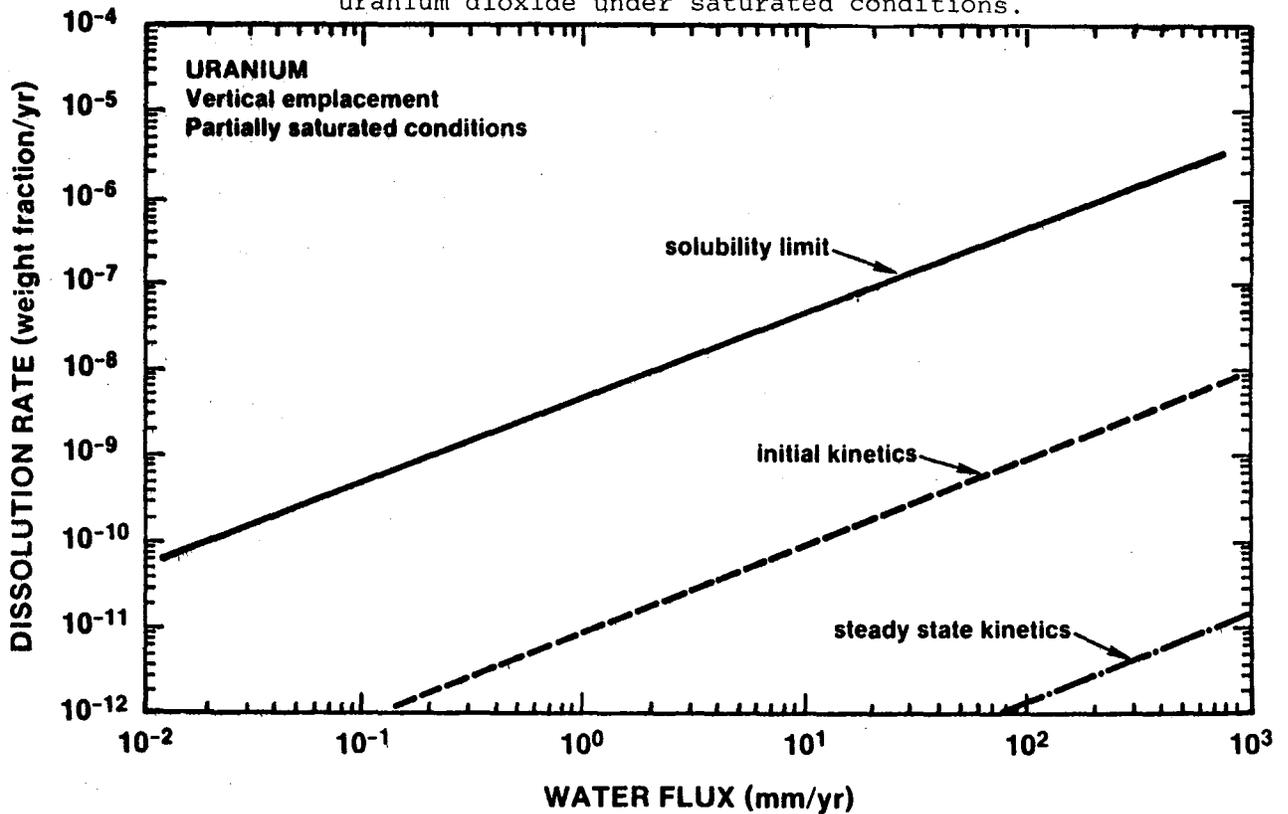


Figure 2. The effect of water flux on the dissolution rate of uranium dioxide under partially saturated conditions.

DATA REQUIREMENTS BASED ON PERFORMANCE ASSESSMENT ANALYSES OF
CONCEPTUAL WASTE PACKAGES IN SALT REPOSITORIES

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ABSTRACT

Performance assessment analyses of conceptual waste packages in salt repositories were conducted as a part of statutory environmental assessments (EAs) for seven potential salt sites. These analyses included simulation of heat transfer, thermal gradient-induced brine migration, waste package corrosion, and dissolution of radionuclides from the waste and provided estimates of source terms for radionuclide migration based on available data. However, essentially none of the available data were site specific; these analyses identify explicitly those parameters for which site specific data are required to refine the estimates given in the EAs. These parameters are (1) thermal conductivity and diffusivity of host rock, (2) brine content of host rock, (3) composition and location of water bearing clay minerals in the host rock, (4) threshold thermal gradient for brine migration, (5) corrosion rates of overpack materials in site specific brines as a function of temperature and radiation level, (6) dissolution behavior of waste forms in site specific brines as a function of temperature and radiation level, (7) solute species and solubility levels as a function of temperature for various radionuclides in site specific brines, and (8) brine "diffusion" coefficients in salt. In addition, simulation models that are being used must be validated insofar as possible with tests in Exploratory Shaft Facilities. This paper will also report on the behavior of these brines as a function of temperature, radiation, and presence of package materials in the laboratory, using a version of the EQ3/6 geochemical equilibrium code which has been modified to accommodate high ionic strengths. The required precision for these parameters will also be discussed. The paper will provide details of these considerations.

(Abstract only available)

SUMMARY OF SESSION II: CONTROLLING MECHANISMS OF RELEASE

The papers presented in Session II and others of this workshop detailed a variety of mechanisms that may affect the release of radionuclides from nuclear waste packages. This summary divides these mechanisms into four broad categories of groundwater access, barrier penetration, waste form dissolution, and radionuclide transport.

Groundwater Access

Several presentations (Braithwaite, Neretnieks, Pigford) demonstrated the central role of flow rate on the quantitative evaluation of radionuclide release rate in source-term calculations. Site-specific conditions for saturated flow (Neretnieks, Pigford), unsaturated flow (Braithwaite, Oversby), and brine migration/diffusive flow (Raines, Storck) were shown to lead to extremely different approaches to source-term modeling and testing. The role of groundwater access on source-term evaluation is perhaps most clear for saturated host rocks such as granite, basalt, and clay. There is a continuous supply, albeit at low flow rates, of water to the waste package and a continuous water phase connecting the waste package to the surface. For salt host rock, the key aspect of groundwater access is the limited amount of water by corrosion of the metallic canister. In unsaturated tuff, the infiltration rate of groundwater is estimated to be extremely low and to occur as discrete droplets. There is nothing inherently superior in any of these flow conditions with respect to safe disposal of nuclear waste.

Another important feature affecting radionuclide release is ambient composition of ambient groundwater (Cleveland). Groundwater composition has been shown to affect both the rate of release and the solubility-limited concentration of released radionuclides. Complexation of radionuclides by dissolved organics should also be of concern to source-term evaluations (Snelman). A caveat to this is the fact that ambient groundwaters can undergo significant changes in composition upon reaction at elevated temperature with host rock and waste package materials (McKinley).

Barrier Penetration

Modeling the time-distributed failure of metallic barriers, rather than assuming simultaneous and total failure, may lead to significant attenuation of the release rate of radionuclides from a repository system (Wick, Rickertsen, Apted). Similar conclusions were reached by the KBS-3 analysis for ^{129}I release even for containment lifetimes of 10^6 years. It was also suggested that the limited rate of aperture growth, or exposure of waste form surface, may provide a limiting mechanism for radionuclide release (Apted), although the demonstration was qualitative and may prove to be difficult to explicitly evaluate.

Related to aperture growth, the suggestion was made that waste components and their alteration (corrosion) products will line the pathways of water entering a waste package. These materials will likely act as chemical buffers and reactive components to reduce radionuclide release (McKinley, Apted, Neretnieks). It was cautioned, however, that corrosion products often can effectively seal and protect underlying surfaces of fresh, unreactive materials such as metals. This would limit the enormous redox buffering capacity represented by metallic barriers, but it should also retard overall corrosion rates.

Waste Form Dissolution

Source-term papers by a number of authors (Neretnieks, Pigford, Snelman, McKinley, Stelte, Wikjord) stressed solubility-limiting to release rate imposed by radionuclide-bearing solids. Three basic types of radionuclide release behavior were defined (Lanza, Avogadro): (1) nuclides that form their own solubility-limiting solids, (2) nuclides that are controlled by matrix-solubility limits of the matrix components of waste forms, and (3) nuclides that do not exhibit solubility-limited release behavior in any form (i.e., leach rate-limited).

Because of the heterogeneity of spent fuel, dissolution and release of radionuclides is unlikely to appear congruent because of the different dissolution properties of the many phases (gap, grain boundaries, and grains) composing spent fuel. There is evidence, however, that UO_2 grains dissolve congruently as a function of solution redox conditions (Shoesmith). Dissolution of borosilicate glass is congruent for time periods greater than several hours, although the subsequent precipitation of surface layer phases may indicate apparent incongruent releases (Wikjord).

Finally, it has been proposed (Neretnieks, Shoesmith) that alpha radiolysis at the waste form/water interface may lead to a locally oxidizing volume of solution. Because of the strong positive correlation between actinide solubility and oxidation potential (McVay), this highly oxidizing solution volume with relatively concentrated alpha-emitting nuclides may migrate away from the waste package. Interaction of such solutions with more reducing materials would eventually promote precipitation of nuclides. This scenario relies on complex interaction of surface area to volume ratios and relative rates of radiolysis, gas migration rates and capacity for redox buffering by solids, scavenging reactions within solution, and the reaction rate of solution redox couples.

Radionuclide Transport

The key role of groundwater flow rate on overall radionuclide release rate has been mentioned under "Groundwater Access." There are additional mechanisms that may further limit release. Reversible (physical) sorption within the waste package may attenuate the release of a limited number of nuclides that have either extremely high sorption coefficients, short half-lives, or both (McKinley, Pigford). Irreversible (chemisorption) sorption, however, can be an effective mechanism for controlling the release of radionuclide in source-term calculations.

Formation and migration of radionuclide-bearing colloids may also affect source-term calculations. Laboratory tests of waste forms (Lanza, Cleveland, McVay) indicate that a high proportion of many release nuclides, especially actinides, occur in a colloidal fraction. Initial work on the transport of such colloids through compacted clay indicates that essentially all the colloids are removed by physical filtration.

RELEASE MECHANISMS AND THEIR ROLE IN THE
SPENT FUEL REPOSITORY PERFORMANCE

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ABSTRACT

The paper presents insights from studies aiming at clarifying the release mechanisms and their role in the overall safety of the final disposal of spent fuel in hard precambrian bedrock.

The expected chemical conditions are defined with respect to the materials introduced into the repository, taking into account their possible long-term changes. The main parameters affecting the barrier performance are identified. The parameters affecting the leaching and the solubility of the actinides in the repository are discussed basing on preliminary experimental and theoretical studies.

The role of release mechanisms for the safety of the overall disposal system under different conditions is discussed. The importance of the source term is increased when the conditions are assumed to be normal, e.g. the engineering barriers of the repository are damaged. The source term modelling requirements and the data needs are evaluated.

1. INTRODUCTION

The possible radiological impacts from final disposal of nuclear wastes can be estimated only by means of predictive mathematical models. An essential part of an overall model system is comprised of a near field modeling which describes the release of radionuclides out of the repository into the surrounding geological host formations. In that an important part consists of a "source term", which by definition describes the mobilization of radionuclides from the wastes themselves.

In this paper the topic has been considered from the point of view of disposal concepts and spent fuel management timetables planned in Finland [1,2]. According to the present plans one is prepared to have a certain part of the spent fuel disposed of within Finnish territory after 2020. The R&D plan includes e.g. disposal site screening before the end of 1985, next safety assessment for extension of the reactor operation licence by the end of 1987, preliminary site selection in 1992 and repository construction application in 2000. Alongside with spent fuel disposal R&D work an option based on the reprocessing and the disposal of immobilized reprocessing waste is under study, as well. This alternative, however, doesn't seem very probable due to unfavourable economics and lack of reprocessing capacity in the near future.

The present concepts concern disposal deep in geological formations, in practice in crystalline rock such as granites, gneiss, gabbro etc., since salt or suitable clay formations do not exist.

The basic design of the repository consists of tunnels with vertical holes for the canisters containing the spent fuel. The disassembled spent fuel pins are enclosed inside copper canisters having a wall thickness of 0,1...0,2 m, a diameter of ca. 0,8 m, height ca. 4,5 m and weight 10...16 tons copper. The space around the pins is filled with lead or copper. The canisters are surrounded by compacted bentonite in the emplacement holes, the tunnels and the shafts are filled with a mixture of quartz and bentonite. Detailed information about the repository and the encapsulation facility is presented in reference [1]. The repository and canister design may alter significantly, specially after the year 1992, when the site characteristics will be more restrictly bounded. Preliminary studies indicate sound reasons for a less sophisticated design [3,4].

In the R&D program the Technical Research Centre of Finland (VTT) plays an active role including experimental as well as modeling work, specially as regarding studies related to safety assessment.

2. MECHANISMS AND INTERACTIONS

The mobilization of radionuclides from the waste is effected by several interactions between the UO_2 -matrix, water, engineered barriers and the surrounding rock: heat, radiation, chemical and mechanical effects. The mobilisation itself comprises dissolution of UO_2 -matrix and its radionuclides, diffusion of certain elements inside the matrix, and dissolution of gaseous elements from the gas gap of the fuel pins. The dissolution process includes interactive surface reactions and speciation and their solubilities in the water phase.

The mechanisms with their interactions should be taken into account with a different accuracy at different repository development phases: one application purpose calls for very sophisticated modeling, another as simplified as possible, and furthermore, a realistic or a conservative approach is to be chosen. So as to render all this possible, the mobilization phenomena and the pertinent physico-chemical dependencies must be studied.

3. CHEMICAL CONDITIONS

In order to be able to assess the corrosion of waste canisters and the leaching and dissolution of spent fuel (UO_2) it is important to know the chemical conditions in the repository.

3.1 The bedrock/groundwater systems

Igneous rock, such as granite, is composed of a small number of major constituents e.g. quartz, feldspars (orthoclase, plagioclase), biotite, hornblende and pyroxenes. In addition there are some accessory minerals such as titanites, apatite, zircon, magnetite, hematite, pyrite, ilmenite, fluorite, chlorite, muscovite, epidote minerals and carbonates etc. that might have some influence on the composition of the groundwater.

The Finnish bedrock is more felsic (containing more quartz and feldspar) than the earth's crust in general. Smaller amounts of FeO , Fe_2O_3 , MgO and CaO and higher contents of SiO_2 and K_2O are observed. Typical of the Finnish bedrock is the high content of felsic granites and migmatites.

The primary rock forming minerals, additional accessory minerals as well as weathering and decomposition products form a very complicated system with the groundwater in bedrock. Some possible chemical effects of the main minerals in granites are listed in Table I.

In addition to these minerals also fluid inclusions might affect the rock-water equilibrium. In the STRIPA project [5] granite bedrock have been found containing fluid inclusions, up to some $10^8/cm^3$ of rock. The fluid inclusions might contain very saline solutions, that is chlorides of Na, K and Ca. Some inclusions containing high concentrations of CO_2 -gas have also been found.

The composition of groundwater in granitic bedrock at greater depths is reported primarily in studies performed in Canada and Sweden. Most results from Finland are limited to the depths of shallow water (< 200 m). Some trends in these data may, however, be extrapolated to greater depths.

The expected groundwater conditions in deep granitic bedrock as based on results available from Canada, Sweden and Finland are listed in Table II.

3.2 The repository/groundwater system

3.2.1 Conditions in the case of an intact canister

As long as the spent fuel canister remains intact, the conditions in the repository will be determined by the interaction of the groundwater

with the buffer and backfill materials. In addition the waste influences the chemical conditions mainly through temperature effects.

The effect of buffer and backfill materials

According to the proposed concepts the backfill consists of sand/bentonite mixtures, approximately 80...90 % of quartz sand and filler and 10...20 % of bentonite. The buffer bentonite Volclay MX-80 comprise 90 % of clay-minerals, 5 % of feldspars and 4 % of quartz. As accessories some calcite, biotite, chlorite, tremolite, titanite, apatite, talc, zircon, leucite, vulcanic glass, pyrite, ferro (ferri-) oxides and some silty sized rock fragments are to be met with. The content of organic materials and sulphide is expected to be low. The content of organic material in bentonite has been analyzed at the Technical Research Centre of Finland (VTT). The measured value was 5000...6000 ppm [6]. The sulphide content is according to KBS less than 200 ppm after oxidation [7].

The groundwater composition alters somewhat after passing through bentonite. The changes are mainly due to dissolution and ion exchange reactions between cations in the mineral and the groundwater components. At the early stages after closure bentonite contains some air, entrapped in the pores of the buffer mass, which will affect the O_2 -content of the water and redox conditions.

Due to temperature effects from the waste canister, the bentonite might undergo an illitization process, which in turn will influence the ion exchange reactions with groundwater. The effect of radiation is expected to be minor. Only a limited space between the canister surface and the bentonite is expected to be affected by the (γ, β) -radiation.

Experimental

There are very few, if any, experimental results available treating the effect bentonite has upon groundwater. Experimental studies on the bentonite-groundwater interactions have been carried out at the VTT. The groundwater used is a synthetic groundwater, the composition of which is given in Table III.

The groundwater represents a typical granitic groundwater well within the range given in Table II although some components such as Fe(II)/Fe(III), sulphides, fluorides and phosphate are missing from the water.

The experiments are performed under static conditions at 25°C in an anaerobic atmosphere (N_2 90 %/ H_2 10 %). Traces of oxygen (< 20 ppm) are present in the anaerobic cabinet. Prior to starting the experiments the water is flushed with nitrogen (N_2). The level of oxygen in the water is measured at the start of the experiment and at the time of sampling. The oxygen level in the sample has remained low (< 0,01 mg/l). The preliminary results of the experiments after 6 months are shown in Figure 1.

In the undisturbed deep groundwaters the $H_2O-CO_2-CaCO_3$ system is stated to buffer the pH to a range 6...10. In contact with bentonite, the original pH of the water (pH 8,2) rises to a higher level (pH 9...10).

The redox conditions in deep groundwaters are taken to be determined by the presence of ferrous minerals, like pyrite FeS , siderite FeCO_3 , and goethite FeOOH and the magnetite Fe_3O_4 /hematite Fe_2O_3 equilibrium. The redox potential, Eh, based on the magnetite/hematite and a goethite/siderite equilibrium is calculated to be (-0,44...0 V) for pH 6...10. The preliminary redox measurements performed with the Ag/AgCl and the glassy carbon electrodes in the bentonite-water system indicate a negative Eh-potential. However, the Eh-values for the samples range from -0,1 to -0,3 V. The reason for this wide range is not yet known. In addition to the Fe II/Fe III-couple several other redox couples, such as S(VI)/S(II), N(V)/N(I), O(0)/O(-II) and organic components, might be present.

The principal anions in the groundwaters are OH , HCO_3 , CO_3 , SO_4 , Cl , F with minor amounts of HPO_4 , PO_4 , NO_3 , and HS . These anions might form complexes with the elements of the nuclear waste (canister and spent fuel). The carbonate concentration in the groundwater is strongly affected by the presence of bentonite, due to dissolution of carbonate minerals. Some dissolution of fluoride and chloride from the bentonite is also observed. No measurable amounts of sulphide ($> 0,1$ mg/l) have been observed.

In addition to the inorganic ligands the concentration of complexing organic compounds (fulvic and humic acids) in the groundwater is of importance. The organic content of groundwater is generally 1...20 mg/l, the fraction of fulvic and humic acids is not known. The increase in the KMnO_4 consumption in the bentonite-water experiments indicates some dissolution of organic material from bentonite, or some bacterial (anaerobic) growth. The composition of the organic component has not been analyzed as yet.

The concentration of cations Ca, Na, Mg and K in the water is influenced by the bentonite due to ion exchange and dissolution effects.

A summary of the expected chemical conditions in the repository prior to canister breakdown has been given in Table II.

3.2.2 Conditions after canister penetration

After the canister has been penetrated the chemical conditions in the repository will in addition to the material effects mentioned earlier be modified by α -radiolysis and the dissolution of spent fuel and cladding materials.

The main radiolysis products are H_2 and H_2O_2 . The yield of these products depending on the amount of Fe(II), HCO_3 , CO_3 , Cl , NO_3 and NO_2 in the groundwater. The net effect of these over time spans seems to be complicated to calculate.

Christensen and Bjergbakke calculated the radiolysis effects for water with a low iron content, ≤ 5 ppm. No further addition of iron e.g. from bentonite was considered. The production after 10^6 year totaled 41 550 mol for 1,4 tons of spent fuel. Irradiation was considered in a 4,2 l water volume in a layer 0,03 mm thick [9].

Due to radiolysis effects the metals Zr, Pb and Cu are expected to be oxidized first by leaving the actinides in their original oxidation states. The metals form hardly dissolvable salts and oxides, such as PbO, PbSO₄ and ZrO₂. The formation of protective layers of oxides will most likely decrease the effectiveness of the metallic reducing agents, leading to an increased oxidation of the spent fuel and higher mobilities of the actinides.

In addition to the Eh-effects the radiation will also influence the pH conditions in the repository. The extent of the effect is not known.

Table II lists the expected groundwater conditions at the time of dissolution of the spent fuel (UO₂).

4. FACTORS AFFECTING THE DISSOLUTION AND LEACHING MECHANISMS

Spent fuel is largely UO₂, with only a small fraction being constituted by other actinides and fission products. The chemical and physical changes that occur during irradiation result in a product that is inhomogeneous on both the micro and macro scale. This inhomogeneity is reflected in the dissolution behaviour e.g. the dissolution of gas gap elements and elements from the fracture surfaces.

4.1 Dissolution mechanisms

The dissolution of UO₂ as modified by the fuel's irradiation history can be described as:

- 1) An almost instantaneous release of soluble nuclides of Cs, I present in easily accessible regions of the fuel pins either at the gas gap or in cracks or porous regions of the pellets.
- 2) A congruent dissolution of UO₂, which releases other radionuclides, such as the actinides in the solid. This is complicated by a perturbation due to the diffusion of certain elements inside the matrix.

Models for the congruent dissolution of fuel are usually based on the solubility of UO₂ in a limited amount of water. This solubility can vary by several orders of magnitude depending on the redox chemistry and groundwater composition. Under oxidizing conditions UO₂ solubility is stated to be limited to about 360 mg/l by the availability of carbonate (about 275 mg/l) [10]. This conclusion is based on theoretical calculations.

The radiolysis may affect the behaviour of the radionuclides via effects on the groundwater, that is mainly Eh and pH changes, or by the radiolytic conversion of crystalline oxides to amorphous or less crystalline oxides thereby decreasing their thermodynamic stability and increasing their solubility.

Among the inorganic ligands generally found in groundwater HCO₃⁻, CO₃²⁻ and OH⁻ are of particular interest owing to their high concentrations as well as to the high stability constants of the complexes they form with actinides.

Experimental

The mechanism of spent fuel UO_2 dissolution has generally been studied using unirradiated UO_2 pellets. So far only some experiments have been performed with spent fuel. Most of the studies have been carried out using deionized water. The mechanism will, however, be more complicated in groundwater conditions. Some suggested oxidation and dissolution mechanisms for UO_2 is shown in Figure 2 [11]

Electrochemical studies performed by Johnson et al. have elucidated some aspects of the initial oxidative dissolution of UO_2 [12]. The UO_2 surface reacts rapidly with dissolved oxygen to produce oxidized surface films. The thickness and composition of said films depend on the redox conditions and solution composition. The effect of oxidized surface films on the leaching and dissolution behaviour of irradiated fuel appears to be of significance, but adequate information on the subject is not to be had at present.

Irradiated fuel dissolution experiments at 25°C have shown that under oxidizing conditions the UO_2 matrix dissolution rates can be enhanced by the presence of complexing agents, such as carbonate. In spite of this result, fission product and actinide releases have been reported to be generally lower in groundwater than in pure water. The reasons for this are not clear but could be explained by processes occurring after the release of the UO_2 species from the fuel i.e. adsorption onto the fuel surface or colloid formation and precipitation processes [12].

Experimental and theoretical studies on the dissolution and leaching behaviour of spent fuel under repository conditions has been studied at the VTT since 1980. Unirradiated UO_2 fuel is used in the experiments. The tests have up till now been performed in natural groundwaters taken at shallow depths (< 70 m) in the Finnish bedrock and at the Stripa mine in Sweden. Recently a series of dissolution experiments with artificial groundwaters was started, the one representing a typical granitic groundwater (Allard) and the other corresponding to the repository conditions taking simultaneously into account the possible effect of bentonite (Table II). In these experiments the pH and redox conditions are varied.

Up till now the dissolution tests of unirradiated UO_2 pellets have been made using the ISO (International Standard Organization) standard method to measure the dissolution rate of uranium in groundwater. The method was modified so that the low oxygen content of groundwater was simulated. The experiment was carried out in an oxygen-free atmosphere in an anaerobic cabinet filled with a mixture of nitrogen and hydrogen (90 % N_2 /10 % H_2). Two different natural groundwaters were used as leachants. The compositions are presented in Table IV. The Olkiluoto groundwater has a relatively high content of HCO_3^- , which is near the upper limit specified for groundwaters in deep granitic bedrock (Table II). The concentration of the main groundwater components is generally smaller for the Stripa groundwater, except for chloride and fluoride.

The groundwaters were made oxygen-free by flushing with N_2 gas. Then the samples with UO_2 pellets were removed into the anaerobic cabinet. The oxygen content in the waters remained at $\lesssim 0,01$ ppm during the experiments. The accurate content could not be measured. The redox potential values of the waters ranged from $-0,4 \dots -0,1$ V.

The dissolution rate of uranium in the natural groundwaters as a function of time up to 400 d is presented in Fig.3. The experiment is still continuing. The dissolution rate is $3 \dots 4 \cdot 10^{-8} \text{ g cm}^{-2} \text{ d}^{-1}$ after 520 d.

During the last dissolution periods precipitation of uranium could be observed in the waters. It seems as if the solubility limit were attained during the period. When the solubility limit is calculated from the measured dissolution rates, the following solubility limits are obtained:

Olkiluoto groundwater: $25 \dots 200 \text{ } \mu\text{g/l}$
Stripa groundwater: $40 \dots 350 \text{ } \mu\text{g/l}$.

Moreover, an autoclave system for dissolution experiments has been planned and constructed, see Fig. 4.

The groundwater is warmed, and made oxygen-free in the supply vessel by flushing with N_2 gas. Then it is let run down in the dissolution vessel where the experiment is carried out. The redox, pressure and temperature conditions may be adjusted. The system has been constructed in a way that the UO_2 pellet does not undergo any variation in pressure during water changing. Finally, the groundwater is let run down in the depletion vessel for sampling. Recently, a redox measurement system with a Pt electrode and a Ag/AgCl reference electrode has been installed in the dissolution vessel.

The first dissolution experiment with the autoclave system has been performed. The purpose was to test the system. The dissolution rate of uranium in natural groundwater (Olkiluoto groundwater) was measured at elevated pressure, 10 MPa, at 60°C .

The dissolution rate as a function of time up to 300 d is presented in Fig. 5. The value is $5 \times 10^{-8} \text{ g cm}^{-2} \text{ d}^{-1}$ after 300 d. The experiment was finished after that.

The preliminary experiments show that the temperature and the pressure do not significantly affect the dissolution rate of UO_2 fuel pellets. No significant difference between the effect of the two natural groundwaters (HCO_3 , SO_4 , Cl, F) upon the dissolution rate is observed.

TABLE I. THE CHEMICAL EFFECTS OF GRANITIC MINERALS

Mineral /weathering product	Chemical effect
<p>Main minerals</p> <p>Quartz 25 - 30 %</p> <p>Feldspar 50 - 75 %</p> <p style="padding-left: 40px;">E.g. orthoclase $KAlSi_3O_8$</p> <p style="padding-left: 40px;">E.g. plagioclase $(Na,Ca)(Al,Si)_4O_8$</p> <p>Amphiboles < 20 %</p> <p style="padding-left: 40px;">E.g. hornblende $Ca_2Na(Mg,Fe)_4$ $(Al,Fe,Ti)_3$ $Si_8O_{22}(OH,F)_2$</p> <p>Micas < 20 %</p> <p style="padding-left: 40px;">E.g. biotite $K(Fe,Mg)_3$ $AlSi_3O_{10}(OH,F)_2$</p> <p>Accessory minerals</p> <p>Magnetite Fe_3O_4</p> <p>Pyrite FeS_2</p> <p>Ilmenite $FeTiO_3$</p> <p>Zircon $ZrSiO_4$</p> <p>Fluorite CaF_2</p> <p>Calcite $CaCO_3$</p> <p>Apatite $Ca_5(F,Cl,OH)$ $(PO_4)_3$</p> <p>Monazite $(Ce,La,Th)PO_4$</p> <p>Weathering products</p> <p>Kaolinite $Al_4(Si_4O_{10})(OH)$</p> <p>Chlorite $(Mg,Fe,Al)_4(Si_4O_{10})(OH)_8$</p> <p>Clay minerals</p>	<p>Source of colloid SiO_2</p> <p>Interstitial K, Na, Ca-exchangable</p> <p>Easily weathered</p> <p>Cation exchangers?</p> <p>Eh-effect, Fe^{2+}-source</p> <p>Eh-effect, Fe^{2+}-, S^{2-}-, SO_4^{2-}-source</p> <p>Partially exchangable (M(IV))?</p> <p>F^--source</p> <p>Ca^{2+}-, HCO_3^--, CO_3^{2-}-source, pH</p> <p>HPO_4^{2-}-, PO_4^{3-}-source</p> <p>Sorption of Ln and An?</p> <p>From feldspars, cation exchanger</p> <p>From amphiboles and micas, cation exchanger</p> <p>Na^+, Ca^{2+}, Mg^{2+}, pH</p>

5. DISCUSSION AND CONCLUSIONS

The importance of understanding the source term mechanisms depends on several factors, the most relevant possibly being:

- the criteria to be applied in assessing the suitability of a disposal system
- the repository development phase.

When the system performance criteria are used, the role of the source term depends on the performance of the other parts of the whole disposal system. If the geosphere is evaluated as reliable and effective, there is no need of high accuracy in the source term estimation. On the other hand, if the geosphere is either ineffective at present or if the probability of such disruptive events, which can weaken essentially its performance in the future, is high enough, the role of the source term becomes emphasized. Particularly in situations, when the other engineered barriers of the repository may be breached, consequently increasing the water flow around the waste, the source term may become very important.

If the criteria concern the performance of subsystems or components, the role of the source term is evidently greater and more independent of the performance of the rest of the system. The level of understanding called for depends, however, on the strictness of the criteria.

If the repository development is in the phase of concept feasibility assessment, the geosphere may be assumed to be rather ineffective, and thus the release mechanisms should be known well enough so that the conservatism of the source term estimate can be relied upon. After the site selection phase, in a phase of engineered barrier design, the source term-related mechanisms must be known even better so as to be able to develop and apply realistic modeling for optimization purposes.

The uncertainty estimates of the performance are of importance and they are to be made. The estimation methods and their contents are dependent on the type of criteria employed and of the repository development phase. An understanding of the mechanisms affecting the source term improves the reliability of the uncertainty estimates, regardless of whether they are made by means of sophisticated or simplified models.

The following research objects are therefore considered important in the near future:

- Groundwater conditions inside the repository, in the surrounding rock and in the near field (disturbed zone), especially changes due to buffer/water chemical interactions and waste/water radiolytic interactions in a realistic repository environment.
- Dissolution mechanisms, speciation and solubility under realistic repository conditions. Identification of the most important dependencies on the various possible factors and quantification of the effects.

The phenomena and the connected mechanisms are to be studied by experimental and theoretical means. In the source term modelling the interactions will be considered more carefully and will be given more attention in the development work to be done.

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TABLE II. CHEMICAL CONDITIONS IN THE REPOSITORY

Component	Natural groundwater	Repository groundwater	
		In case of intact canister	After canister penetration
pH	6...10	6...10(11)	4(6)...10
Eh(V)	-0,44...0	-0,4...0	-0,4...pos.values
Conductivity mS/m	30...500		
O ₂ mg/l	< 1	> 1	> 1
HCO ₃ ⁻ mg/l	100...400	400...600	400...600
CO ₃ ²⁻ "			
SO ₄ ²⁻ "	1...100	1...50	≤ 50
HS ⁻ "	0,1...1	1...3	< 1
HPO ₄ ²⁻ "	< 0,4	≤ 0,4	≤ 0,4
PO ₄ ³⁻ "	≤ 0,01	≤ 0,01	≤ 0,01
NO ₃ ⁻ "	0,01...0,05	0,01...0,05	0,01...0,05
NO ₂ ⁻ "	0,01...0,6	0,01...0,6	0,01...0,6
Cl ⁻ "	5...100	5...100	5...100
F ⁻ "	0,5...7,5	≤ 7,5	≤ 7,5
Ca ²⁺ "	10...100	≤ 20	≤ 20
Mg ²⁺ "	1...65	≤ 5	≤ 5
Fe _{tot} "	0,02...5	1...10	1...10
Mn ²⁺ "	0,02...0,7	0,02...0,2	≤ 0,2
K ⁺ "	0,2...10	≤ 5	≤ 5
Na ⁺ "	10...500	300...500	300...500
NH ₄ ⁺ "	< 0,1	≤ 0,1	≤ 0,1
Al ³⁺ "		≤ 0,02	≤ 0,02
Cu, Zr, Pb compounds			
SiO ₂ "	2...20	> 2...20	2...20
Org. compounds	1...20	30...40	≤ 30
Colloids "	0,5...1	≥ 1	≥ 1
Micro-org. "			
Gases:			
H ₂ , H ₂ O ₂ mol/l		≤ 360	≤ 41 500
Temperature °C	8...13	max. 70°C	8...13

TABLE III. COMPOSITION OF THE SYNTHETIC GROUND-WATER ACCORDING TO B. ALLARD [8].

	Conc [M]	mg/l
HCO ₃	2 x 10 ⁻³	123
SiO ₂	2 x 10 ⁻⁴	12
SO ₄	1 x 10 ⁻⁴	9,6
Cl ⁻	2 x 10 ⁻³	70
Ca	4,5 x 10 ⁻⁴	18
Mg	1,8 x 10 ⁻⁴	4,3
K	1 x 10 ⁻⁴	3,9
Na	2,8 x 10 ⁻³	65
pH ~ 8,2		

TABLE IV. COMPOSITION OF GROUNDWATERS USED IN UO₂ DISSOLUTION EXPERIMENTS.

	Olkiluoto ground-water	Stripa ground-water
pH	8.2	8.3
Conductivity (25°C)	8.7 mS/m	28.0 mS/m
HCO ₃	360 mg/l	86 mg/l
F	0.47 "	5.25 "
NO ₃	< 0.1 "	0.02 "
NO ₂	< 0.1 "	< 0.001 "
NH ₄	< 0.01 "	< 0.01 "
Cl ⁻	20 "	37 "
SO ₄	180 "	6.0 "
PO ₄	0.011 "	< 0.1 "
Fe	0.04 "	< 0.02 "
Mn	1.29 "	< 0.02 "
Ca	69 "	13.6 "
Mg	39 "	0.25 "
Na	77 "	50 "
K	17 "	0.26 "
Si	13 "	< 1 " (SiO ₂)

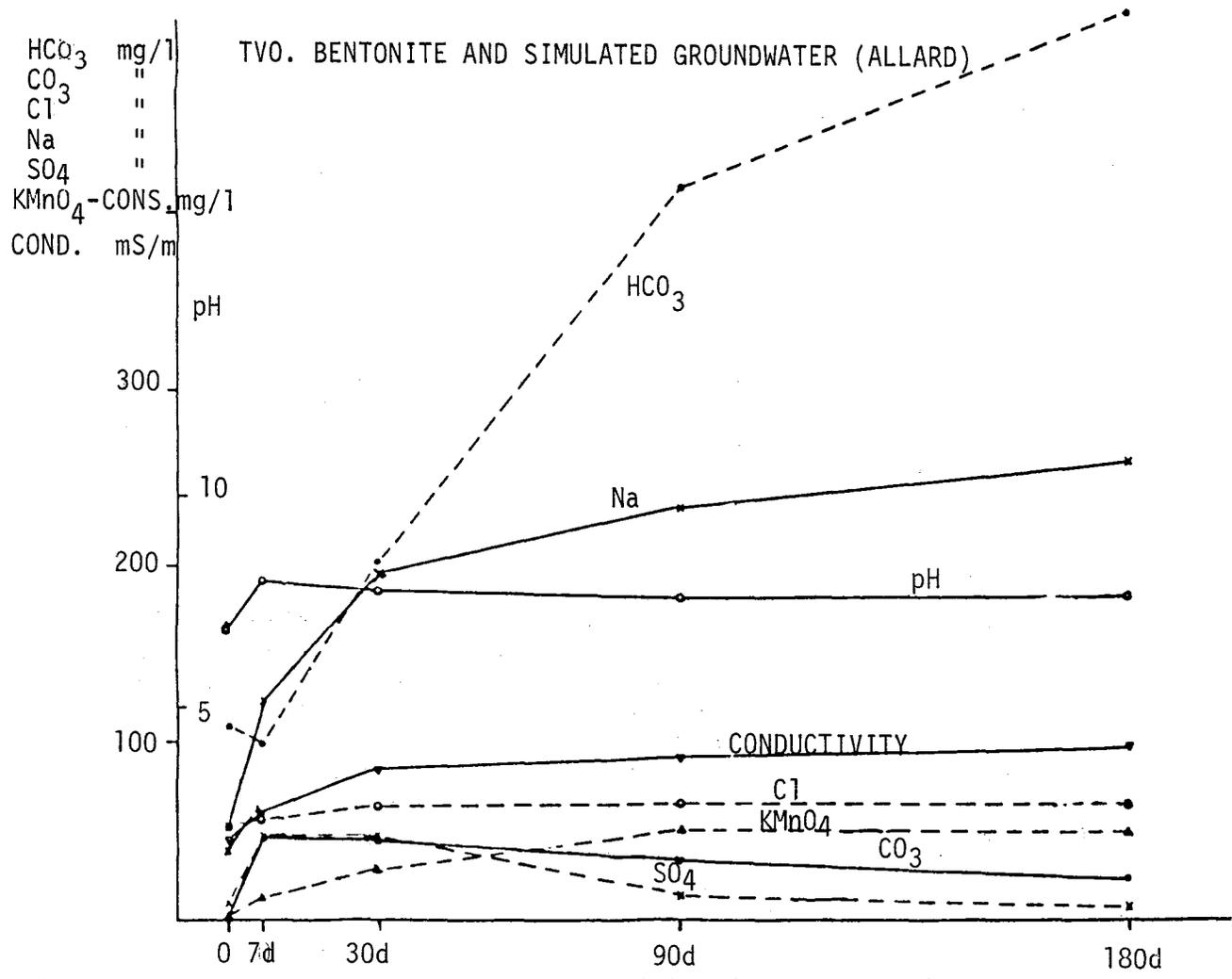


Figure 1. Changes in groundwater composition due to bentonite.

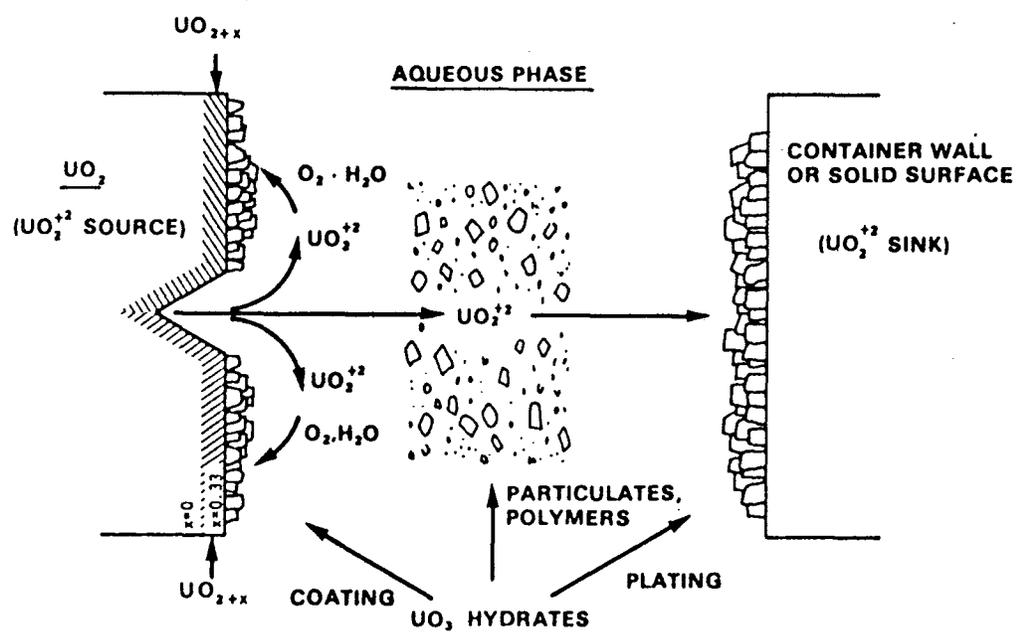


Figure 2. Oxidation and dissolution mechanisms for UO_2 [11].

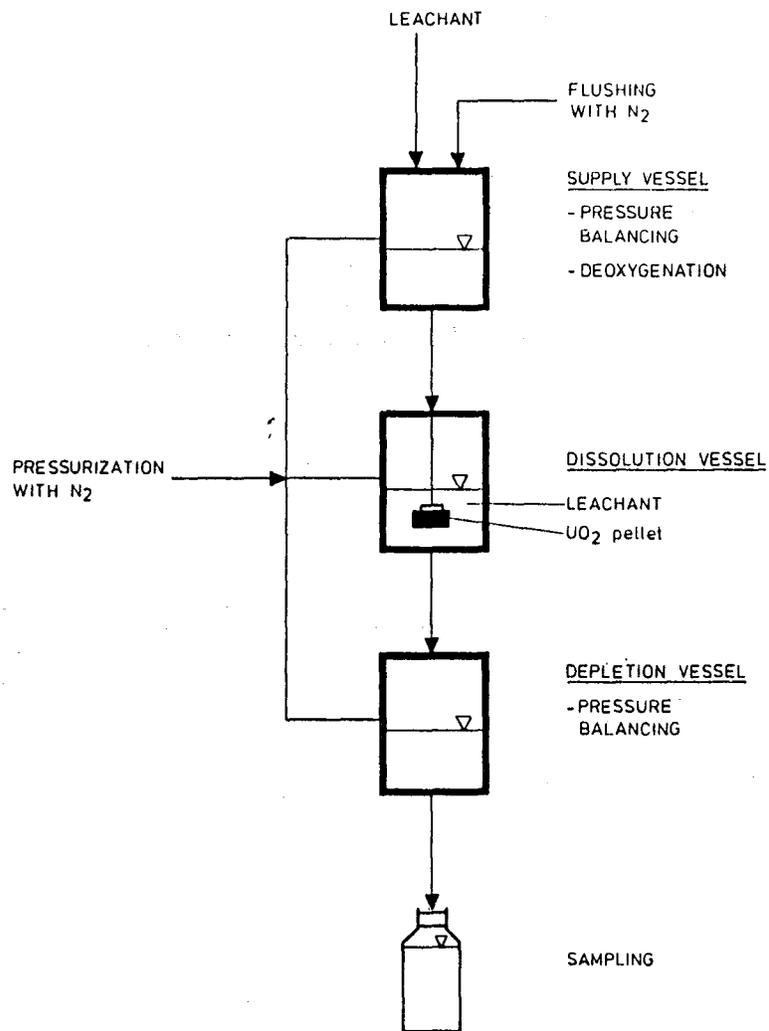


Figure 4. Dissolution at elevated pressure.

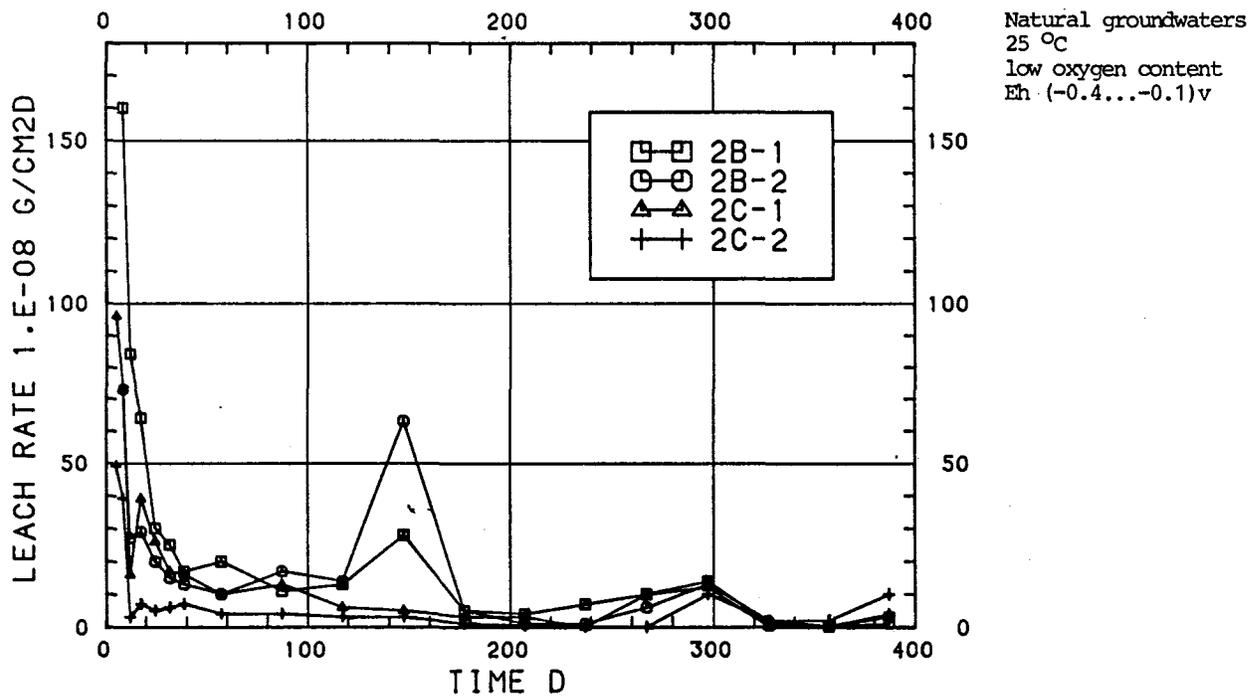


Figure 3. U-dissolution rate as a function of time (25°C).

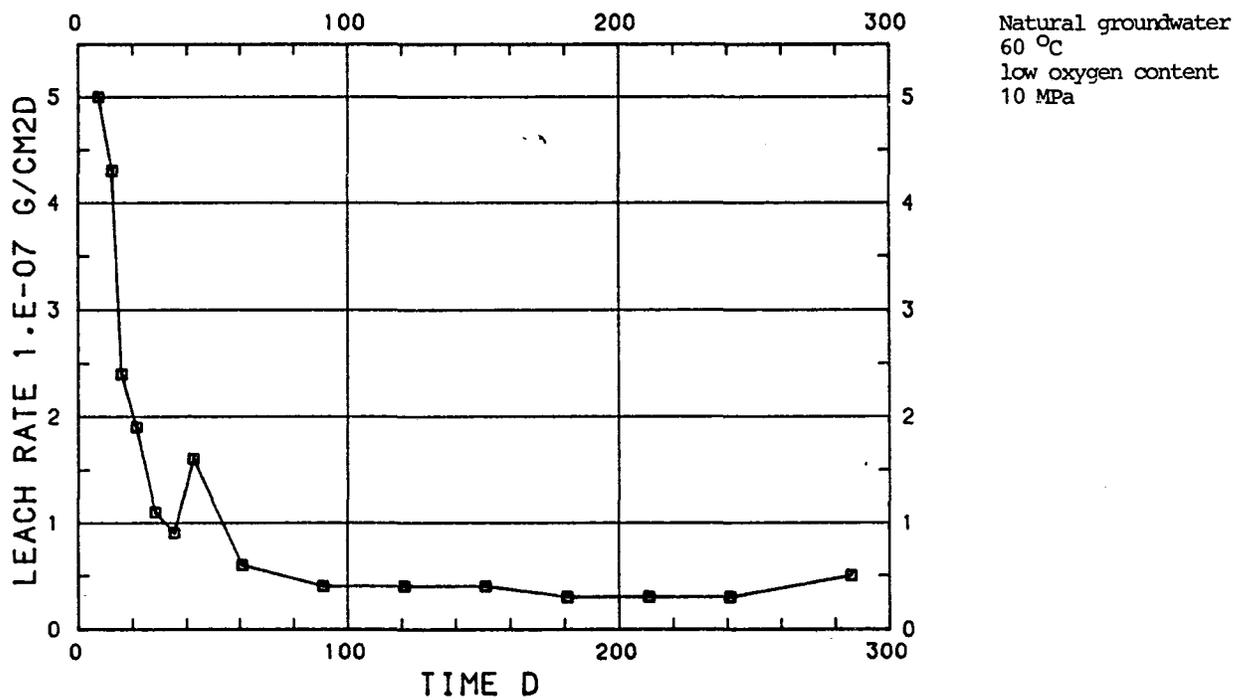


Figure 5. U-dissolution rate as a function of time (60°C, 10 MPa).

LEACHING OF PLUTONIUM FROM A BOROSILICATE GLASS
BY SELECTED GROUND WATERS

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ABSTRACT

The leachability and speciation of plutonium from a borosilicate glass (Battelle 80-207) by eight actual ground waters of diverse chemical compositions has been determined. Waters from alluvial deposits in the Hualapai Valley (Arizona) and from Grande Ronde Basalt (Washington) leached plutonium most efficiently at 25°C and 90°C respectively. Leaching was incongruent with plutonium removed slower than glass-matrix dissolution. The results indicate the need to determine leachability of actual waste forms with actual ground waters that would contact the waste in the event of a repository breach.

INTRODUCTION

The U.S. Geological Survey program to study the geochemical behavior of the transuranium elements in ground waters from rock types that are being considered as possible hosts for nuclear-waste repositories has involved three approaches: 1) single-phase speciation of added plutonium, neptunium, and americium in 12 ground waters and 2 surface waters as a function of time and temperature [1-7]; 2) determination of thermodynamic parameters for complexes with ions common in ground waters [8-10]; 3) determination of the leachability and speciation of plutonium from a radioactive waste glass by selected ground waters used in the single-phase speciation studies. This paper describes results of the latter study.

A theory for glass leaching has been formulated from existing data using deionized water as leachant. In this theory, the initial stages of leaching follow a diffusion process in which the alkali-metal ions are selectively leached from the surface of the glass, leaving behind a porous, silica-enriched hydrated layer. As this dealkalinized layer thickens, the metal diffusion rate becomes progressively slower until the diffusion rate equals the rate of dissolution of the silica-enriched layer. At this time, dissolution of the glass appears to become congruent. Barkatt and associates [11] observed that when polyvalent cations are present in the glass matrix, they tend to be retained in the dealkalinized layer until all available sites in the layer have been saturated, after which they are released at rates much greater than those measured initially. Thus the release rate of polyvalent ions should increase with increasing leach time.

One consequence of the theory is that the thickness and structure of the surface layer is probably dependent on the chemical composition of the leaching solvent. In fact, there were observable differences in the depth and structure of the surface layer in glasses leached by deionized water compared to glasses leached by brines [12]. However, few leaching studies have utilized actual ground waters, the leachants that would actually contact the wastes should a repository be breached [1, 13-15]. In this paper, the results of a study using eight ground waters to leach a plutonium-containing borosilicate glass waste form are presented. We will show that the quantity, chemical form, and physical form of the plutonium leached from the glass are highly dependent on the chemical composition of the ground-water.

EXPERIMENTAL

The waters used were from: 1) Grande Ronde Basalt underlying the Hanford reservation in Washington; 2) tuff at the Nevada Test Site (NTS); 3) Cretaceous shale of the Northern Great Plains; 4) Climax stock granite at the NTS; 5) Crystal Pool, which drains the carbonate aquifer underlying NTS; 6) well 5C at NTS, which penetrates alluvial fill; 7) Rentfrow well, which penetrates into the Permian Yeso formation in the Tularosa Basin in New Mexico; and 8) Red Lake South well, which penetrates alluvial fill in the Hualapai Valley in Arizona. Deionized water was included for comparison to other studies. Ground-water compositions are shown in Table I.

The leaching studies were conducted with 5-mm glass cubes (Battelle 80-207 [16]) and contained 0.04 weight percent plutonium. The chemical composi-

tion of the glass is given in Table II. All leaching experiments were conducted using the Battelle static leach test MCC-1 procedure [17] with two modifications: 1) Only two temperatures were used (25° and 90°C); and 2) the sampling periods were 30, 90, 180, and 360 days. The surface-area-to-volume ratio (SA/V) requirement was met by using three cubes (area of 150mm² each) and 45 mL ground water contained in tightly sealed Savillex (1) Teflon jars. Weight loss from these jars averaged less than 1 percent, even after 360 days at 90°C. After the stipulated leaching period, the waters were sampled before and after filtration through 0.05- μ m Nuclepore filters and the oxidation-state distribution of plutonium in the filtrates was determined by procedures given in [18], involving PrF₃ carrier precipitation to determine Pu(III) and Pu(IV) concentrations, PrF₃ precipitation following NaHSO₃ reduction for total plutonium concentration, and thenoyltrifluoroacetone (TTA) extraction for Pu(IV) concentration. Plutonium (V+VI) concentrations were calculated by subtracting the Pu(III) and (IV) concentrations from the total plutonium concentration. In addition, the glass cubes and containers were rinsed with 0.5 M HClO₄, and the resulting solutions were analyzed to determine the quantity of sorbed plutonium. Because the plutonium was not isotopically pure and the glass contained a small amount of americium, all plutonium analyses required ion-exchange purification followed by alpha-spectrometric analysis as described in [19]. The concentrations reported are for Pu-239.

To determine whether the mechanism of leaching was consistent with that formulated by Barkatt [11] for deionized water, experiments at 25° and 90°C were performed utilizing plutonium-free glass cubes otherwise similar to those used in the plutonium leaching experiments. The chemical compositions of the three ground waters (basalt, shale, and tuff) used as leachants in these experiments were determined on aliquots that had contacted the glass for 180 days, and on aliquots receiving the same treatment in the absence of glass cubes. Changes in chemical composition between the two sets of waters were attributed to material leached from the glass.

RESULTS AND DISCUSSION

Results of the plutonium speciation experiments are shown in Figures 1 and 2. The data at each time period were obtained from a single experiment. The insoluble-sorbed fraction is the quantity of plutonium removed from the glass cube surfaces and the Teflon vessel walls by rinsing with dilute HClO₄, and represents the fraction of plutonium that was leached from the glass, but subsequently sorbed. The insoluble-suspended fraction is the difference between the total plutonium concentration in the ground water before and after filtration through a 0.05- μ m filter, whereas the soluble fraction is the concentration of plutonium that passed through the filter, and is defined as being in solution, although colloidal material smaller than 0.05 μ m might be present in this fraction. Within experimental error, which we estimate based on counting statistics, agreement of the individual oxidation state analyses and previously reported [1-7] single-phase experiments to be \pm 20%, the sum of the concentrations in each of the oxidation states should equal the concentration of plutonium in the soluble fraction.

The quantity of plutonium leached from the glass (soluble, insoluble-sorbed, and insoluble-suspended), its physical form and its oxidation-state

(1) The use of trade names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

distribution all depended on which ground water was used as leachant. At 25°C, the basalt, Crystal Pool, Rentfrow and Red Lake South ground waters were about equally effective leachants, whereas well 5C maintained the most plutonium in solution. At 90°C, the basalt removed the most plutonium and maintained the highest concentration in solution. With the exception of the basalt and tuff ground waters, more plutonium was leached at room temperature. In general, more remained in solution after 180 days than after 360 days, indicating some mechanism for removing the plutonium from solution once it was released from the glass. An auxiliary experiment in which both radioactive and non-radioactive glass cubes were leached together in the same Teflon vessel showed that the amount of plutonium rinsed off the non-radioactive cube was about 70 percent of that rinsed from the radioactive one, indicating that most of this loosely-held plutonium was sorbed from the solution with only a minor fraction being nascent. With only a few exceptions less than 10 percent of the plutonium removed from the glass at 360 days was in true solution.

The oxidation-state distributions at 25°C (Figure 2) did not differ in kind from the distributions reported in single-phase speciation experiments [1-7]. In waters that oxidized plutonium in the single-phase studies, notably the Rentfrow water, the leached plutonium in solution was principally in the upper oxidation states. Similarly, in waters that reduced plutonium, e.g. the basalt, the leached plutonium was mostly in the lower oxidation states. However, the 90°C data indicate a larger percentage of oxidized plutonium than in the single-phase studies. Moreover, the Pu(IV) concentration was significant in most of the glass leachates at both temperatures, whereas Pu(IV) was observed in the single-phase experiments only in ground waters containing appreciable concentrations of strongly complexing ligands. One possible explanation is that the Pu(IV) was associated with very small colloids, small enough to pass through the 0.05- μ m filter, and extractable by TTA. This possibility is reasonable in light of the overwhelming majority of particulate-associated plutonium. Alternatively, since all the plutonium present in the glass is in the tetravalent state (PuO₂), it is possible the Pu(IV) observed may not have had time to equilibrate with the water.

The most striking result on display in these figures is the strong dependence of leaching behavior on ground-water composition. This dependence is summarized in Table III, which indicates that with only a single exception, all of the waters are more effective leachants than deionized water, some by a large factor. The hazard of attempting to use deionized-water leaching results to predict actual ground-water behavior is obvious.

In an attempt to determine the mechanism for plutonium removal from the glass, a set of experiments was performed to monitor the change in chemical composition of ground water during glass leaching. Basalt, shale, and tuff ground waters were selected because they represent extremes in composition. The components monitored were SiO₂, as a measure of the glass-matrix dissolution; Na, representing release of the mobile alkali metals; Mg, an indicator of the release of the less-mobile alkaline earth metals; Fe, because of its very high concentration in the glass, and to monitor release of multi-valent metals from the glass; and Pu.

Ground-water composition changes after 180 days' leaching are shown in Table IV. Only small changes in composition occurred at 25°C; greater changes at 90°C. With the exception of the tuff water, there was no signi-

ficant increase in the sodium-ion concentration, in marked contrast with the reported increase when deionized water was used as leachant [11]. At 90°C, significant quantities of iron were leached, especially by the basalt water. Only modest increases in silica concentration were observed.

There were two compositional changes not caused by leaching, but by the temperature change. Except for the basalt water, the concentrations of calcium and magnesium decreased when the temperature was increased from 25° to 90°C, because of the negative temperature coefficient of solubility for several calcium and magnesium salts, notably the sulfates, causing them to precipitate at 90°C. The calcium and magnesium concentrations were too low to achieve saturation in the basalt water.

To gain a better insight into the leaching mechanism, a more useful comparison is the normalized mass loss coefficient (NL) [17], the quantity of glass which, upon total dissolution, would cause the observed increase in concentration of a given glass component in the leachant. It relates the quantity of each component released from the glass to the concentration of that component within the glass. By comparing the NL for several components it is possible to determine whether one component was being preferentially leached from the glass, or whether all components were being released in a congruent fashion, that is, strictly as a result of matrix dissolution. A large NL value indicates extensive leaching of that component. The NL is calculated using the following equation:

$$(NL)_{i,T} = \frac{V_L \cdot C_{i,L}}{SA \cdot C_{i,g}}$$

where: $(NL)_{i,T}$ = grams of glass dissolved per unit area in total time T necessary to produce the measured concentration of component i (gm/cm²)

V_L = volume of leachant (L)

$C_{i,L}$ = concentration of species i in the leachant (moles/L)

SA = surface area of the glass leached (cm²)

$C_{i,g}$ = concentration of species i in the glass (moles/g)

The calculated NL values for the three waters at 90°C and 180 days are given in Table V. If NL_{silica} is the indicator for glass-matrix dissolution, sodium is removed preferentially from the glass except in the shale water, whereas iron and plutonium are removed at rates slower than glass-matrix dissolution. For at least these three waters, the quantity of material removed from the glass, be it silica, sodium, magnesium, iron, or plutonium, depends on which water is leachant. The tuff water is the most effective solvent for the glass matrix (as indicated by the largest NL value for silica) whereas the basalt water is the most effective leachant for iron and plutonium. Only the shale water failed to leach any of the monitored glass components appreciably. These results indicate that different ground waters leach different components preferentially. Predicting the durability of waste glasses based on leaching studies utilizing deionized water may not be conservative, but in fact may be optimistic. An example is the leaching of pluton-

ium at 90°C, where all the ground waters were more effective leachants than deionized water. It is obvious that the composition of ground water contacting the waste glass in an actual repository may be altered by passage through the backfill material, and also by dissolution of canister corrosion products. However, these alterations would most probably make the ground water leaching behavior even more dissimilar to that of deionized water, further demonstrating the hazard of attempting to predict repository glass leachability from deionized-water results.

CONCLUSIONS

The quantity of plutonium leached from Battelle 80-207 glass depends on the chemical composition of the ground water used as leachant. The water from Grande Ronde Basalt, which contained approximately 50 mg/L fluoride, was the most effective leachant for plutonium at 90°C and the water from Red Lake South well, which was quite oxidizing, was the most effective leachant at 25°C. Tuff ground water was most effective at dissolving the glass matrix, but was not effective for removing plutonium from the glass, whereas shale ground water was the least effective leachant. In general, after 360 days greater than 90% of the plutonium removed from the glass by all of the waters was either sorbed to the glass or Teflon container walls, or was suspended in the leachant. The quantity of plutonium in solution, i.e. that passed through a 0.05- μ m filter, was less after 360 days than it was after 180 days. Plutonium (IV) was more prevalent in the glass leachates than in experiments in which dissolved plutonium was added to these same ground waters, suggesting possible sorption of insoluble Pu(IV) onto dispersed colloidal material smaller than 0.05 μ m. At least in the time frame of this study, the glass was leached incongruently with sodium removed faster than the glass matrix, and plutonium and iron being removed more slowly than the matrix. Based on these results, the leaching of Battelle 80-207 glass by actual ground waters is, in general, consistent with the leaching theory developed utilizing data from deionized-water experiments. However, with only a few exceptions, all the waters were significantly more effective leachants for plutonium than deionized water at both temperatures.

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Table I. Groundwater Compositions (mg/L except pH)

Solute	Basalt	Tuff	Shale	Granite	Crystal Pool	Well 5C	Rentfrow	Red Lake South
Alkalinity (as CaCO ₃)	146	98	530	140	256	265	80	90
Calcium	<0.1	10	100	300	49	2	550	28
Iron	0.3	0.007	0.01	0.007	0.03	0.01	0.05	0.01
Magnesium	<1	3	50	3	21	0.4	210	24
Manganese	0.005	0.001	0.3	0.03	<0.001	<0.001	0.008	0.084
Potassium	3.0	4.2	24	2.3	8.7	6.3	5.2	3.9
Sodium	300	50	700	300	75	140	380	280
Strontium	0.01	0.05	3	5	1.0	0.018	9.9	2.5
Silica	100	70	10	10	27	57	17	15
Chloride	140	7	61	73	22	10	150	480
Fluoride	52	2.3	0.1	0.8	1.9	1.0	2.3	1.9
Phosphate	0.1	<0.01	0.02	0.02	<0.01	<0.01	<0.01	<0.01
Sulfate	75	19	2000	980	90	29	2700	23
pH	9.3	7.8	8.4	8.3	7.5	9.0	7.6	7.9

Table II. Composition of Battelle 80-207 Borosilicate Glass

Component	Weight Percent
Al ₂ O ₃	3.65
B ₂ O ₃	9.74
BaO	0.14
CaO	10.44
CuO	2.17
Fe ₂ O ₃	10.12
K ₂ O	1.97
Li ₂ O	1.89
MgO	3.18
Na ₂ O	7.27
P ₂ O ₅	2.00
SiO ₂	39.81
SrO	0.07
TiO ₂	4.75
ZnO	0.29
ZrO ₂	1.09
PuO ₂	0.04

Table III
Total Plutonium Leached in 360 Days by Various Ground Waters

Ground Water	25°C		90°C	
	Pu Leached (pCi/L)	Normalized (D.I.=1)	Pu Leached (pCi/L)	Normalized (D.I.=1)
Basalt	69,700	12.0	77,200	34.2
Deionized (D.I.)	5,830	1.00	2,260	1.00
Tuff	3,930	0.67	6,910	3.06
Granite	6,210	1.06	24,000	10.7
Shale	8,840	1.52	2,500	1.11
Crystal Pool	97,700	16.7	12,700	5.63
Red Lake Well	185,000	31.7	3,400	1.51
Rentfrow	73,600	12.6	8,550	3.79
Well 5C	17,300	2.96	12,000	5.30

Table IV
Ground Water Composition (mg/L)
Before and After 180-Day Glass Leach

Water	Condition	F	Na	Ca	Mg	Fe	SiO ₂
Basalt	25°C Before	53	260	1.5	0.07	0.190	110
	25°C After	53	270	3.0	0.6	0.170	110
	90°C Before	55	280	1.6	0.07	0.210	120
	90°C After	55	290	7.2	2.0	4.40	150
Shale	25°C Before	-	940	50	56	<0.009	14
	25°C After	-	960	51	57	0.030	13
	90°C Before	-	1000	10	40	<0.009	0.5
	90°C After	-	1000	18	19	0.010	0.9
Tuff	25°C Before	-	46	13	2.1	<0.009	65
	25°C After	-	50	13	2.3	0.080	61
	90°C Before	-	49	1.4	0.09	<0.009	60
	90°C After	-	72	9.4	0.7	0.140	120

Table V
Normalized Mass Loss (NL x 10⁴) For Various
Components at 90°C and 180 Days (g/cm²)
[N.C. indicates insignificant aqueous concentration change]

Ground Water	SiO ₂	Na	Mg	Fe	Pu
Basalt	7.5	18.5	10.1	6.0	0.180
Shale	0.1	N.C.	N.C.	N.C.	0.006
Tuff	15.1	42.6	3.2	0.2	0.009

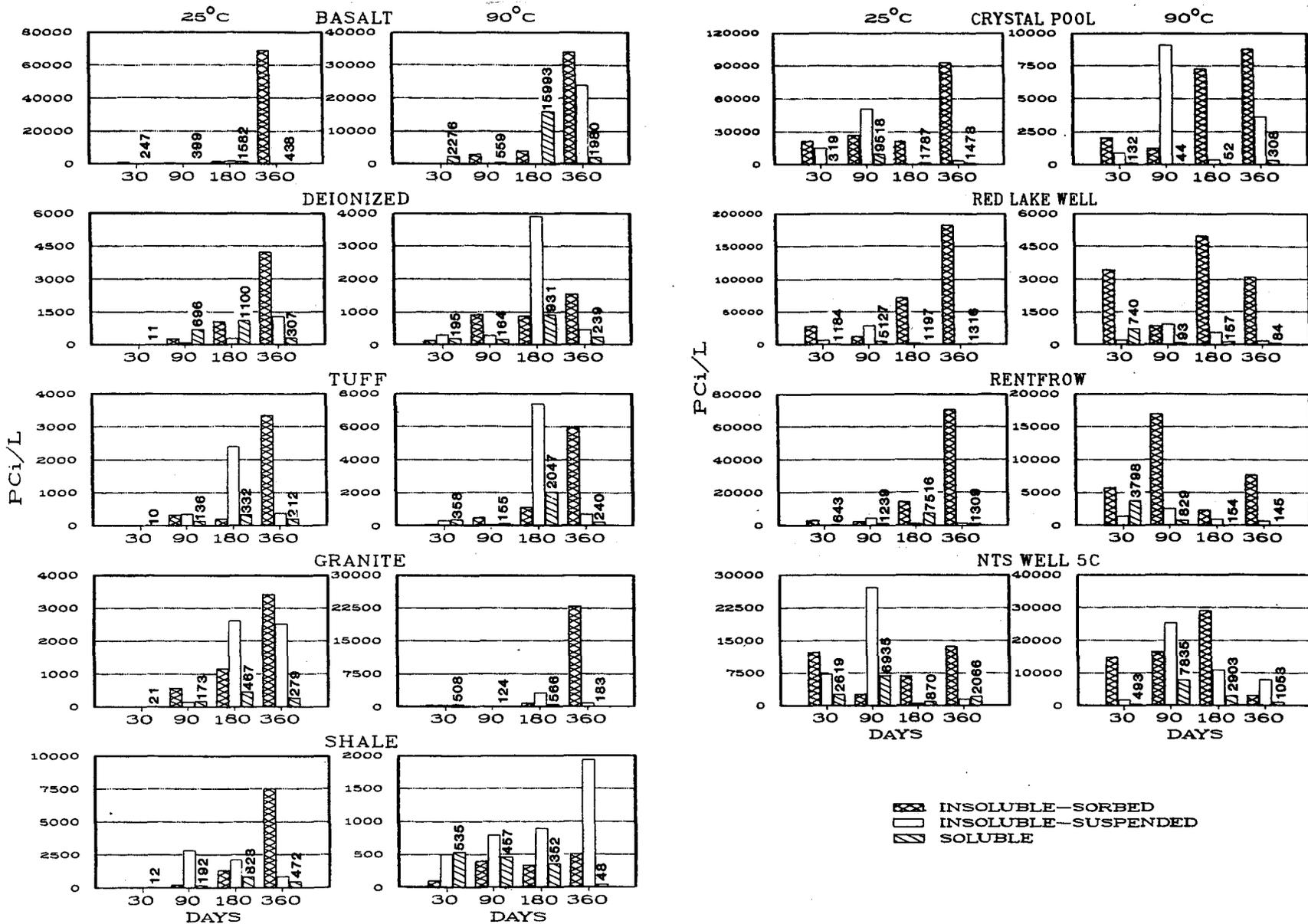


Figure 1. Physical form of plutonium leached from Battelle 80-207 glass by selected ground waters.

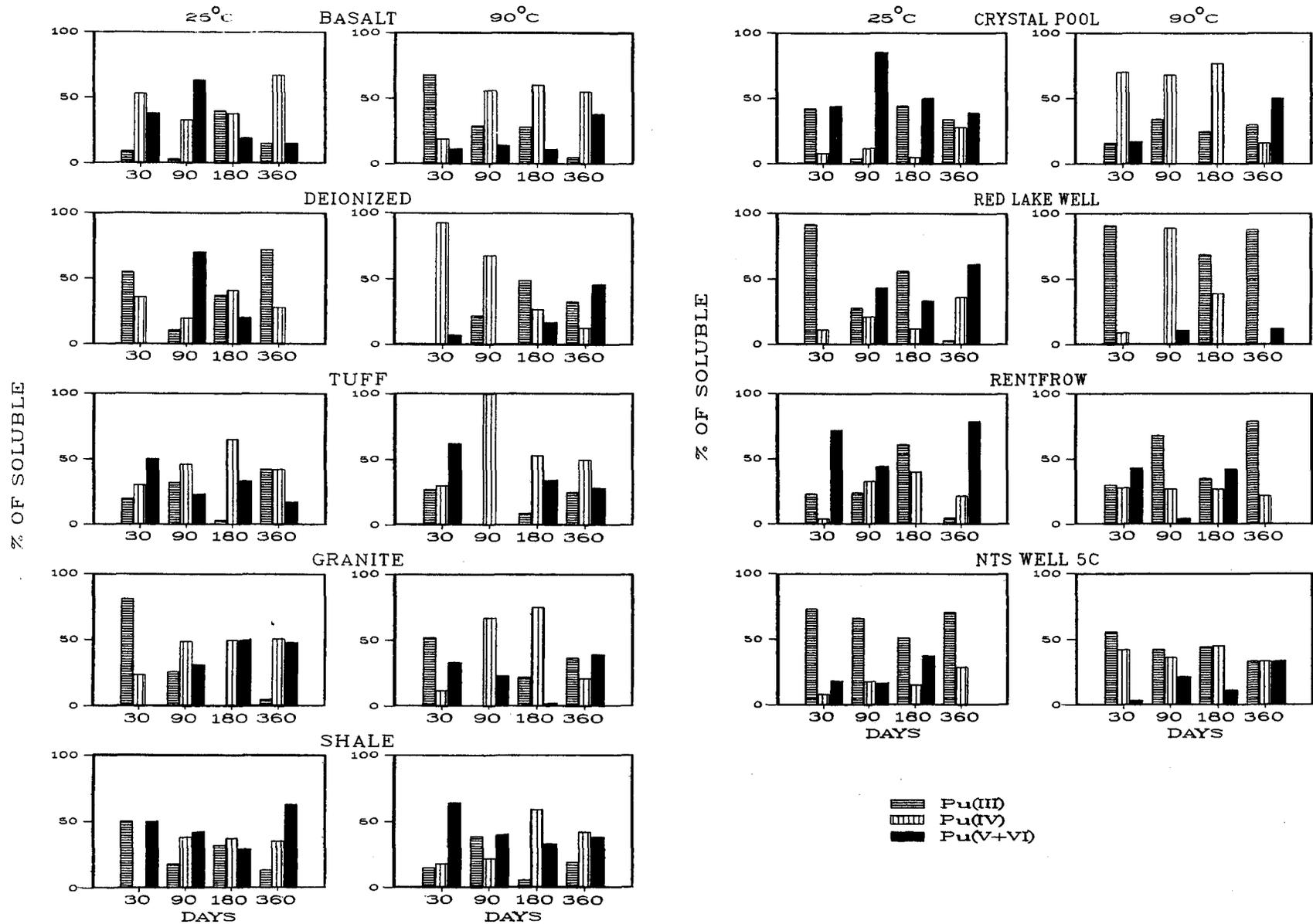


Figure 2. Oxidation-state distribution of soluble plutonium leached from Battelle 80-207 glass.

THE QUANTIFICATION OF SOURCE-TERM PROFILES
FROM NEAR-FIELD GEOCHEMICAL MODELS

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ABSTRACT

A geochemical model of the near-field is described which quantitatively treats the processes of engineered barrier degradation, buffering of aqueous chemistry by solid phases, nuclide solubilisation and transport through the near-field and release to the far-field. The radionuclide source-terms derived from this model are compared with those from a simpler model used for repository safety analysis.

INTRODUCTION

As part of the safety assessment for high-level waste repositories, radionuclide source-terms to the far-field must be defined for subsequent migration modelling. In recent analyses [1, 2] rather simple near-field models have been used to derive such source-terms which are intended to be, if not realistic, at least conservative from a safety point of view. A more realistic approach is needed, however, in order to assess the degree of conservatism in such simple models, evaluate the importance of particular near-field barriers in determining the source-term and identify key areas in which information is lacking. In this paper a simple but fairly comprehensive model of the Swiss near-field is described which allows quantitative evaluation of engineered barrier lifetimes, gross variations in aqueous chemistry in various regions of the near-field, nuclide solubilisation and transport to the far field [3]. Resultant release profiles are compared with those derived from a simple conservative model.

DESCRIPTION OF THE SWISS NEAR-FIELD

The reference Swiss disposal scheme involves emplacement of vitrified high-level waste, encapsulated in cast iron (or steel), in a granitic host rock at a depth of about 1300 m. Waste containers are positioned horizontally in the centre of 3.7 m diameter drifts which are backfilled with compressed bentonite (Fig. 1). For safety analysis, a repository containing 5895 waste canister is considered. The material inventory in the engineered barriers surrounding each canister is summarised in table 1. The near-field also includes the mechanically damaged rock around the tunnel which is considered to extend about 4 m beyond the drift wall.

Table I

Material inventory in the near-field (per canister)

Material	Volume (m ³)	Mass (kg)
Glass	0.15	405
Steel fabrication container	0.01	75
Fabrication void	0.03	-
Canister	0.9	6.5×10^3
Backfill (water saturated)	52.8	1.1×10^5

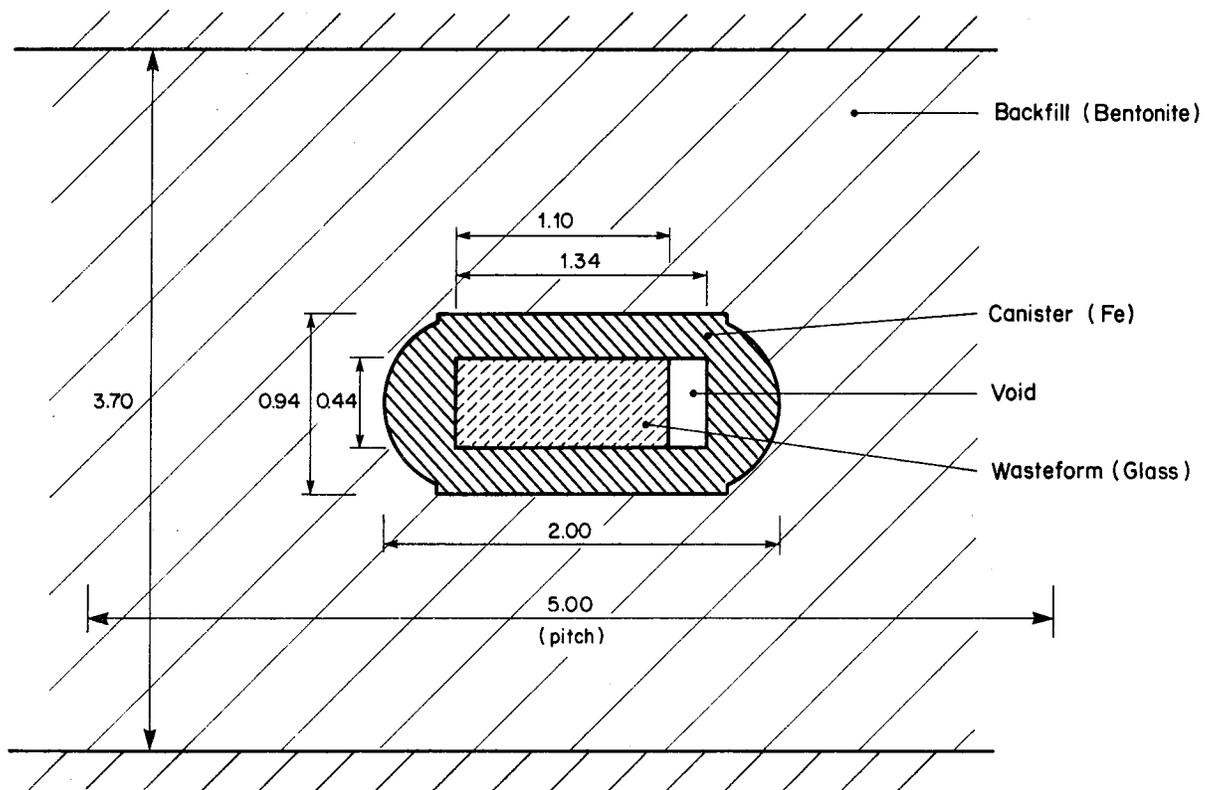


Fig. 1: Reference Swiss disposal geometry (dimensions in metres)

NEAR-FIELD MODELS

The conservative model used to derive source-terms for migration modelling assumes that all waste canisters fail 1000 years after emplacement. The waste glass matrix then dissolves congruently at a rate dependent only on the exposed surface area (10^{-7} g/cm²/day for the base case). A simple computer code evaluates this release taking into account variation in surface area as dissolution progresses, radioactive decay/ingrowth and possible solubility constraints [4]. The solubility calculations assume that the entire water flux through the repository is 'available' for saturation and that effective solubility for multiple-isotope elements is proportional to their relative isotopic abundance in the source at that time. Input solubility limits for the actinides and Tc are calculated for far-field conditions by the thermodynamic equilibrium code MINEQL/EIR [5] while values for other elements are taken from the literature.

A more realistic model of the near-field first requires an evaluation of possible reactions between groundwater and repository materials which allows quantification of engineered barrier longevity and gross variations in water chemistry between different zones in this region. Solubility limits can then

be estimated for near-field conditions. These solubilities can be combined with the previously described glass dissolution model and a more realistically evaluated 'available' groundwater flux to derive radionuclide input functions at the inside of the bentonite backfill. A very simple diffusive transport calculation then allows source-term functions outside the bentonite to be derived. This treatment explicitly includes examination of possible perturbing processes such as radiolysis and colloid formation during leaching or at redox fronts.

GEOCHEMICAL REACTIONS IN THE NEAR-FIELD

The materials used for the engineered near-field barriers are thermodynamically unstable in the presence of host-rock groundwater and resultant reactions will alter the chemistry of both solid and liquid phases.

Reaction of bentonite with groundwater would involve ion-exchange of solution cations for Na⁺ (as sodium montmorillonite is the main mineral component of the reference bentonite), solution pH would increase to a value in the range 7 - 8.5 with an associated decrease in redox potential [3, 6]. Some illitisation of the montmorillonite would also occur but, even if the very slow kinetics of such reaction were ignored, the low rate of supply of K⁺ would limit reaction to \lesssim 2% of the total buffer in a period of 10⁶ y. Both such stoichiometric calculations and observation of natural analogues [7] justify the further assumption that constant chemical and hydrologic conditions prevail within the backfill for periods > 10⁶ years for the base-case scenario.

Based on an empirical corrosion rate of 50 μ /yr, the iron canister is assumed to fail mechanically after about 1000 years but this calculation is very conservative in the extrapolation of laboratory corrosion-rates and pitting measurements to the long timescale involved. Taking into account the additional decrease in corrosion kinetics resulting from the more alkaline conditions realistically expected in the near-field and possible physical or thermodynamic inhibition due to build-up of corrosion product layers or any hydrogen produced by anoxic corrosion [3], corrosion rates at least an order of magnitude lower than the reference value may be realistically expected. Even after canister failure remnant iron and oxy-hydroxide corrosion products would be oxidised only very slowly in the near-field environment and total conversion to a fully oxidised form (eg. Fe₂O₃) would be expected to take > 10⁶ y [7]. In addition, the deep granitic groundwater is actually oversaturated in Fe²⁺ at the higher pH of the near-field and hence continuous, slow precipitation of Fe(OH)₂ (or FeSiO₄) would be expected in this region.

The differences between Eh/pH conditions found in the near-field and those expected on the basis of the geochemical reactions above are illustrated in table 2. Limiting elemental solubilities of some species calculated by MINEQL/EIR are also presented in this table [3, 5] from which it can be seen that a quite significant decrease is observed in near-field conditions for the case of Tc. Although the general applicability of such thermodynamic codes, and even of the entire Eh concept, as applied to low temperature groundwaters has been questioned (eg. [8]), the porous canister corrosion products would be expected to provide an almost ideal redox buffer and thus agreement between

'canister-zone' solubilities and far-field values used in the conservative model may provide an important justification for the latter. Species which may be more soluble in a near-field environment (eg. Pu) are thus identified as worthy of more detailed study if the conservative model assumes solubility limited release. It should be noted that, for many relevant fission product elements, solubility data are even more sparse than for the actinides and the literature values used for modelling are order of magnitude estimates which do not justify analysis of the type above.

Table II

Solubility limits in the near- and far-fields

	Canister	Bentonite	Far-field
pH	7 - 8.5	7 - 8.5	6.8
E ⁰ *	0 - 220	220 - 407	220 - 407
Log Solubility (M)			
Tc	-8	-4.5	-4.3
Th	-8	-8	-7.8
U	-9	-9	-8.6
Np	-8	-5	-8.7
Pu	-3	-6.5	-7.0
Am	-4.7	-4.7	-4.3

* Redox conditions assumed to be given by $E_h = E^0 - 59 \text{ pH (mV)}$
 nb E⁰ = 0 iron/magnetite or H₂/H⁺ equilibria
 E⁰ = 220 haematite/magnetite equilibrium
 E⁰ = 407 ferric hydroxide/siderite equilibrium.

HYDROLOGIC CONSTRAINTS

The conservative model pessimistically assumes that released radionuclides may saturate the entire water flux flowing through the repository and ignores retardation in the bentonite backfill. Radionuclides may then be classified as either solubility limited or matrix dissolution limited depending on which process constrains their release to the far-field.

Current hydrologic models indicate that, for the reference repository, more than 90% of the total water flux occurs in discrete 'kakirite' zones which can be identified and avoided during emplacement. In addition, of the water flowing between emplacement drifts only that within 2-4 m (accounting for the mechanically damaged zone) can be reasonably expected to be available for nuclide uptake [1, 3]. It is thus reasonable to assume that the available flux for nuclide uptake is 2 orders of magnitude lower than the total flux and still conservatively neglect the further reduction in 'available flux' caused by transfer resistances at the glass/canister, canister/bentonite and bentonite/rock interfaces.

Solute transport through the bentonite backfill will occur predominantly by diffusion. From experimental and theoretical studies, the pore structure of compressed bentonite is expected to preclude transport of colloids or suspended particulates [eg. 9] and, based on previous arguments, this situation is expected to persist for $> 10^6$ y. Solute retardation in such a medium is poorly understood at present but, for semi-quantitative calculations, it should be reasonable to assume a constant distribution coefficient (K_d), reversible sorption model [10]. From a simple, infinite porous medium calculation [3], times calculated for breakthrough of 1% of the inner surface concentration at the tunnel wall range from about 1000 years for poorly retarded anionic species (eg. I, $K_d = 0.005 \text{ m}^3/\text{kg}$) to about 10^6 y for strongly sorbed species (eg. Zr, Pu, Am, Th etc., $K_d = 5 \text{ m}^3/\text{kg}$).

The effect of these two processes can be clearly seen if the output profile for the '4n+1' chain derived from the conservative model (Fig. 2a - [4]) is compared to that from a semi-quantitative analysis of this realistic model (Fig. 2b). Retardation delays output to such an extent that some unsupported nuclides decay completely within the bentonite (Cm-245, Am-241). For long-lived species (e.g. Np-237) this delay has little effect on their output concentrations - although in cases where delays $\lambda 10^6$ years occur the significance of further calculations is debateable. In intermediate cases, excess releases of relatively short-lived daughters decay during transit and hence source concentrations to the far-field are at secular equilibrium with long-lived parents (e.g. U-233, Th-229). The nuclide release rate, whenever it occurs, is directly affected by the water flux only for solubility limited species (and their supported daughters) when it is directly proportional to this parameter.

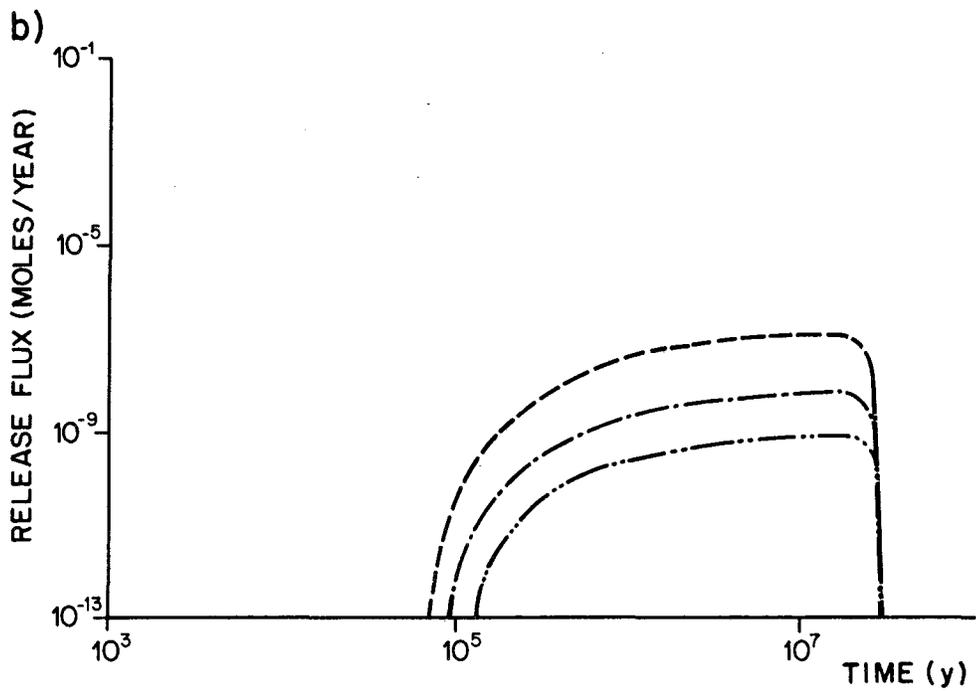
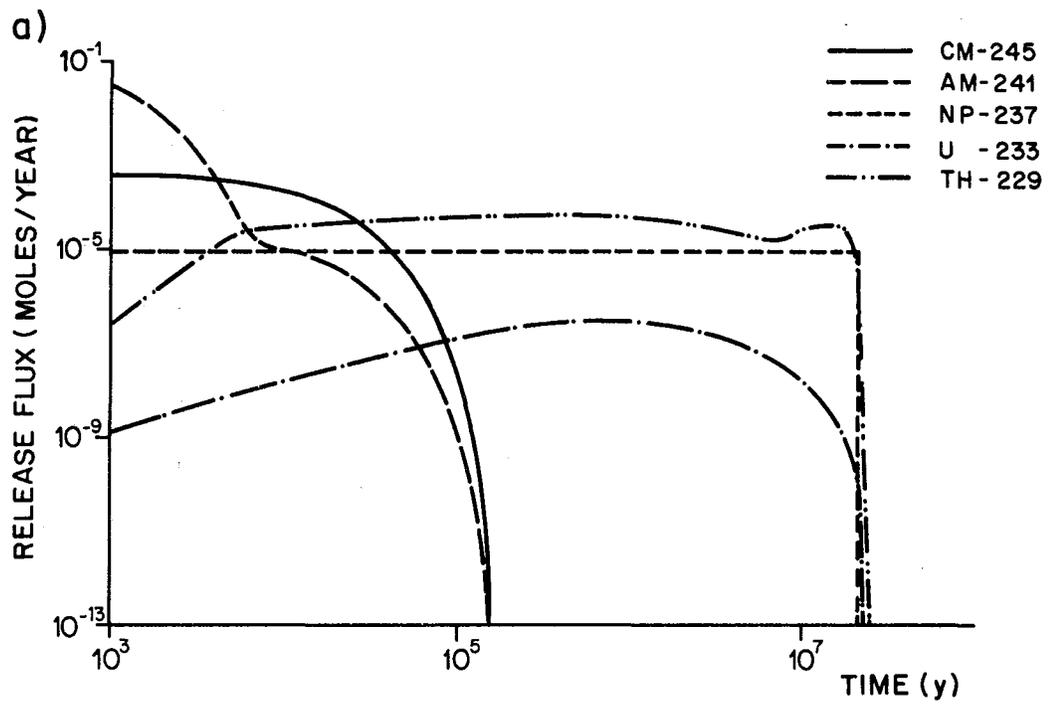


Fig. 2: Radionuclide release rates to the far-field from the entire repository: a) conservative, b) realistic model.

RADIOLYSIS

Although it will not be discussed in detail, the consequences of the radiolysis of water have been considered in evaluating realistic geochemistry. From the assumptions that 1) radiolysis occurs predominantly due to alpha decay, 2) all the energy from 0.3% of all alpha decays in the period $10^3 - 10^6$ y causes radiolysis and 3) that all 'reductant' (H_2) produced is lost to the system without recombination, it was calculated that about 450 moles/canister of net oxidant (represented as H_2O_2) could be produced in the first 10^6 y [3]. Although such radiolysis might cause more oxidising conditions to prevail in the micro-environment of the glass surface, it could be easily buffered by the canister corrosion products (eg. if the entire canister were initially corroded to Fe_3O_4 , this 'radiolytic oxidant' could be consumed by conversion of < 2% of the canister mass to Fe_2O_3). Any redox front formed (eg. [11]) and associated colloidal precipitates would thus be contained within the bentonite barrier. If a redox gradient exists between the glass surface and the buffering corrosion products, net solubility will be determined by the lowest value encountered which could be considerably lower than the 'canister' value in some cases (eg. Pu).

CONCLUSIONS

A simple geochemical analysis of the near-field for the reference Swiss HLW disposal scheme indicates that a chemical environment (reducing, slightly alkaline) will be established in this region which, together with the low availability of water, will limit the release rates of many radionuclides. The physical properties of the backfill - preventing colloid transport and severely retarding diffusion of many dissolved species - will result in many nuclides decaying completely within this region and the release of others being delayed for very long periods. Both these hydrologic and chemical properties would appear to be stable over a timescale of about 10^6 y and any radiolytic effects would be contained within the canister corrosion products and have no influence on far-field release functions.

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A CONCEPTUAL MODEL FOR REPOSITORY SOURCE-TERM EVALUATION

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ABSTRACT

A new source-term model is described that will yield probabilistically determined estimates of the times-to-penetration by various corrosion mechanisms for metallic barriers of waste packages. After penetration, the model evaluates radionuclide release rates as a function of groundwater hydrology, dissolution/precipitation reactions, sorption processes, inventory changes, and variations in the geochemical/radiation environment. Integrated repository releases will be calculated over time by summing the probabilistically generated releases from the individual waste packages.

INTRODUCTION

The U. S. Department of Energy (DOE) is developing a performance assessment strategy to demonstrate compliance with the standards and technical requirements for the safe isolation of high-level nuclear waste (HLW) set by the U. S. Environmental Protection Agency (EPA) and the U. S. Nuclear Regulatory Commission (NRC). The post-closure portion of the performance assessment strategy requires coordination between site-specific research and model development, and expert technical judgment on expected and disruptive scenarios.

Post-closure performance assessment of the geologic repository system can be divided into a Source Term Model and a Contaminant Transport Model (Figure 1). The Source Term Model would be used to estimate the expected range for canister lifetime and containment radionuclide release rates from the population of waste packages, as well as provide input to the Contaminant Transport Model. The Contaminant Transport Model would then estimate cumulative releases to the accessible environment.

This paper focuses on the structure and components of one approach to a Source Term Model. In addition, it identifies processes that should be considered for assessment of the performance of the canister, cladding, and spent fuel components of the engineered barrier system. A companion paper [1]

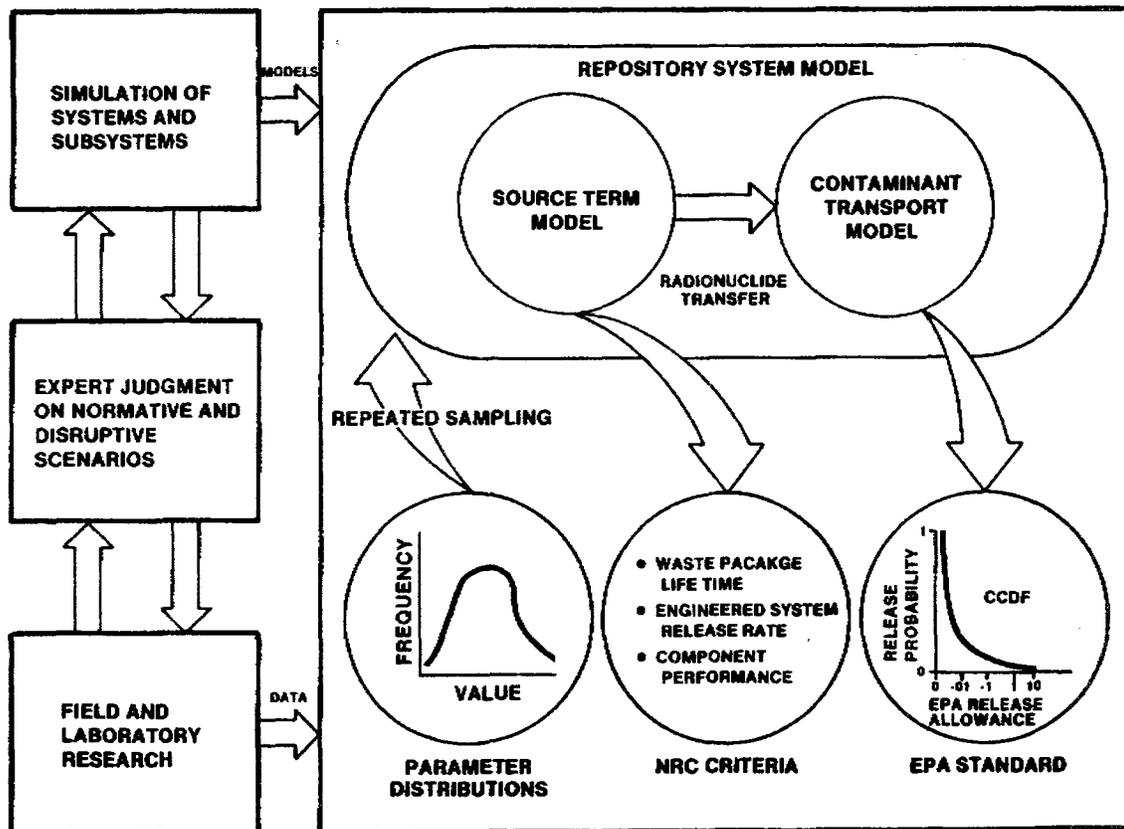


Figure 1. Components of Geologic Repository System Post-Closure Performance Assessment Strategy (after Lyon, 1982)

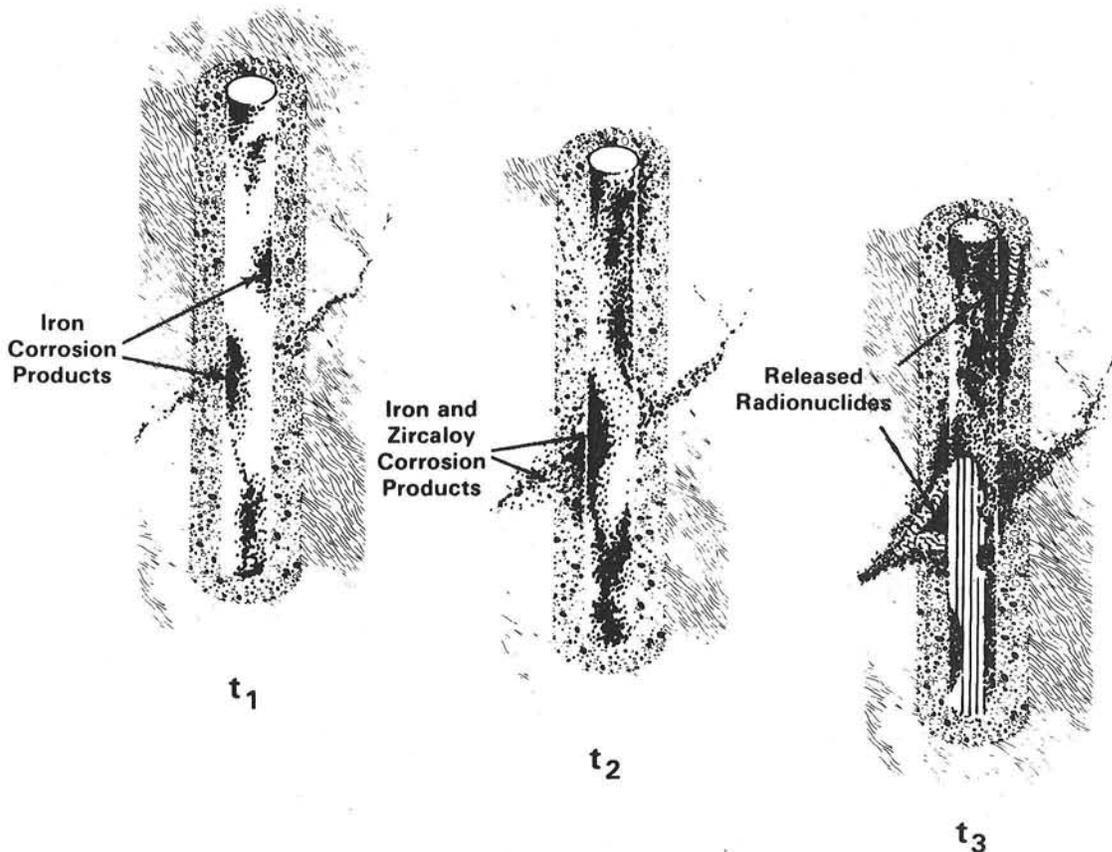


Figure 2. Schematic of Waste Package Barrier Penetration and Radionuclide Release

addresses the need for a broad, inclusive approach to performance assessment and the potential ramifications of such an approach. This Source Term Model (Figure 1) would provide the means to assess compliance with NRC performance criteria for waste package lifetime and engineered barrier system release rate [2]. It is recognized that limitations in data and models may require that such a model be used in conjunction with conservative bounding assumptions on a site- and design-specific basis.

As presently conceived, this model will evaluate radionuclide releases from a realistic waste package/repository configuration, avoiding the physically impossible scenarios that are often called "worst case." There are two components to the Source Term Model. The Barrier Penetration Model simulates water penetration of the container and the Zircaloy cladding before reaching the spent fuel (Figure 2, t_1 - t_2). After penetration of the metallic barriers, the release of waste to the water and migration outward through corroded openings (Figure 2, t_3) will be calculated by a Release Model. Release of radionuclides from the waste package will be controlled by the limited exposed surface area of the spent fuel as well as chemical interactions with primary and corrosion products that will line exit paths. By accounting for these processes and events, a Source Term Model can be used to establish a more realistic failure scenario. Results from this model can also be used to guide the future testing and design modifications in order to reduce uncertainty in performance of the engineered barrier system.

The Source Term Model proposed here differs from several existing waste package performance assessment models such as BARRIER [3] and WAPPA [4] in that it will stochastically estimate the distribution of canister failures and radionuclide releases over time from the total population of waste packages. Similar probabilistically-based approaches have been adopted by the Canadian [5,6] and Swedish [7] nuclear waste repository programs, and proposed for at least one U. S. program [8].

BARRIER PENETRATION MODEL

Model Description

The Barrier Penetration Model is designed to estimate the time-to-penetration of a typical waste package under repository conditions in as realistic a manner as the current state of knowledge allows. For modeling purposes, a barrier is defined as "penetrated" at the time that its net thickness becomes zero at some locale. The barrier penetration event is preceded by a "damage" period and followed by an aperture "growth" period. "Damage" is defined as a reduction in the local net thickness of a barrier via corrosion or fracture propagation. Aperture growth is defined as the subsequent (post-penetration) change in the cross-sectional area of local penetrated regions. Note that aperture growth can mean an increase in aperture size or numbers (as in corrosion processes) or a decrease, as in the plugging of a small fracture by corrosion products.

The corrosion of barriers is linked sequentially in a time-dependent fashion. The time at which the first barrier is penetrated initiates corrosion of the next barrier. In addition, the progress of corrosion for all barriers is tracked by an aperture growth model.

Model Structure

The model is composed of a time-linked sequence of modules, a structure that allows for a widely ranging mix of stochastic and deterministic components and one that is easily modified to incorporate current information. The model is driven by a set of input information that describes the canister, its contents, and the repository environment.

Figure 3 reveals in a general way the modular structure and basic logic of the Barrier Penetration Model. It contains modules that describe the steam corrosion mechanism and penetration models for canister (low-carbon steel in this example) and Zircaloy (Zry) barriers. The modules are ordered in time. The specific model in each depends upon a number of factors, an important one of which is the host medium (basalt, salt, tuff, granite).

The model will perform as follows. Parameters are chosen to describe the repository design, the canister and its contents, and initial environmental and ambient conditions [5,8]. Appropriate probability distributions will be assigned to describe the ranges and variability of initial values of these parameters. A canister is then selected randomly from the "population" of canisters defined by these initial distributions.

Figure 4 shows detail for a possible model of the time-to-penetration of a low-carbon steel (LCS) barrier. Parameters and variables that change spatially and temporally are updated as necessary. The updated values become

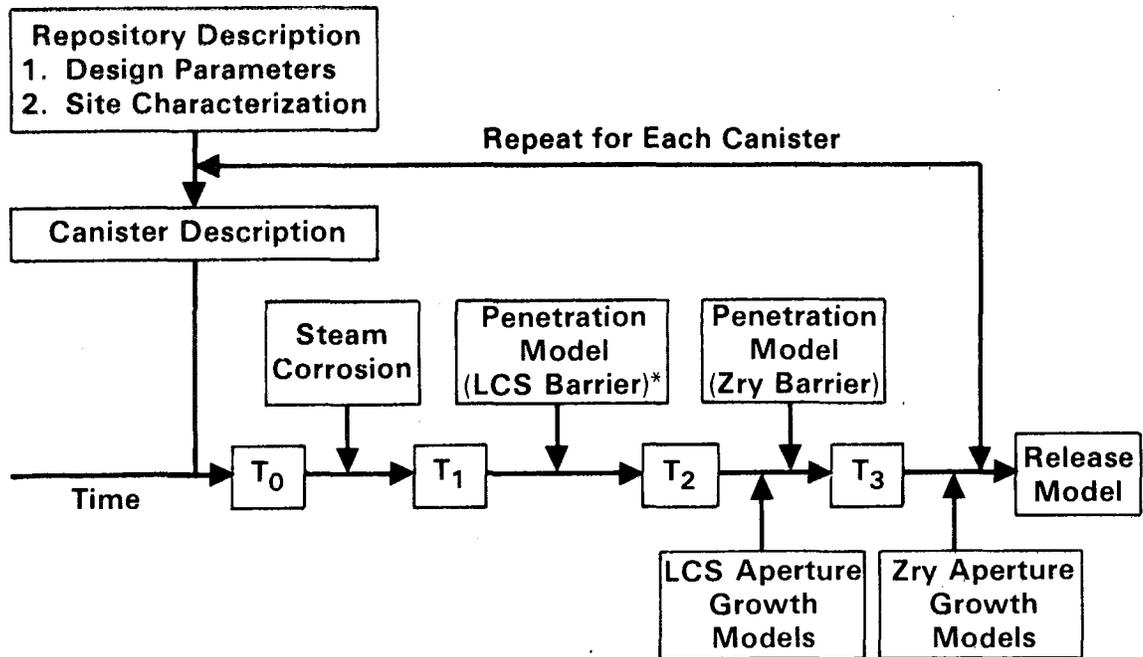


Figure 3. Flow Chart for Barrier Penetration Model

inputs to the LCS corrosion model. Corrosion of the LCS barrier is caused by a number of interdependent, time-dependent physical degradation processes such as uniform corrosion, stress corrosion, pitting, and fracture. All degradation processes are simulated through time until at least one of them results in penetration. A decision as to whether to continue simulation of LCS corrosion can be made at that time. The decision depends largely upon the nature of the model for aperture change (discussed below). The overall model can incorporate different corrosion mechanisms for Zircaloy than for LCS.

A specific example of a corrosion (penetration) rate model is that of Westerman and others [9], who present a model for uniform corrosion of LCS in a salt environment. The authors used laboratory data to develop an equation that relates uniform penetration rate to temperature, radiation dose rate, flow rate, and other parameters. The parameters in such a model can be assigned uncertainties on the basis of best available information from site characterization and design studies. Deterministic models will be used, where available, in connection with estimates of parameter uncertainty. Where suitable mechanistic models are unavailable, probability models (distributions) will be used instead.

Before the Barrier Penetration Model can be implemented, aperture growth models must be developed. For the various barriers, these models specify the nature of corrosion products and how the corroded surface area changes with time; this directly affects the release of radionuclides. A "worst case" model would specify that the area of the failed surface becomes maximal at the time of penetration. For this model, there is no need to track corrosion mechanisms for additional time. A more realistic model would specify the rate of aperture change with time by taking account of the effects of important corrosion mechanism and products. In this case, it is worthwhile to continue simulation of LCS corrosion after penetration of the LCS barrier because the cumulative effect of various corrosion mechanisms could be significant.

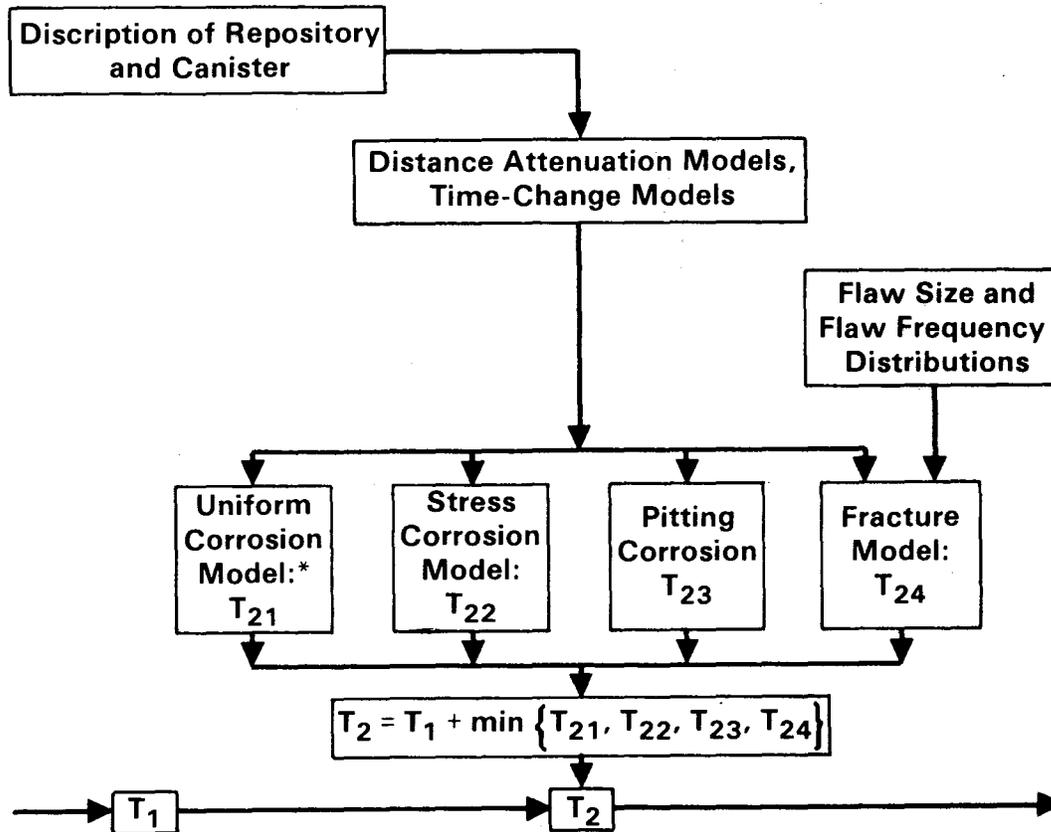


Figure 4. Detail of Corrosion Mechanisms including including Barrier Penetration Model

The model, as presently formulated, will simulate one canister at a time until a repository is developed. This procedure is based on the assumption that the waste packages behave independently; that is, that the penetration of one canister does not affect the penetration times of its neighbors. If this simplifying assumption is determined to be unrealistic, it will be necessary to simultaneously simulate the times-to-penetration of all the canisters in the repository.

The Barrier Penetration Model takes into account not only spatial and temporal variability in geochemical parameters and canister descriptors, but also uncertainties in their initial values. Insofar as possible, parameter values and their uncertainties are estimated from actual data. The alternative is to systematically postulate an array of plausible scenarios and examine their consequences. Models that describe spatial and temporal changes depend, of course, upon the host material and descriptors of both repository and canister design.

Model Inputs

The Barrier Penetration Model will be driven by a number of parameters. Model inputs consist of the set of initial values and uncertainties for these parameters [5,8]. Where appropriate, initial values will be selected from probability distributions that describe the range and variability of the input parameters. The input parameters fall naturally into three classes:

environmental and/or geochemical parameters, repository design parameters, and parameters that describe the canister and its contents.

Environmental and geochemical parameters include the following: host material (e.g., basalt, salt, tuff, granite), temperature, pressure, solid phases, pH, Eh, radiation fields, and groundwater flow descriptors (rates, direction, etc.). Repository design parameters include the following: number of canisters, number and type of engineered barriers, and time of closure. Canister descriptors include the following: dimensions, composition (e.g., LCS) and thickness, waste type (spent fuel, commercial high-level waste), initial radiation, dose rate, initial temperature at centerline, and the probability that a canister contains pre-damaged fuel rods.

Model Outputs

The basic output of the Barrier Penetration Model is a series of stochastically determined times-to-penetration. This output can be described as a point process of canister penetration times. This process depends upon the values established for model input parameters.

In addition, output is structured to understand the factors that affect penetration times and, more importantly, to drive the Release Model. Output for the first purpose includes a breakdown by barrier and corrosion mechanism of the times-to-penetration for the simulated canister. The values of parameters at the time of penetration, which are needed to estimate leach rates and chemical reaction times, are outputs for the second purpose. These parameters include temperature, redox conditions, pH, Eh, F⁻, Cl⁻, and S⁻². Unless aperture growth occurs over a short period of time, a necessary output from the Barrier Penetration Model will be information about aperture growth (composition and growth rates of alteration phases, for example) for use in the Release Model.

The point process of canister penetrations can be used to estimate the probability of canister penetration at any specified time and to give an associated estimate of uncertainty. Such information is crucial to assessing compliance with NRC regulations regarding waste package (canister) lifetime [2]. Moreover, these times can be used in connection with the Release Model to estimate total repository release.

RELEASE MODEL

Model Description

Predicting the rate of radionuclide release subsequent to the loss of physical containment is a vital part of the overall performance assessment of geologic repositories. The purpose of the Release Model is to calculate expected radionuclide releases and subsequent migration for a range of different repository conditions. This model will use the output of the Barrier Penetration Model and additional site-specific data to evaluate conformance to both the engineered barrier release rate limit set by NRC and the EPA limits on radionuclide release from the repository to the accessible environment.

The Release Model within our Source Term Model will be coupled in two parts (Figure 5). The first part represents release and uses a generalized

mass transport theory [10,11], combined with chemical mass balance and mass action constraints within the engineered barrier system, to calculate radionuclide release rates. This first part will be initiated by the output parameters from the Barrier Penetration Model. These include initial environmental conditions, exposed surface area for the waste form from corrosion-aperture growth calculations, and the starting time for waste form/water interaction. The second part, representing migration, will apply subsequent chemical and physical processes that may retard or attenuate the migration of radionuclides within the engineered barrier system. The following sections address the structure of the Release Model and describe the necessary inputs to as well as the desired output from such a model.

Model Structure (Release and Migration)

Previous models for radionuclide release have been published on both a repository-specific [12,13] and generic basis [10,14]. A common aspect of most of these approaches is the use of mass transport theory. This theory has recently been considerably expanded so that exact analytical solutions for waste package performance assessment now exist [10]. Use of such analytical mass transport solutions provides for simple and accurate calculations of

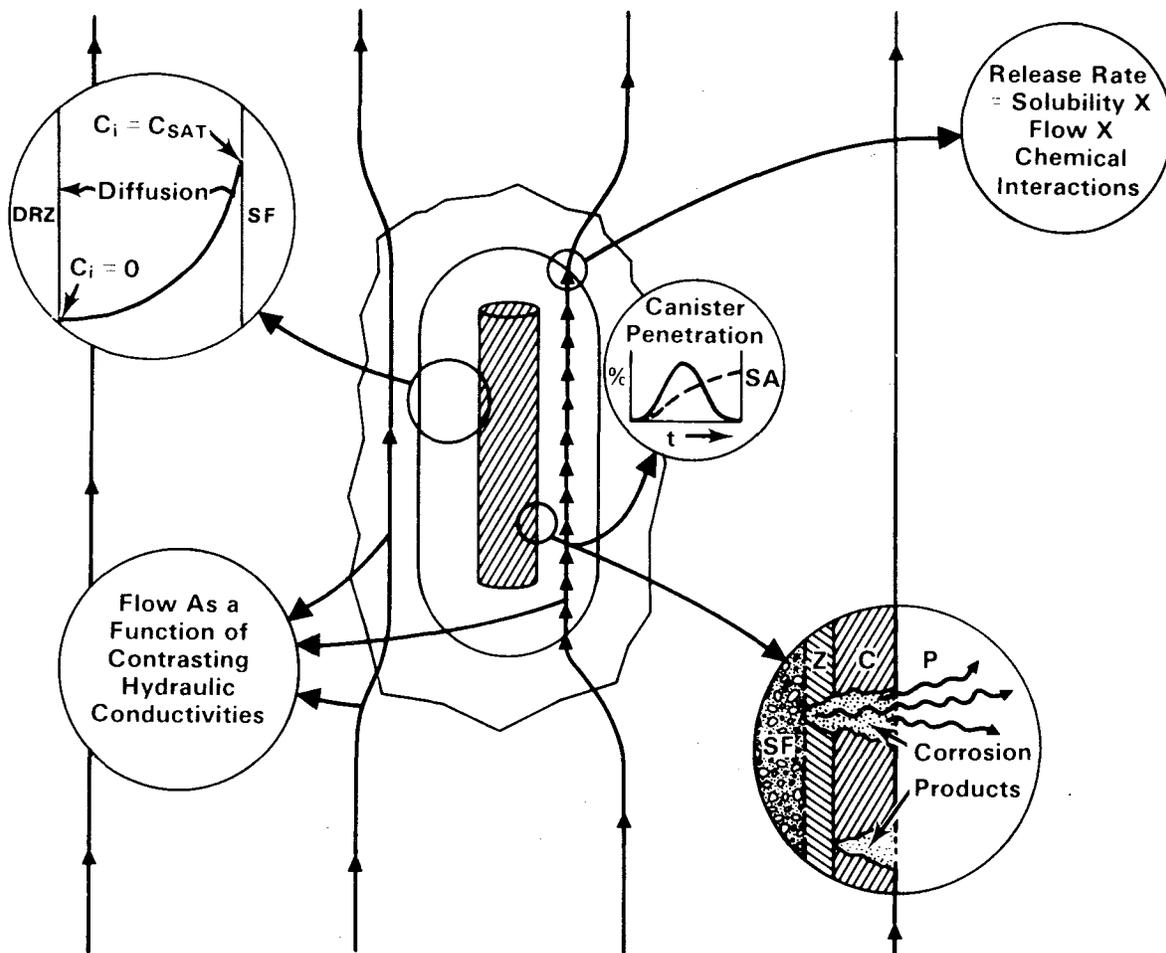


Figure 5. Schematic of Processes Affecting Release Model of Repository Source-Term Model (after Lyon, 1982)

release rates from waste/barrier/rock systems. In addition, this approach can be used to parametrically determine the limits of validity for the model and sensitivity of the results to design and environmental factors. The relevance of mass transport models to the extremely different conditions of proposed repositories (e.g., saturated versus unsaturated groundwater flow, groundwater flow versus brine migration) has recently been addressed, but is not yet resolved [15].

There remain several modifications to present mass transport models that are needed to simulate important aspects of the repository setting. The effect of the extremely limited surface area of the waste form exposed directly to groundwater must be included, and the nature of flow in and around such a penetrated canister should be estimated. The application of saturated flow models to conditions of two-phase flow needs to be addressed. Further review of the approach equating fracture flow to equivalent porous flow is also required. In addition, much of the data on waste form/groundwater interaction does not accurately represent actual repository conditions [10] and are, therefore, of questionable use in mass transport modeling. These limitations notwithstanding, release rate calculations based on mass transport calculations provide a technically defensible and programmatically achievable approach to the assessment of a repository source term.

Upon release from the waste form surface, radionuclides will migrate away by fluid flow or solute transport. Within a homogeneous porous packing (backfill/buffer) material or a water-filled void space around a waste canister, the migration of radionuclides can be expressed by the exact analytical equations previously developed from mass transport theory. Transport within the engineered barrier system may be retarded or attenuated by chemical or physical processes. Mass transport equations modified by several such processes, including radioactive decay and sorption, have been derived for radionuclide migration [10,11].

The effect of reversible sorption on radionuclide migration has been extensively studied [16-19]. Over the relatively short pathways in the engineered barrier system, sorption does not significantly mitigate the steady-state release rate of radionuclides [10]. Exceptions occur for radionuclides with short half-lives (e.g., cesium-137, strontium-90) or with extremely high sorption coefficients. Irreversible sorption (co-precipitation), in which sorbed radionuclides could become incorporated within the sorbing phase (including corrosion products), may also be an important process [18,19].

Colloid formation and transport represents a potentially significant perturbation to mass transport models of radionuclide release and migration [20,21]. If colloidal particles form and are not filtered, they may transport additional radionuclides at the water velocity. Studies of colloid transport through clay and sand packing/backfill materials have demonstrated that physical filtration and aggregation effectively prevent the migration of radionuclide-bearing colloids [20,21]. Furthermore, the general reports of radionuclide concentrations in waste form "leach" solutions filtered through an approximately 400 nm filter undoubtedly includes a large colloidal fraction [22]. Release rates based on such test results would, therefore, overestimate the amount of radionuclides that are truly soluble and transportable. Empirical corrections to radionuclide migration rates arising from colloid transport will be applied, as necessary, on a site-specific basis.

Current radionuclide migration models require improvements in several areas. Relevant waste package and geochemical reactions are typically observed to be at nonequilibrium (or steady-state) conditions, although they are generally treated as controlled by equilibrium solubility constraints [23]. Directly coupled or iteratively coupled migration models linking chemical reactions and fluid flow [24] have been applied to far-field waste contaminant transport, but the data base and code development for application to radionuclide migration are still lacking. Conversely, there may not be a need to incorporate such coupling over the limited dimensions of the engineering barrier system. Coupling of radiolytic reaction rates with geochemical reaction rates may be needed to evaluate potential pH and redox effects on radionuclide solubility and transport.

Model Inputs

The initial environmental conditions used in the Release Model are derived from the output of the Barrier Penetration Model. These correspond to the temperature, pressure, radiation field, groundwater chemistry, etc., at the time of first loss of containment. The results of the aperture growth calculation are also used in the Release Model to determine available waste form surface area exposed to water (or steam), the composition of corrosion products, and the changes in the corrosion aperture with time.

In addition, specific data on properties of waste forms, individual radionuclides, and hydrodynamic parameters are required. These data include: identity of solubility-limiting phases, dissolution rate of waste form matrix at long time periods, sorption isotherms for radionuclides on fresh and altered engineered barrier materials, waste form inventories of radionuclides 1000 years after emplacement, convective flow direction and rate, aqueous diffusion coefficients of radionuclides, and the porosity (or distribution of fractures) in engineered barrier systems.

Model Output

The Release Model will provide an estimate of radionuclide release rates for the overall repository system as a function of time. Integrated engineering system releases for all radionuclides are calculated by summing releases from the individual waste packages that have lost containment (Barrier Penetration Model) and are undergoing slow radionuclide release (Release Model).

The output from this model can be structured to show the progressive effects on the release rate by successively including the distribution of canister failures, time-dependent exposure of waste form surface area, geochemical interaction effects, and radioactive decay in the model. By considering the effects of these separate factors on radionuclide release, it should be possible to evaluate their relative importance and, therefore, to help guide future research and testing.

SUMMARY

As part of DOE's overall HLW repository postclosure performance assessment strategy (Figure 1), a Repository Source Term Model is being developed [1]. This model evaluates engineered barrier system performance stochastically by sampling from ranges of input parameters that vary as a

function of time and of repository population variability. The model simulates canister penetration and aperture growth as a function of time (Figure 5). After canister penetration, Zircaloy corrosion is modeled, estimating cladding penetration and aperture growth as well as the resulting exposed surface area of spent fuel to groundwater. The model simulates the release of radionuclides from spent fuel using mass transport theory and appropriate site-specific constraints. Physico-chemical interactions between migrating radionuclides and engineered barrier materials, including corrosion products of iron and Zircaloy, are also explicitly included in the analysis.

This new model will be used to assess radionuclide releases to the geosphere as a function of the probabilistically determined failures in population of waste packages. The input and overall structure of this model will be flexible to accommodate site-specific features of engineered barrier systems. The model will also permit assessment of compliance with the NRC requirements on waste package lifetime and engineered barrier system release rate, as well as evaluation of importance to safety of system components.

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SUMMARY OF SESSION III: EXPERIMENTS AND SPECIAL EFFECTS

The papers in Session III were all based on experimental studies and generally focused on interpretation of underlying mechanisms of important processes (e.g., radiolysis, dissolution and leachate transport). The Canadian work (Shoesmith) in this area seems particularly significant. It involves the continual development of novel methodology and imaginative planning of long-timescale experiments (lasting several years) that are important in this area of research. The experimental studies themselves can be classified as either simple, in which a single process is examined, or integral, in which more complex and hopefully realistic combinations of processes are studied. From the papers presented, it is evident that these experiment types are complementary and, if coordinated, can yield much more valuable information than either could in isolation.

Two general observations can be noted from the session. First, experimental studies of the near field are extremely medium-site and disposal design-specific. Although some experimental techniques may be commonly applicable, important near-field phenomena for, say, disposal of spent fuel in the unsaturated zone in tuff, mixed I/HLW in salt and vitrified HLW in granite are likely to be very different. Second, despite the elaboration of data requirements by modelers in the preceding sessions, very little direct feedback from experimentalists to model development was evident. In order to specify "realistic" experimental conditions and model processes, much more extensive two-way communication is required. These two considerations bring out the need to tailor each experimental effort to fit both the specific environment and system being studied and the models being used to describe them.

SYSTEM TESTS FOR STUDYING THE RELEASE OF RADIOACTIVITY FROM
HIGH-LEVEL WASTE FORMS UNDER GEOLOGICAL DISPOSAL CONDITIONS

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ABSTRACT

Canadian studies are focused on a multibarrier concept of disposing of high-level wastes in plutonic rock. There has been considerable effort to specify the components of the underground vault and the physical, geochemical, mechanical and radiological conditions of the disposal environment. The post-closure assessment of the disposal concept requires a reliable prediction of the flux of radionuclides from the vault to the geosphere as a function of time. This paper describes the multicomponent system tests and facilities designed to determine the performance of the engineered barriers of the vault under geological disposal conditions.

1. INTRODUCTION

Canadian research and development on the disposal of high-level nuclear waste is currently in a concept-assessment phase. The disposal concept receiving the greatest attention is based on a system of engineered barriers in a deep underground vault surrounded by a massive natural barrier of plutonic rock. The engineered barriers include the waste form consisting of either used CANDU fuel or solidified wastes arising from the recycling of used fuel, a corrosion-resistant container, and an impermeable buffer material surrounding the container. The engineered components will be emplaced in boreholes in the floor of the underground vault. The post-closure assessment of the performance of the vault requires a reliable prediction of the flux of radionuclides at the vault-geosphere interface (i.e. a source term) over a period of thousands of years.

In 1960, researchers of Atomic Energy of Canada Limited initiated a pioneering field test to evaluate the performance of a vitrified high-level waste form in a natural soil-groundwater environment at ambient temperature. Twenty-five, 2-kg hemispheres of radioactive aluminosilicate glass (15 CaO: 9 Na₂O:4 K₂O:20 Al₂O₃:52 SiO₂, wt%) containing 21 TBq (570 Ci) of mixed fission products were buried in a sandy-soil aquifer at the Chalk River Nuclear Laboratories. The release and migration of Sr-90 and Cs-137 has been derived from the record of field data and compared to laboratory leaching studies of a hemisphere retrieved in 1978 [1]. After 15 years of burial, the leach rate of the glass decreased from its initial value by more than 3 orders of magnitude. The field data have been interpreted on the basis of a protective layer on the glass surface [2]. A leaching model has been proposed which describes the loss of radionuclides by diffusion from a nondissolving waste form through an inert mineralized layer into an open water system [3].

In the last decade, the concept of a multibarrier vault deep within plutonic rock has evolved, based on extensive laboratory tests on various waste forms, containers and buffer materials. Today, the experimental program is focusing on multicomponent tests under the conditions anticipated in an underground disposal vault. This report describes the laboratory facilities and equipment that have been constructed at the Whiteshell Nuclear Research Establishment (WNRE) to carry out such tests. The facilities include:

1. lead-shielded cells with remote manipulators for the fabrication and testing of high-level waste forms (located in the WNRE hot cell facility);
2. concrete canisters for interactive tests involving radioactive waste forms and other vault components (located in a canister storage area of the WNRE hot cell facility);
3. concrete canisters containing used UO₂ fuel to study the behaviour of materials in a gamma field (located in the WNRE waste management area);
4. an experimental facility containing used ThO₂ fuel to study the behaviour of materials in a gamma field (located in the fuel storage pool of the WR-1 reactor, a 40-MWt, organic-cooled, D₂O-moderated research reactor at WNRE);

5. an underground research laboratory constructed in plutonic rock in the Precambrian Shield (located on the Lac du Bonnet batholith a few kilometers from WNRE).

2. REFERENCE VAULT CONDITIONS

The physical, chemical, mechanical, radiological and geological conditions expected in an underground vault for high-level wastes will depend upon many factors, including the choice of host rock and engineered barriers; groundwater chemistry; type, quantity and loading of the waste form; and size, depth and configuration of the vault. The anticipated vault conditions are subject to revision as new laboratory and field data are generated and the disposal strategy is optimized. The vault conditions currently assumed in conceptual engineering studies are: borehole emplacement at 1000 m depth in granitic rock; highly saline Na^+ , Ca^{2+} , Cl^- -type groundwater; 10 MPa hydrostatic pressure and 30 MPa lithostatic pressure; high-level waste forms comprising used fuel or vitrified recycle wastes; titanium containers surrounded by a mixture of 50% sand and 50% clay; maximum container skin temperature of 100°C . In the research programs, the effects of variations in parameters and components are being investigated and reviewed.

3. INTERMEDIATE-LEVEL SHIELDED CELLS FOR FABRICATION AND TESTING OF RADIOACTIVE WASTE FORMS

To understand the possible reactions and interactions involving radionuclides, waste forms, container and buffer materials, rock and groundwater, it is necessary to conduct experiments with waste forms loaded with radioactive fission products and actinides. In such experiments, the radionuclides serve as tracers which can be used to help elucidate the processes of dissolution and alteration of the waste form, as well as migration, sorption and precipitation of the released radionuclides.

Irradiated CANDU fuel pellets are readily available in the Canadian Nuclear Power Program and fuel recycle waste forms can be fabricated from limited quantities of high-level liquid wastes arising from small-scale, fuel-recycle experiments. To carry out the fabrication and testing of radioactive waste forms, an experimental facility consisting of five intermediate-level lead-shielded cells has been constructed as an extension of the existing hot cells at WNRE. Each cell (Figure 1) is mounted on a structural steel bench, equipped with remote manipulators, and provided with active drainage, ventilation, process chemicals, vacuum, compressed air, and a Halon fire-suppression system. Shielding is provided by 100-mm thick interlocking lead bricks designed to allow safe handling of a maximum of 590 GBq (16 Ci) of mixed fission products.

Three of the cells (Figure 2) are interconnected with transfer ports and equipped for the fabrication and testing of high-level waste glasses and glass-ceramics. The required operations include feed preparation, melting, annealing, crystallization and leaching. The fourth cell is equipped to study the dissolution behaviour of irradiated fuel in aqueous systems under both static and dynamic flow conditions at temperatures up to 150°C . The fifth cell is provided with titrimetric, colorimetric, potentiometric, ion-exchange and chromatographic equipment for the chemical analysis of leachate solutions. Samples are transferred out of the facility for mass spectrometry, atomic absorption spectrophotometry and radiochemical analyses.

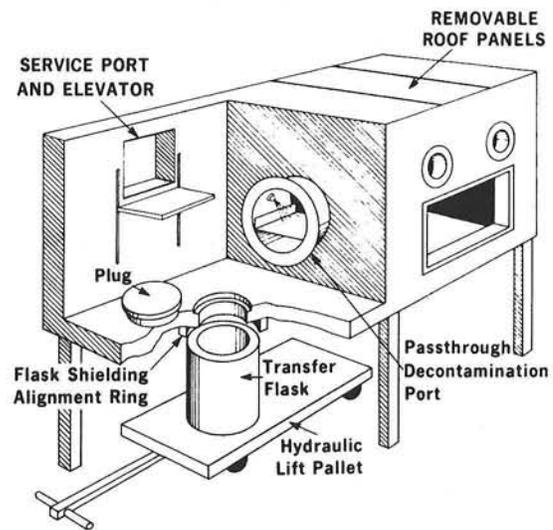


Figure 1: Schematic of a lead-shielded cell for intermediate-level experiments

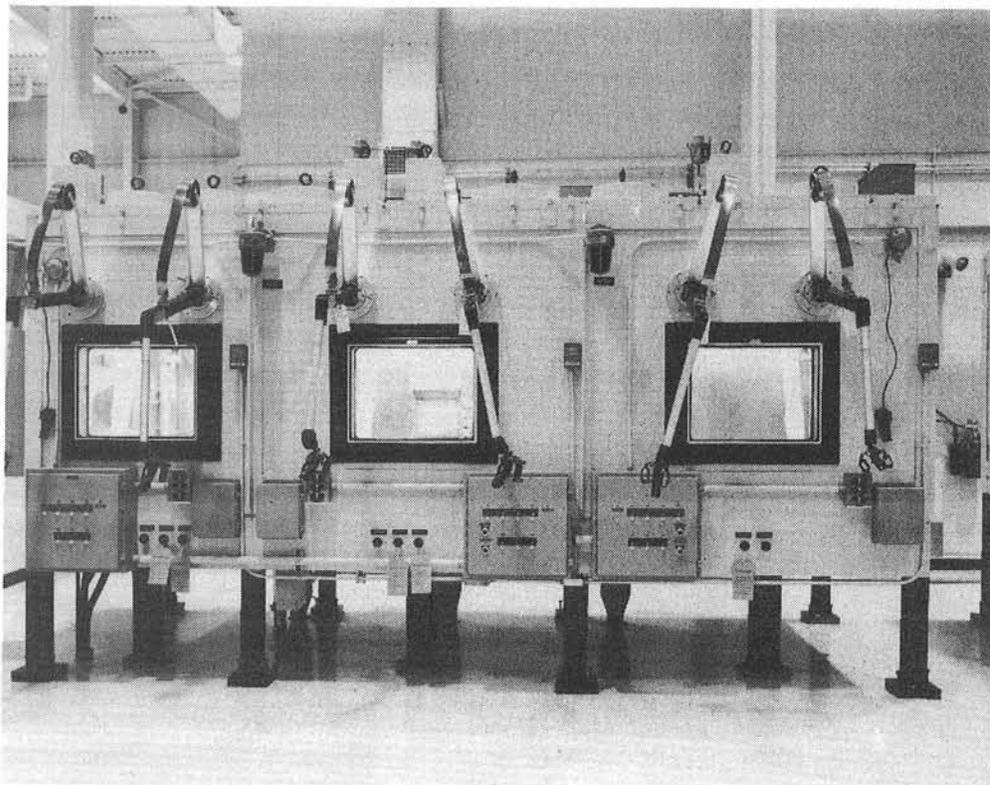


Figure 2: Photograph of three interconnected intermediate-level cells.

4. MULTICOMPONENT SYSTEM TESTS USING SHIELDED CONCRETE CANISTERS

High-activity experiments are being conducted in shielded canisters constructed of concrete and steel. These free-standing modules provide a more cost-effective approach for long-term experiments than the use of space within hot cells. Two types of experiments are being carried out. In the first, described elsewhere [4], an irradiated fuel bundle provides a gamma-field to study the corrosion behavior of metallic container materials. The shielded canisters are designed to accept one 22-kg, 5-year cooled CANDU fuel bundle with a burnup of 860 GJ/kg U (10,000 MWd/MgU) [4].

In the second type of experiment, radioactive waste forms (used fuel and glasses or ceramics loaded with fission products) are sealed in pressure vessels along with other engineered and geological components of an underground vault. The experiments are statistically designed in order to assess the relative importance of the buffer and container materials, the groundwater, and the ratio of the surface area of the waste form to the volume of the solution (SA/V) on the durability of the waste form. Figure 3 is a cut-away drawing of a canister with a removable secondary containment vessel (SCV) and retaining basket designed to accommodate up to 18 individual pressure vessels made from ASTM grade 2 or grade 12 titanium. Figure 4 shows three pressure vessels mounted in a retaining basket in front of the SCV. A piezoresistive pressure transducer is attached to the head of one of the vessels. The S-shaped service penetrations indicated in Figure 3 accommodate a ventilation line from the SCV and electrical leads connecting thermocouples and transducers to a computerized, data-acquisition system. Each titanium vessel is assembled in a hot cell, prepressurized with argon, and loaded into the basket within the SCV as shown in Figure 4. The SCV is placed in the shielded concrete canister according to the procedures described in [5].

Figure 5 shows a schematic cross-section of a pressure vessel lined with a cup fabricated from granite. A "minican" made from ASTM grade 2 titanium holds either used fuel or radioactive glass, sandwiched between pellets of compressed clay and metal discs. This waste package is in contact with groundwater of ionic strength simulating either fresh granitic groundwater at shallow depths, or highly saline groundwater of the type found at 500 to 1000 m depth throughout the Canadian Shield [6]. Thus, the waste package configuration resembles a "minivault," containing all components expected to be present in an actual disposal vault.

Table I gives the range of the variations of the parameters in the statistically-designed experiments. Nine parameters are considered, the last four of which are held constant within one concrete canister.

At the end of each experiment, the leach solutions will be analyzed for fission products and actinides. The surfaces of the waste form, metal and rock will be investigated using a shielded scanning electron microscope fitted with an energy dispersive X-ray analyzer. Surface scrapings from the waste form will be analyzed by a shielded X-ray diffractometer.

From the analytical results, the leach rates or solubilities of nuclear waste forms will be estimated for conditions resembling those in a disposal vault. Also, the parameters which have a major influence on the leaching and dissolution behaviour of high-level waste forms will be identified.

Figure 3: Cut-away of a concrete canister for high-level experiments.

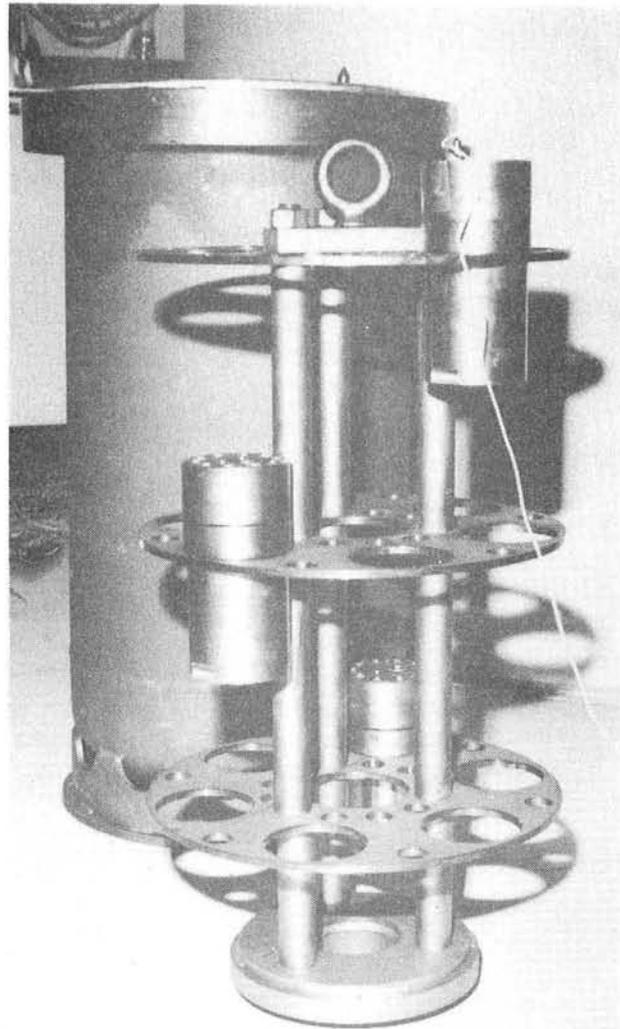
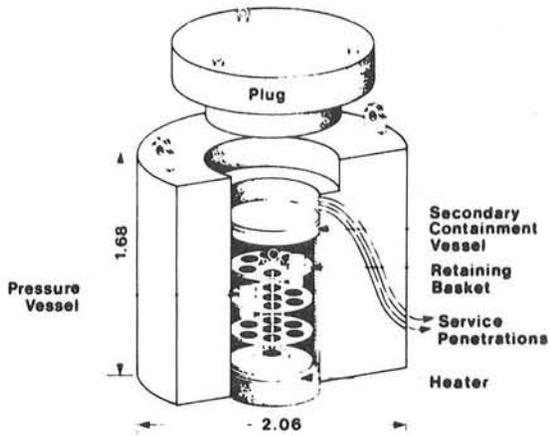


Figure 4: Pressure vessels mounted in a retaining basket in front of a secondary containment vessel.

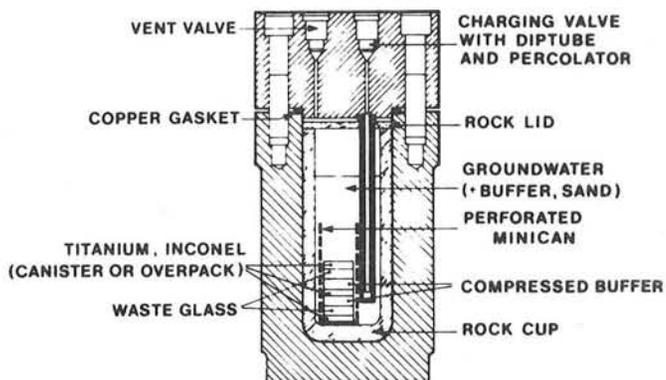


Figure 5: Pressure vessel with "minican" to simulate the components of a disposal vault.

Table I: Experimental Parameters Varied During the Research Project

Parameter		Range of Variation
(i)	Waste form	Used UO ₂ fuel Fuel recycle waste glass
(ii)	Buffer material [7,8]	Ca-montmorillonite (CEC ^a = 1360 meq/kg) Illite (CEC = 160 meq/kg) Na-montmorillonite (CEC = 820 meq/kg)
(iii)	Groundwater [9]	Granite groundwater (I ^b = 1.4 x 10 ⁻³ mol/L) Standard Canadian Shield Saline Solution (SCSSS) (I = 1.37 mol/L)
(iv)	Container material [10]	ASTM grade-2 titanium ASTM grade-12 titanium Inconel 625
(v)	SA/V ratio	12 - 120 m ⁻¹
(vi)	Rock material	Granite Gabbro
(vii)	Pressure	10 MPa (hydrostatic, 1000-m depth) 30 MPa (lithostatic, 1000-m depth)
(viii)	Reaction time } (ix) Temperature }	6 months at 200°C 6 months at 150°C 12 months at 100°C 24 months at 50°C
a) CEC = cation exchange capacity		b) I = ionic strength

5. EXPERIMENTS TO INVESTIGATE EFFECTS OF GAMMA RADIOLYSIS

Several studies are underway to assess the relative importance of solution radiolysis on radionuclide release from candidate waste forms. Since groundwater close to a waste package will initially be subjected to gamma radiation from fission products (principally ¹³⁷Cs), it is necessary to understand the radiolysis processes which could enhance container corrosion and radionuclide release from the waste form by such mechanisms as changes in radionuclide valency or production of reactive radiolysis products.

Several waste forms, doped with U and inactive Cs, Sr and La, were sealed in silica capsules containing the various components of a multibarrier disposal environment (Table II). The capsules were put into titanium pressure vessels, placed in a gamma irradiation facility consisting of a shielded concrete canister with an inner basket holding up to 12 experiments (Figure 6) and heated to 100°C for 485 days. Used UO₂ fuel elements provide a gamma dose rate of 400 R/h inside the titanium pressure vessels. The leachants in the capsules were analyzed for the major constituents and dopants, and surface

analyses were performed on the specimen coupons using secondary-ion mass-spectrometry and scanning electron microscopy. Initial results are given in [11].

A second facility (Figure 7) for studying radiolysis effects is nearing completion. The facility will be located under 5 m water in the fuel storage bay of the WR-1 experimental reactor and will use a hollow-core, fast-neutron, ThO₂-fuel assembly to provide a gamma dose rate in the range of 10⁵ to 10⁶ R/h. A pressure vessel containing sealed experimental capsules will be filled with a thermal transfer fluid and heated to 100 to 150°C. Sealed capsules containing components shown in Table II will be removed periodically so that radiolysis effects can be followed as a function of time. The experiments will investigate the fundamental aspects of radiolysis in simple systems and provide a basis for modelling radiolysis effects under vault conditions.

Table II: Components Used in Gamma-Radiolysis Experiments

Component	Type
Waste form	Glass - aluminosilicate, borosilicate Glass ceramic - titanosilicate
Leachant (~7 mL)	Deionized water Granite groundwater Standard Canadian Shield Saline Solution
Container	Stainless steel Titanium
Buffer	Sodium bentonite clay
Rock	Granite Gabbro
Atmosphere (~0.1 kPa)	Air Argon

6. IN-SITU EXPERIMENTS PROPOSED FOR AN UNDERGROUND RESEARCH LABORATORY

An underground research laboratory (URL) is being constructed in a previously undisturbed batholith in the Canadian Shield near WNRE [12]. Multicomponent experiments on the interactions between nonradioactive waste forms, engineered barriers, granitic rocks and groundwaters will be conducted in the URL. These multicomponent experiments are currently planned to begin after August 1986 when URL construction will be complete.

Metallic containers will be placed in vertical boreholes in the vault floor and separated from the host rock by a compacted clay-based buffer [13]. The buffer material will support the container and minimize the rate at which radionuclides migrate from a breached container to the geosphere. It has been suggested [14] that the principal component of the buffer material should be

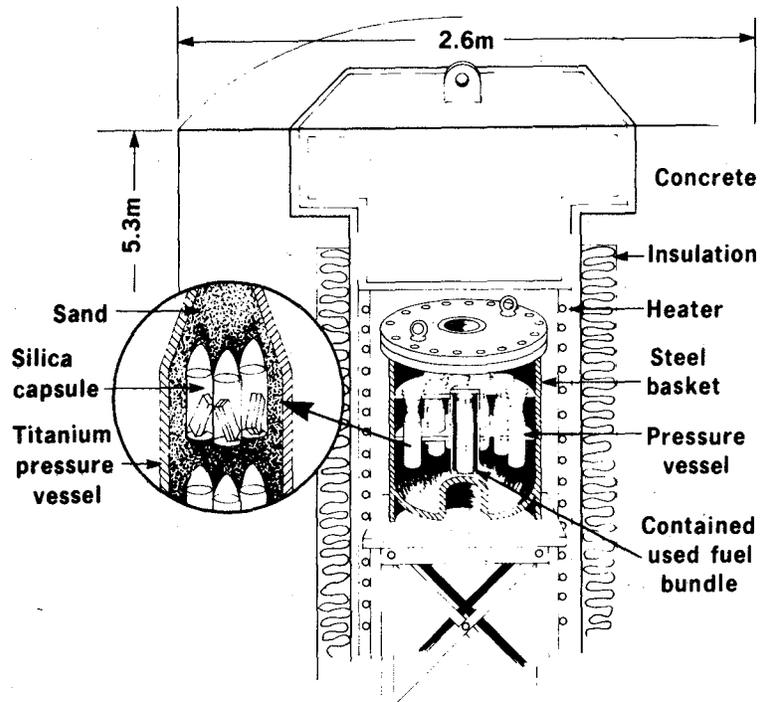


Figure 6: Shielded concrete canister irradiated internally by a UO_2 fuel bundle

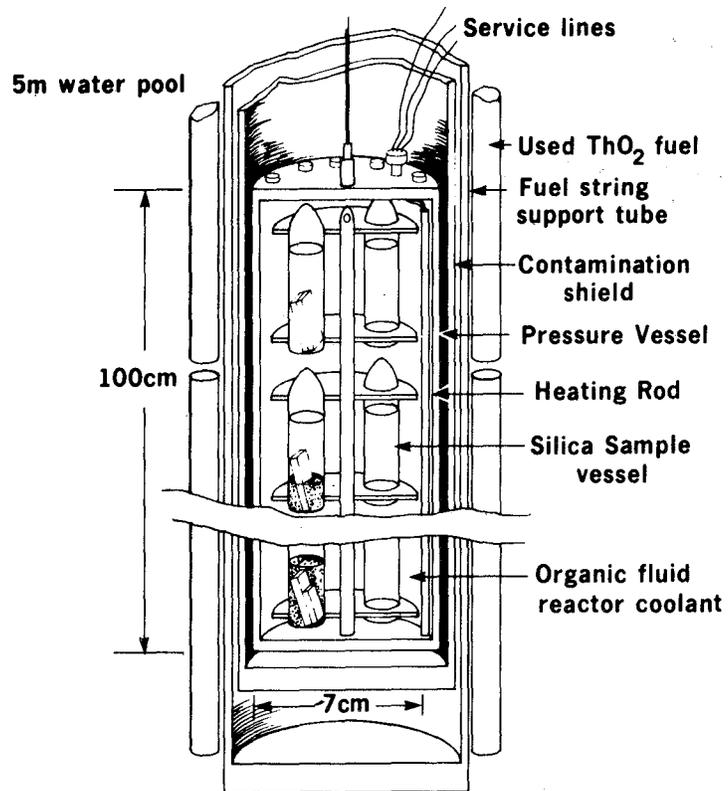


Figure 7: Gamma irradiation facility located in a fuel storage pool for the WR-1 reactor.

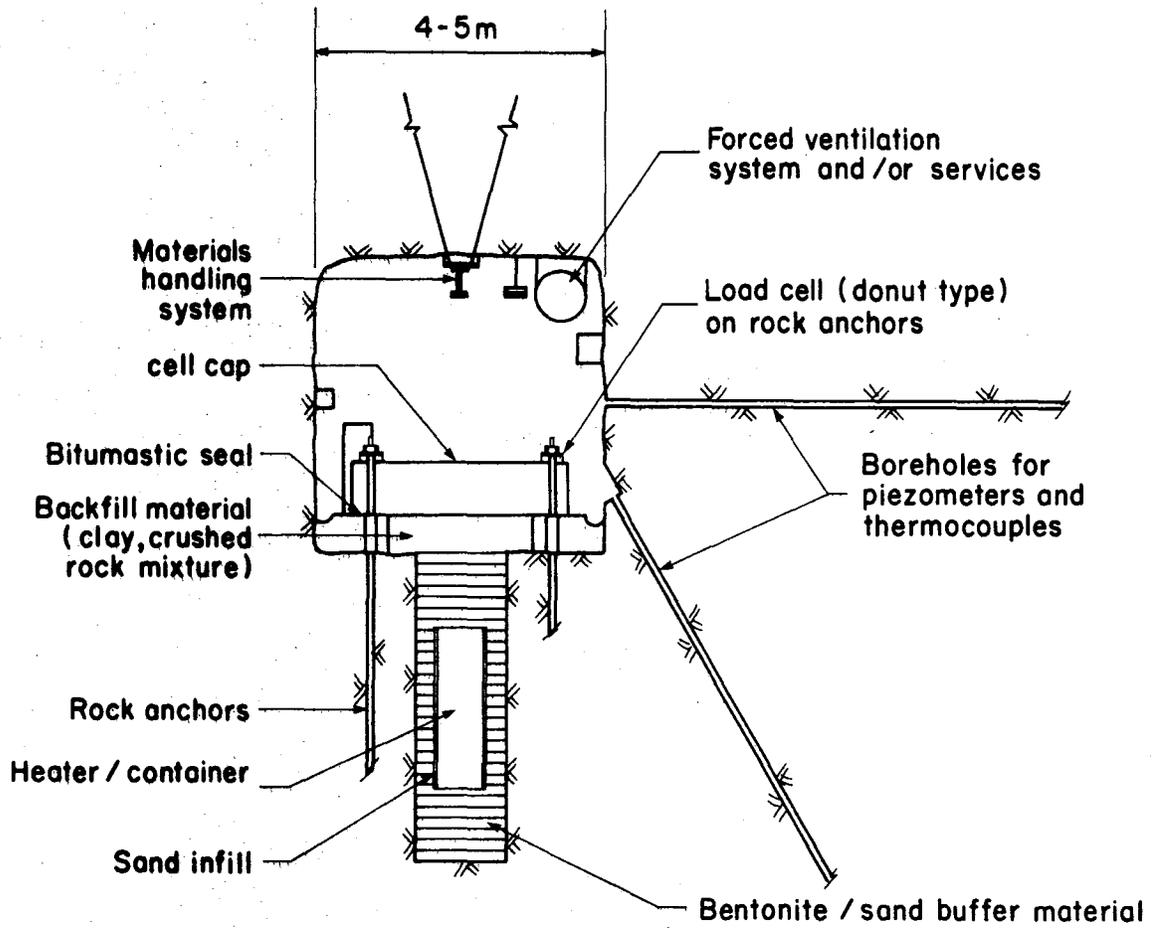


Figure 8: Design for buffer mass tests in boreholes of the underground research laboratory.

sodium bentonite because it retards the migration of radionuclides and swells on exposure to water. Swelling will lead to self-healing if fractures develop in the buffer. Available data [15,16] indicate that the important physical properties of the buffer are optimum when the bentonite clay is mixed with a graded sand in a mass ratio of approximately 1:1.

Tests to determine the nature of the physical interaction between the container, buffer, host rock and groundwater are now being designed for emplacement in the URL. A conceptual design for the first experiment is shown in Figure 8. The granitic rock, the buffer and the container will be extensively instrumented to provide a detailed history of changes in the total stresses, pore water pressures, temperatures and moisture distributions within, and around, the buffer. In addition to the measurements required to describe buffer behaviour, consideration is being given to the inclusion of simulated waste glass coupons within the buffer mass. The coupons will be examined before and after the test by surface-analysis techniques to determine the extent of interaction between the glass and the other components of the experiment.

Alternative test configurations for including waste forms within the buffer material can be considered, provided they do not interfere with the buffer mass tests. For example, it may be possible to include small heated "pineapple" test assemblies, in which glass coupons are placed in contact with various buffer and/or container materials, either within the buffer mass or in a small diameter hole drilled at the base of the emplacement borehole.

7. SUMMARY

Canada has carried out the world's longest field evaluation of a durable active waste glass. Interactive tests involving waste forms, engineered barriers, groundwaters and rocks are being carried out under simulated disposal conditions in shielded concrete canisters. In-situ, nonradioactive tests in an underground research laboratory are being planned. The tests will improve our understanding of the behaviour of the man-made materials in an underground disposal vault and help determine source terms for the environmental and safety assessment of the vault.

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STUDY OF THE RELEASE OF VARIOUS ELEMENTS FROM HLW GLASSES
IN CONTACT WITH POROUS MEDIA

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ABSTRACT

When a borosilicate glass incorporating HLW is embedded in a static porous media the leached elements diffuse into the media. The release of the various elements from the glass is governed by different mechanisms. Soluble elements (such as Cs or Tc) will be released as a direct consequence of the glass degradation. The release of elements which are less soluble than silica, on the contrary, will be dominated by the solubility limit and by the subsequent diffusion in the porous media. An integral experiment has been devised which allows at the same time to measure the leaching rate and the diffusion of the various species in the porous media.

INTRODUCTION

In the description of the release of radionuclides from the conditioned waste it is customary to speak of a near field region. In this region are coupled the phenomena of corrosion, leaching, complexation reaction, diffusion and reprecipitation. It is difficult to define physically the boundaries of the near field. Certainly they comprehend the engineered part of the repository.

Many concepts of final repository are actually at the study. In most of the concepts in between the glass container and the repository wall, a compacted porous material is foreseen. The use of a backfilling porous material is generally accepted for both granite and clay repositories. In the case of clay repository or of a subseabed emplacement even the main barrier is a wet porous material. It appears then that it is worthwhile to study the mechanisms which dominate the leaching of the glass and the release of the various elements.

As far as leaching of the glass is concerned a porous material filled by interstitial water presents aspects which are quite peculiar. The system cannot be considered equivalent to a static condition due to the fact that by diffusion the product released by the glass can migrate. Possible saturation effects depend then on diffusion rate. Nor can it be considered equivalent to a dynamic condition as the migration rate, depending on adsorption and diffusion, varies with the various elements. It appears then that a leaching test specific for glass embedded in a porous media must allow not only to evaluate the glass degradation but also the release and diffusion of the various elements.

PRELIMINARY EXPERIMENTS

In a first study aimed at the understanding of the main mechanism of leaching in porous media, a very simple leaching system was utilized. The glass investigated was a borosilicate glass containing 20% in weight of simulated waste oxides. Its silica content is 48%; the detailed composition is reported in [1].

Different types of wet porous media were utilized. Firstly a series of tests were conducted with a mixture of montmorillonite and sand. Other tests were conducted using a mixture made of montmorillonite, sand and Fe_2O_3 . From these mixtures a paste was obtained using distilled water. A second series was conducted using only sand wetted as before with distilled water. Finally a series of tests has been conducted using red clay sea sediments extracted from the CV2 site wetted by sea water.

The experiments were conducted in glass ampoules in which 30 cc of a dilute paste was introduced. Over the paste an equal volume of water was placed and then the ampoules were sealed. Experiments were performed at 30, 50 and 80°C. Every three weeks an ampoule was removed and the sample extracted. The tests were terminated after 60 weeks. More details on those tests are given in [1].

The weight loss data obtained at 80 and 30°C using distilled water are

reported in Figs. 1 and 2. The data are exposed in a log-log diagram. A linear relationship is the expression of a relation of the type $\Delta W/S = at^n$. As Lutze [2] pointed out a value $n = 1$ is representative of a dissolution attack while a value $n = 0.5$ underlines the predominance of diffusion mechanisms. In the three diagrams are also reported data corresponding to weight losses in slowly renewed water which were obtained previously [3]. We will consider these data as a basis for evaluation if saturation effects are present.

At 80°C it can be seen that the attack of the glass in montmorillonite and montmorillonite + Fe₂O₃ in a first time follows closely that occurring in slowly renewed water. Both seem to follow a dissolution kinetic. After about 100 days the leaching rate changes passing to a kinetic depending on saturation controlled by diffusion phenomena. The glass sample immersed in sand not only shows a lower leaching rate, but also from the beginning, a kinetic dominated by saturation and diffusion phenomena. The relatively high scattering of the data has to be attributed mainly to the very low weight losses. Lowering the temperature the attack in montmorillonite tends to increase in respect to slowly renewed water. We note that the weight losses in montmorillonite are practically the same at 50 and 80°C. In the presence of montmorillonite dissolution seems the predominant mechanism. Tests in sand were conducted at 50°C and showed the same picture as in the tests at 80°C, low attack rate and diffusion predominance.

A first interpretation of this complex behaviour can be attempted considering as a main phenomenon of leaching the dissolution and absorption of SiO₂. In a porous system, we can assume that the interstitial water in contact with the glass reaches rapidly the saturation limit. As a consequence, the silica dissolution rate will be governed by the diffusion of silica in the porous media. For the case of montmorillonite it has to be noted that clay can absorb silica. Following the data of Tau [4] at room temperature the initial Kd value is around 200 cm³/g. As a consequence the silica released by the glass is readily adsorbed by the montmorillonite and the glass behaves like in renewed water following a direct dissolution kinetic.

Only after a certain time, when sufficient silica has been released to saturate the montmorillonite surrounding the glass, saturation appears and diffusion of silica begins to be the rate determining step. Such an effect is easily apparent in the data at 80°C. In montmorillonite at lower temperature the weight losses are even higher than in the case of the slowly renewed water, indicating that probably silica adsorption interferes in the process of the surface gel formation.

The importance of the dissolved silica in the leaching phenomena is underlined by the tests performed with the glass immersed in sand. In this case the interstitial water contains yet an elevated amount of dissolved silica; as a consequence the dissolution potential is lowered and weight losses are very low.

The tests performed with Fe₂O₃ do not differ appreciably from those with montmorillonite. McVay [5] has noted that the presence of iron tends to accelerate the leaching process due to the formation of a highly insoluble silicate. In our case it seems that such an effect is covered by the influence of absorption of the clay. Tests with real corrosion products are needed in

order to verify this point. In Fig. 3 the data referred to leaching in red clay sea sediments are shown. Sea sediments present an interesting phenomenon. At their original temperature (2-4°C) they are in equilibrium with the interstitial water which has an appreciable concentration of dissolved silica, ~ 10 ppm. When tests are performed at higher temperature the system sea water-sediment is temporarily disturbed. At 30 and 50°C the disturbance is not so strong to avoid saturation effects and a diffusion system seems prevalent, but at 80°C, where the unbalance is maximum, a preliminary period of dissolution is noted.

In order to verify if the increase in temperature influences also the tests performed with a mixture of montmorillonite and sand, a test was devised in which the wet mixture was pre-treated for six months at 80°C. Afterwards a test was performed at 50°C as usual. The results are exposed in Fig. 4. It can be seen that the pre-treatment of the mixture changes the kinetic of the weight losses, probably due to saturation effects. It appears clearly that in performing the experiments, care should be taken in trying to be in a condition of equilibrium of the system porous media-interstitial water at the temperature of the test.

COLUMN EXPERIMENTS

Preliminary experiments have shown the importance of diffusion phenomena in the evaluation of the rate of degradation of the glass. Besides, it appeared clearly that it was necessary to be able to evaluate the release of the various elements which are not released congruently. It seemed necessary, then, that the leaching apparatus could allow to measure, at the same time, the diffusion of the released elements.

In the diffusion experiments it is essential to have a well defined geometry of the system in order to be able to apply simple mathematical models. In general a cylinder of the porous matter pressed against a source is used. In such experiments the source term is a sheet of filter paper soaked in a solution containing a radioactive element [6]. Following these lines a design has been developed. In this apparatus a cylinder of porous material wet by its interstitial water is pressed by a piston against a glass block [7]. In order to avoid that the porous material dries during the experiments, it is necessary to keep it in a tight system. For this reason the piston is equipped with two O-rings while in the lower part the porous material is kept tight by the use of an O-ring which is pressed against the shoulders of the crucible. The system is tested at the helium leak detector and it is considered acceptable if it shows a leak lower than 10^{-8} l/s. In order to keep constant in time the contact pressure between the wet porous material and the glass sample, the upper piston is pressurized by a hydraulic system up to a maximum pressure of 2.5 MPa. Every sample is extracted successively every three weeks. The extracted unit is then dismantled in order to recuperate the glass sample.

When the glass is put in contact with the clay the surface layer which results from the leaching process can easily absorb products contained in the clay. As a consequence the weight loss measurements are not very significant. It was decided to evaluate the weight losses after having taken out the gel layer and consider this value as an index of the glass degradation rate. The

cylinder containing the porous material after the test is positioned in an apparatus which allows, using a micrometric screw, to extrude progressively the porous material from the cylindrical body. The extruded part can be sliced, using a blade, and analysed for the diffused elements. This system allows to separate slices of a minimum thickness of 0.5 mm. The slices of clay are analysed by neutron activation techniques.

A preliminary series of tests has been performed using Boom clay at the temperature of 75°C up to a maximum time of 106 days. The glass degradation follows a linear dependence from time. Even taking into account that the surface layer has been removed, the values are rather high and higher by a factor of 5 than those obtained in renewed water. A linear regression gives as a best estimate the following relationship:

$$\Delta W/S = 8.6 \cdot 10^{-5} t \quad (2)$$

If we compare these results with those obtained previously in the ampoule tests it appears that the times of exposure used allow to obtain data referred to periods in which the absorption of the released silica is prevalent. An experimental evidence of the influence of diffusion on the rate of degradation probably needs a longer leaching time.

In order to be able to evaluate the release and diffusion of the various elements it is worthwhile to classify them following their specific leaching rate and their solubility limits. If we assume that the degradation rate is dependent from the leaching rate of silicon, which composes the basic structure of the glass, we can define the following three classes:

- i) elements having a leaching coefficient higher than that of silicon;
- ii) elements having a leaching coefficient equal to or lower than that of silicon and a global solubility limit higher than that of silicon oxide;
- iii) elements having a leaching coefficient equal to or lower than that of silicon and a global solubility limit lower than that of silicon oxide.

In the first class are comprised the alkalis, which can be released from the glass by interdiffusion with H_3O^+ . Cesium is the most important element in this class. However, in normal conditions for complex glasses the release rate due to diffusion is not prevalent in respect to the degradation rate. Only for conditions of advanced saturation alkalis can be released at a higher rate than silicon. We will consider, then, the first class together with the second one.

Elements of the second class, having an elevated solubility, as soon as they are freed from the glass, due to the breakage of the polymeric Si-O-Si network, begin to diffuse. Their release rate will be proportional to the degradation rate of the glass. We have seen previously that in this series of tests the degradation rate is constant during the time of exposure. As a consequence the elements of the second class will be released as a constant flow during the exposure time.

Elements of the third class even if freed by the glass degradation once reached the solubility limits of the various possible chemical species will not be released anymore. The release of the third class, then, will be dominated by the diffusion of the various possible chemical species and will be independent from the glass degradation rate.

The release of the elements of the first and second class corresponds to the diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (3)$$

having as a boundary condition

$$-D \left. \frac{\partial c}{\partial x} \right|_{x=0} = \emptyset \quad (4)$$

where \emptyset is the constant flux at the surface. Assuming that the column is infinite and that thickness of the leached glass is negligible in comparison with the diffusion path, using the method of the Laplace transform, it is possible to obtain the following concentration distribution

$$c = \emptyset/D [\sqrt{2Dt/\pi} \cdot \exp(-x^2/4Dt) - x \operatorname{erfc}(x/2\sqrt{Dt})] \quad (5)$$

The concentration at the interface will be

$$c_0 = 2\emptyset\sqrt{t/\pi \cdot D} \quad (6)$$

The distribution of iron (Fig. 5) into the clay follows closely the distribution described by eq. (5). For elements of the third class the diffusion equation will have the boundary condition

$$c|_{x=0} = c_0 \quad (7)$$

The distribution of the concentrations of the element is given for this case [8] by the following expression

$$c = c_0 \operatorname{erfc}(x/2\sqrt{Dt}) \quad (8)$$

The amount of the element released by the glass is

$$M = 2c_0 \sqrt{Dt/\pi} \quad (9)$$

It has to be underlined that for this class the amount released is independent from the rate of degradation of the glass. The release is governed by the solubility limit of the migrating species and by its diffusion coefficient. Uranium distribution into the clay (Fig. 6) follows closely the distribution described by eq. (8). Cesium shows a high diffusion coefficient in clay so that for the tests made at longer times it was not possible to accept the approximation of an infinite column. The solution proposed by Crank [8] for a sheet having a continuous diffusion flux F at the surface has been utilized. Using a best fitting routine the concentration data for Cs, U, Co, Fe, La, Ce, Eu and Hf have been analysed in order to obtain the corresponding diffusion coefficient. Table I gives the obtained results.

TABLE I - Diffusion coefficients in clay

Element	D (cm ² /s)	Element	D (cm ² /s)
Cs	5.2·10 ⁻⁷	La	1.8·10 ⁻⁹
U	1.2·10 ⁻⁸	Ce	1·10 ⁻⁹
Co	4.8·10 ⁻⁹	Eu	3.9·10 ⁻¹⁰
Fe	2·10 ⁻⁹	HF	7.6·10 ⁻¹¹

CONCLUSIONS

The column experiments allow to study at the same time the leaching of the glass and the diffusional release of the various elements in the surrounding porous media. It appears clearly from the experiment that in considering the glass as a source of the various elements, it is necessary to make a distinction between soluble species, which are released following the kinetic of the glass degradation, and insoluble ones which are released by solubilization and diffusion. For these elements, then, the evaluation of their release is strictly linked to the studies on speciation and to the evaluation of the solubility limits.

A continuation of the study is needed in order to evaluate the influence on the degradation rate of a pre-treatment time at test temperature. The influence of corrosion products on the degradation rate and on the diffusion of the various elements is also to be investigated.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the courtesy of Mr. Bonne (SCK/CEN) for the supply of the Boom clay, the assistance of Mr. Pietra for the nuclear activation analysis, and the assistance of Mr. Saltelli for the analytical treatment of the diffusion equations.

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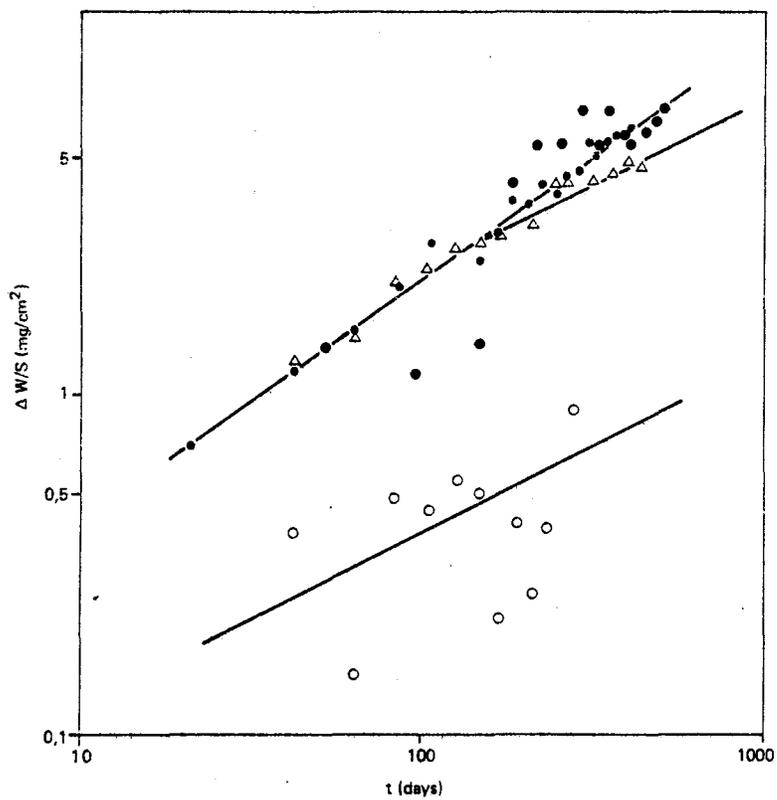


Fig. 1 Specific weight losses at 80°C in various porous media:
 • renewed water; Δ mont + sand; o sand.

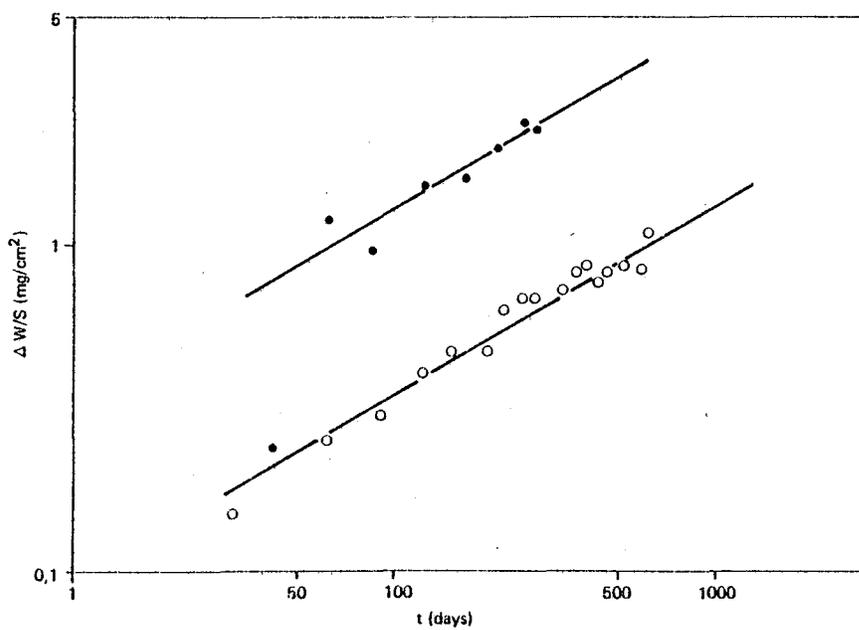


Fig. 2 Specific weight losses at 30°C in various porous media:
 • mont + sand; o renewed water.

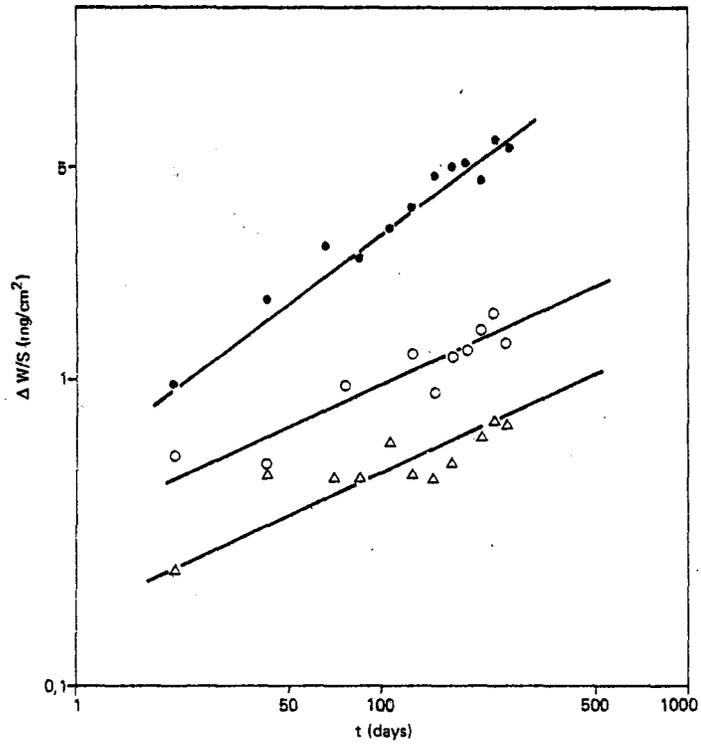


Fig. 3 Specific weight losses in sea sediments at various temperatures: • 80°C; o 50°C; Δ 30°C.

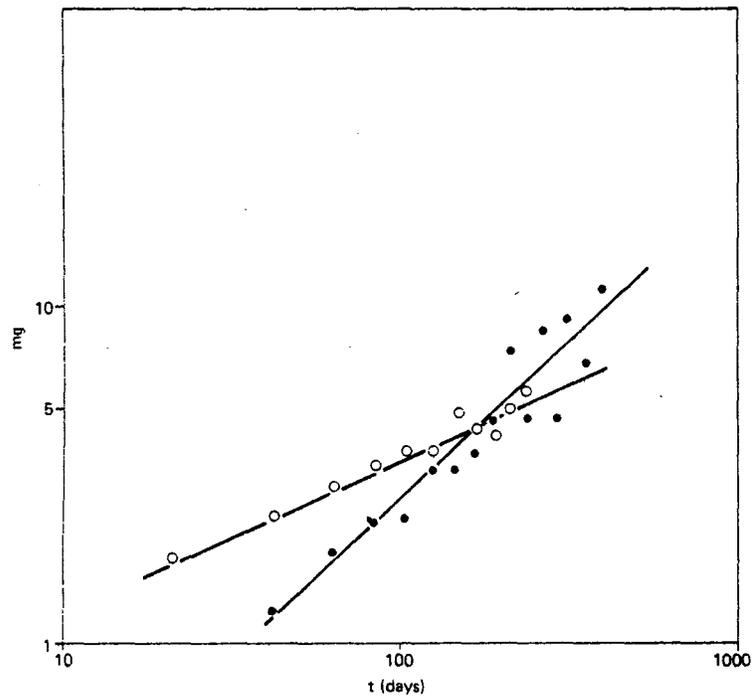


Fig. 4 Leaching at 50°C in montmorillonite sand mixtures: o pretreated at 80°C; • fresh mixture.

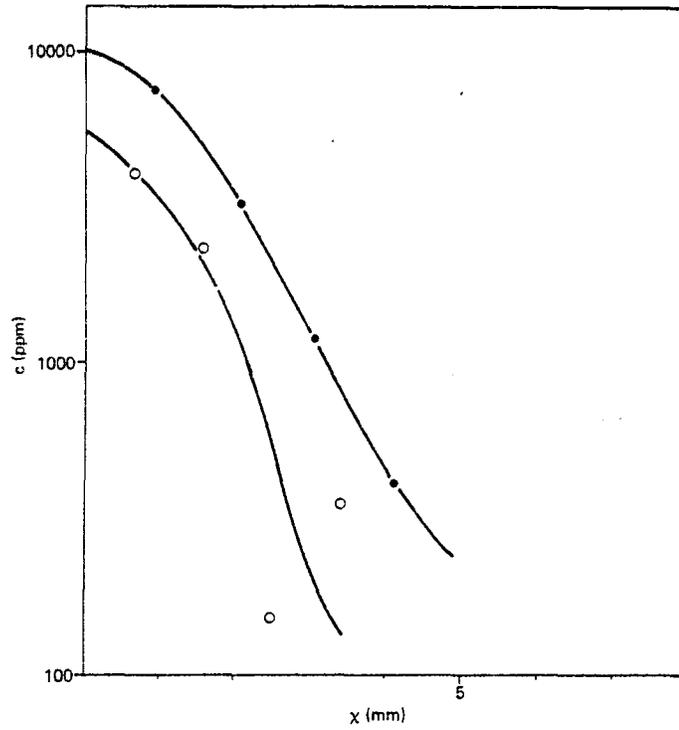


Fig. 5 Diffusion of iron in clay at 75°C after ○ 63 days; ● 106 days.

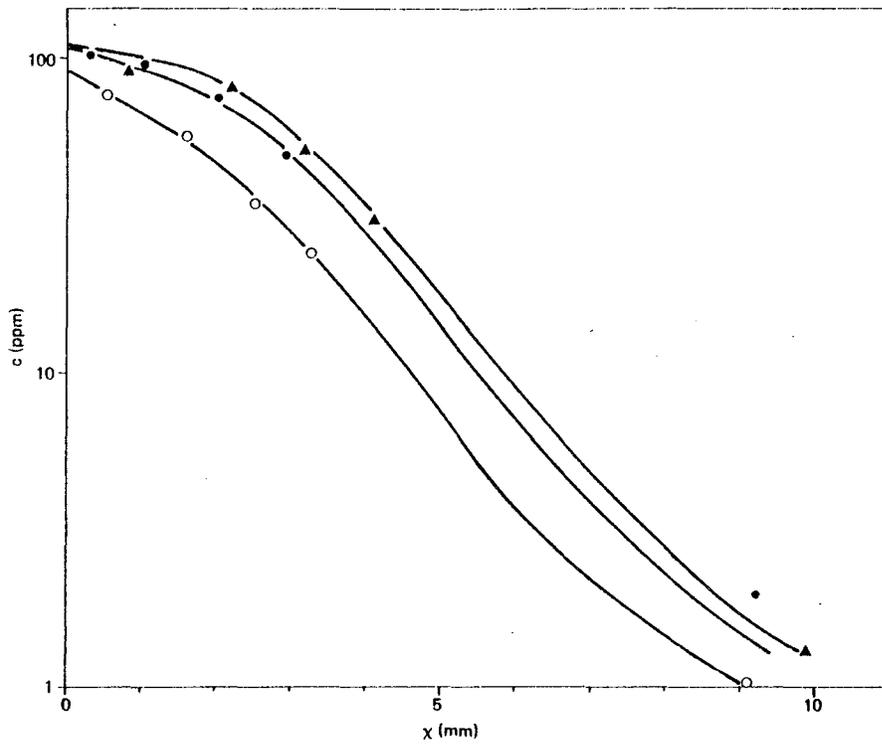


Fig. 6 Diffusion of uranium in clay at 75°C after ○ 43 days; ● 63 days; ▲ 84 days.

LABORATORY SIMULATION OF RADIONUCLIDE GEOLOGICAL MIGRATION

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ABSTRACT

The quantitative description of radionuclide migration in the geosphere demands that the physico-chemical characteristics of species released from the source term are considered.

Laboratory experiments which allowed the identification of the migration mechanisms involved are described; the physical model adopted corresponds to porous media permeated with fresh and/or saline ground water. The waste form considered is the vitrified high level waste and problems connected with the transport of colloidal as well as of soluble species are discussed following a theoretical and experimental approach.

1. INTRODUCTION

The dispersion behaviour of radionuclides in the geosphere depends upon their physico-chemical characteristics and two main classes may be identified : colloidal and soluble species. For the soluble species, the interactions will be dependent upon the valence state and speciation of the nuclide while for the colloidal species the size distribution and the electric charge carried by the particles governs their retention.

The programme being undertaken by the Joint Research Centre at Ispra in the field of geochemical interactions concerns the laboratory simulation of the release and transport through the geosphere of radionuclides leached from vitrified HLW.

Conditions existing around the Boom clay formation in Belgium and the Gorleben salt dome in Germany have been chosen as reference cases. In both cases migration towards the biosphere, following release from the repository, may occur through porous argillaceous formations surrounding the disposal site. It is this porous material that is being used in laboratory percolation experiments.

The working methodology adopted is based on a type of feed-back loop established between simulation experiments, physico-chemical forms determination and model development.

In laboratory simulation experiments, the leachant solution flows over a borosilicate glass containing the nuclide to be studied and then through a column containing the geologic material. At intervals the column is disconnected and the activity profile recorded by gamma-scanning. Percolation experiments under normal atmospheric conditions (oxic conditions) or in special boxes under nitrogen containing 0.1% CO₂ (anoxic conditions) are performed in order to control the effect of the redox potential of the system.

2. Results and discussions

2.1. Salt rock disposal option

In the salt system condition, the leaching solution (a saturated brine of composition reported in TAB.I), is in equilibrium with the porous geologic material. Figure 1 reports the contamination profiles of Americium (oxic conditions), for three different loading volumes, in a column filled with a typical soil overlying the salt rock dome (95% silica, 5% consisting of clay material, magnetite and rutile) . The observed trend suggests the existence of a saturation effect. Figure 2 shows the breakthrough curve which confirms the saturation of the retention capacity after 250-300 days.

The retardation factor R_f determined from the ratio between the velocities of the water and of the radionuclide or from the ratio of the total activity retained in the column to the activity at the outlet at saturation, ranges around 200. The corresponding K_d term consequently assumes a value of 53 ml.g⁻¹.

The batch Kd measured at the same Am concentration of the column influent (75 ml g⁻¹) is in good agreement with the partition coefficient determined from the column parameters. This fact suggests that sorption reactions are at equilibrium in the column; the slightly higher Kd in the static system may be a consequence of the break down of soil particles during the shaking procedure (1).

The same experiments performed with Neptunium doped glass, under oxic conditions, gave similar results showing that sorption phenomena are the result of reversible equilibrium reactions in this case also. A linear sorption isotherm, corresponding to a Kd of 8, was in fact determined from which the same retardation factor of 29 obtained by column data was derived. This indicates an equilibrium reaction but a weaker retention in respect to Americium. In percolation experiments with Neptunium under anoxic conditions, the activity retained by the column increases by a factor 4 corresponding to a R_f of 119. Figure 3 reports schematically the breakthrough curves for the various cases studied.

The results of batch experiments reported in figure 4 were compared with the curve shape given by conventional sorption models.

The least square analysis of the Langmuir equation

$$\frac{1}{K_d} = \frac{1}{bK} + \frac{C_{Am}^{eq}}{b}$$

gave the best fit allowing the evaluation of the apparent binding energy K which results in 8,1.10¹¹ l. mole⁻¹ for Am and several orders of magnitude lower for Np. The adsorption maxima b of the soil material were also evaluated and compared with the column data. For the Am leachate concentration of 10⁻¹⁰ M, the value obtained has the same order of magnitude (3.6-7.6.10⁻⁹ m.mole. g⁻¹) in both cases indicating the total saturation of the available sites, while for the Np leachate concentration of 1.5.10⁻⁷ M column saturation is reached below the adsorption maximum. Definite quantitative data for Neptunium are not yet available.

The differences observed in column behaviour result from the different characteristics of the interacting species. Owing to the difficulties associated with a direct identification of soluble chemical forms of Americium and Neptunium, the equilibrium distribution of species was determined from literature data, taking into account only homogeneous chemical reactions. Table II gives a summary of the stability constant values at 1M ionic strength for Americium and Neptunium interaction with the major inorganic ligands in brine. The available data refer to ionic media different than those of interest in this study. The assumption that the activity coefficients do not vary with ionic strength above 1M is an approximation, due to the lack of any reliable model in predicting such a dependence.

The computer modelling output suggests that Am(III) should exist mainly as a mixture of the first two chloro-complexes in brine. Figure 5 shows how the percentage of americium chloro-complexes (AmCl₂⁺ + AmCl₂⁺) in a 5.4M Cl⁻

ions solution, varies with pH and $\sum \text{CO}_2$. The complementary volume represents the sum of americium carbonate complexes.

The partitioning of the Np(V) soluble species is reported in figure 6 from which it appears that, apart from the Neptunyl ion, the only complexed form present in saturated brine solution is the neutral NpO_2Cl species. The stronger interaction of Americium compared with Neptunium with active sites of the soil is clearly the result of the higher ionic potential of Am soluble species.

2.2. Clay disposal option

In the case of the clay disposal system, a flow of water having composition reported in Table I leaches the simulated vitrified waste and then percolates through the columns filled with the porous strata overlying the Boom clay.

The flow corresponds to a linear velocity of about 27 m per year. The sand layer has 34% porosity, a permeability of about 10^{-4} m/s and contains 20.8 % of glauconite clay mineral.

In parallel with column percolation experiments, ultrafiltration tests of the glass leachate through membranes having different porosities were carried out. For the case of Americium the results of filtration experiments are shown in figure 7 while in figure 8 the column profiles in molar units are reported for three different loading volumes. The Am content in the water at the column outlet reached the value of $(3.5 - 6.6) \cdot 10^{-13}$ M very rapidly at the beginning of the loading phase and remained constant throughout the experiment while the leachate inlet concentration was fixed at $3.8 \cdot 10^{-10}$ M.

The large percentage of Am retained on the filtering membranes suggests that the transport is largely dominated by the colloidal species; it is also evident from the smooth shape of the curve in figure 7, that the colloid size is better described as a distribution rather than as a single value. If the trend of the size distribution is assumed to be representative also of the distribution of the filter coefficient in the classical filtration equation (2), a satisfactory fit is obtained between theoretical and experimental data. This is reported in figure 9 for the 170 days percolation experiment. This confirms that for a convective fresh water system the predominating process of retention in a porous medium is colloidal filtration.

For percolation experiments shorter than 170 days, a plateau at Am concentration $2 \cdot 10^{-10}$ M appears in the final portion of the column. This plateau shows two apparently contrasting features a) it is established very rapidly (within 28 days), and b) it does not increase with time. The existence of the plateau cannot be due to the activity in the interstitial water because a concentration factor of about 10^3 between the plateau and the outlet concentration exists. If this retention were due to colloid filtration we should observe an increase of the plateau with time, which is not the case. It must also be considered that the Am, soluble plus particulate, concentration in the interstitial water is not constant within the column, varying between the inlet value of $3.8 \cdot 10^{-10}$ M and the outlet of $5 \cdot 10^{-13}$ M, mainly as a

consequence of the filtration mechanism. The Am interstitial concentration tends to increase with time as the pulse moves within the column.

As the plateau is much likely given by soluble adsorbed species rather than filtered microcolloids, the constancy of the Am concentration on the plateau suggests that the adsorbed Am has reached its saturation value, and it is not affected by any further increase of the Am concentration in the liquid phase. This phenomenon can be described by a Langmuir isotherm. With this assumption it is possible to verify (2) that a column outlet concentration of $5 \cdot 10^{-13}$ M can be reached very rapidly even if the concentration factor is close to 10^3 .

The column migration pattern of Americium in its various physico-chemical forms present in the leachate is therefore governed by the fixation of the colloidal fraction in the first layers of the column. The behaviour in the remaining portion of the column is the result of the migration of soluble species and their sorption capabilities. A distribution diagramme of Am soluble species as a function of pH for a chemical environment typical of the clay aquifer has been developed (3) and is reported in figure 10.

Under "field conditions" the colloidal fraction will be retained after some meters (or tens of metres); only soluble forms will migrate in a region far from the source and the various soluble ions will be in equilibrium among themselves. When AmCO_3^+ and $\text{Am}(\text{CO}_3)_2^-$ migrate in equilibrium, the overall Am-pulse should travel with an average retention factor governed by the ratio of the equilibrium concentration of the two complexed species present (4).

3. Conclusions

With column simulation experiments three predominating processes have been identified:

- colloid filtration governed by a distribution of values of filter coefficient; this process is particularly effective during the percolation of a fresh water leachate through a porous formation
- a sorption phenomenon adequately described by a Langmuir isotherm; the Americium species reach the maximum adsorption value in both systems analyzed while for Neptunium a linear sorption isotherm was determined for the salt aquifer
- escape of unretained species; experimental evidence indicates that in the case of fresh water aquifers, a small fraction of Americium in the form of carbonate complexes flows through the column with very little retention. In the case of a brine aquifer the chlorocomplexes interact with geologic material through equilibrium reactions resulting in retardation factors of 204 and 29 respectively for Americium and Neptunium.

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TABLE I

Major Ion concentration in the solution used (Molar Units)

	BRINE SOLUTION	CLAY AQUIFER
Na ⁺	5.48	2.4 · 10 ⁻³
K ⁺	1.9 · 10 ⁻³	2.0 · 10 ⁻⁴
Mg ²⁺	1.1 · 10 ⁻³	1.3 · 10 ⁻⁴
Ca ²⁺	4.1 · 10 ⁻³	7.6 · 10 ⁻⁵
Fe(tot)	-	1.8 · 10 ⁻⁶
Cl ⁻	5.48	1.8 · 10 ⁻⁴
SO ₄ ²⁻	5.6 · 10 ⁻³	5.2 · 10 ⁻⁶
ΣCO ₂	10 ⁻⁵ · 10 ⁻⁴	3.4 · 10 ⁻³
pH	4 - 6	8.35

TABLE II

Stability Constant Values in the Speciation Modelling

<u>Species</u>	<u>log β</u>
Am OH ²⁺	6.1
Am (OH) ⁺	9.48
Am Cl ₂ ²⁺	0.487
Am Cl ₂ ⁺	0.033
Am CO ₃ ⁺	5.81
Am (CO ₃) ₂ ⁻	11.8
Am OH (CO ₃) ₂ ²⁻	15.9
NpO ₂ OH	5.1
NpO ₂ Cl	0.4
NpO ₂ CO ₃ ⁻	4.6

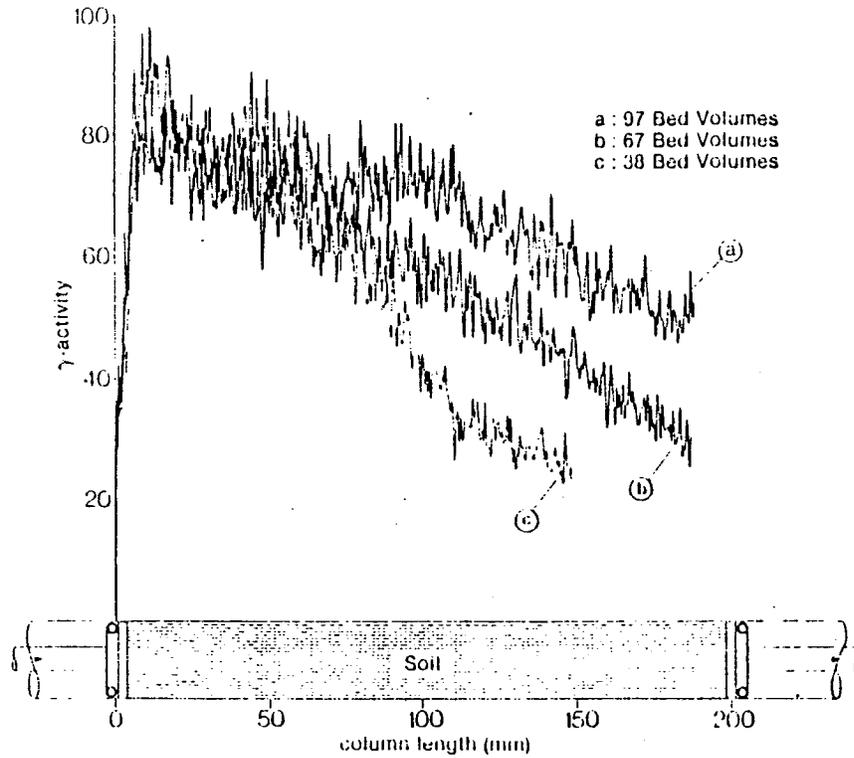


Figure 1 : γ -scanning profiles of the soil column loaded with ^{241}Am glass leachate at different bed volumes of brine solutions.

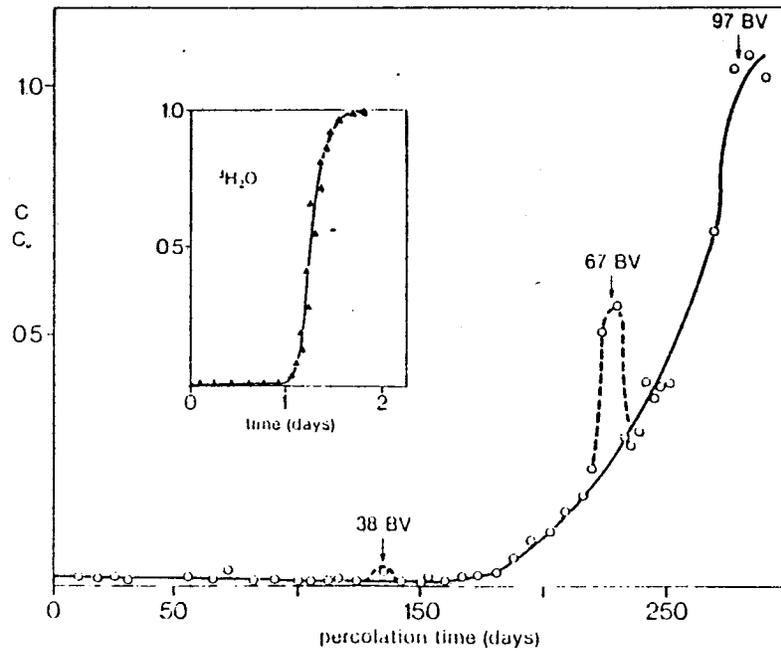


Figure 2 : breakthrough curve of the brine Am leachate (the peaks shown correspond to activity redistribution inside the column during the scanning operation)

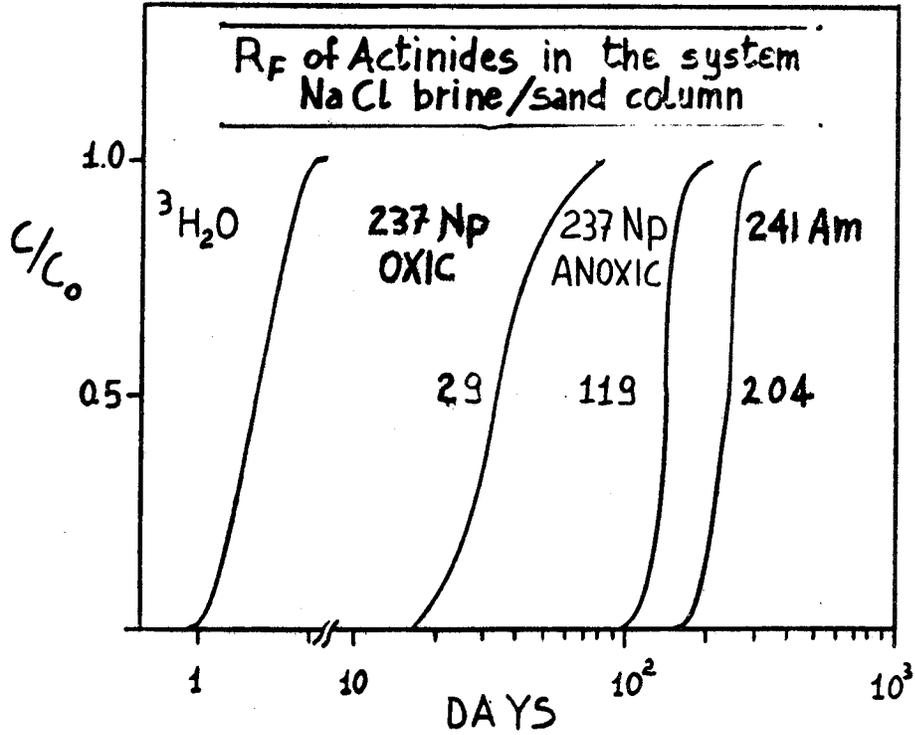


Figure 3 : breakthrough curves of Am and Np for the various situations studied

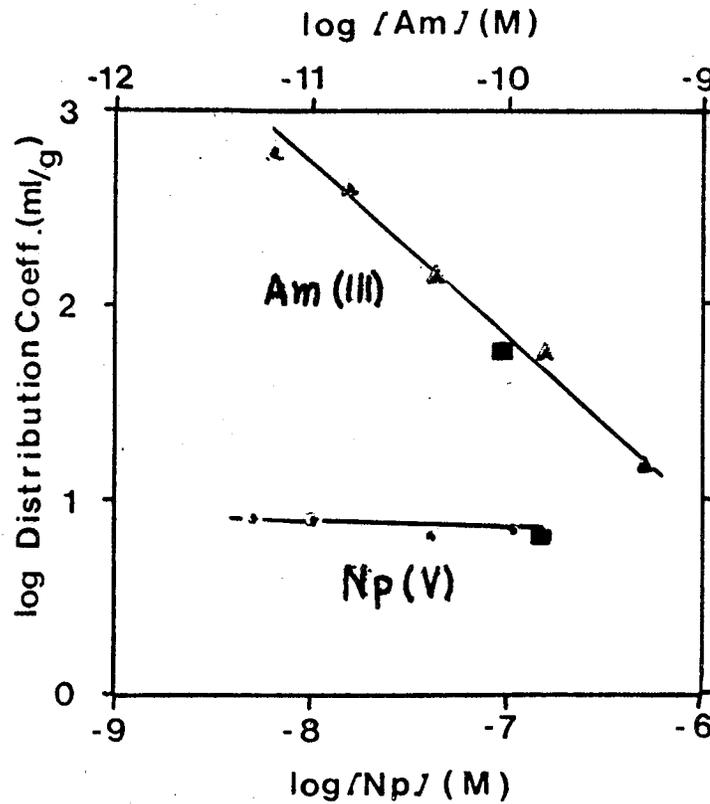


Figure 4 : Adsorption isotherms of Am and Np (square points correspond to column influent concentrations)

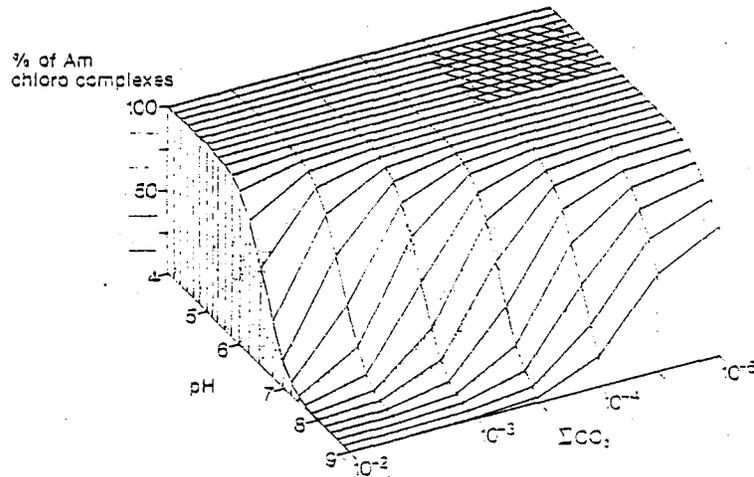


Figure 5 : Influence of pH and ΣCO_2 on the amount of Am-chloro complexes $\text{AmCl}^{2+} + \text{AmCl}_2^+$ in a brine solution ($\text{Cl}^- = 5.4\text{M}$)

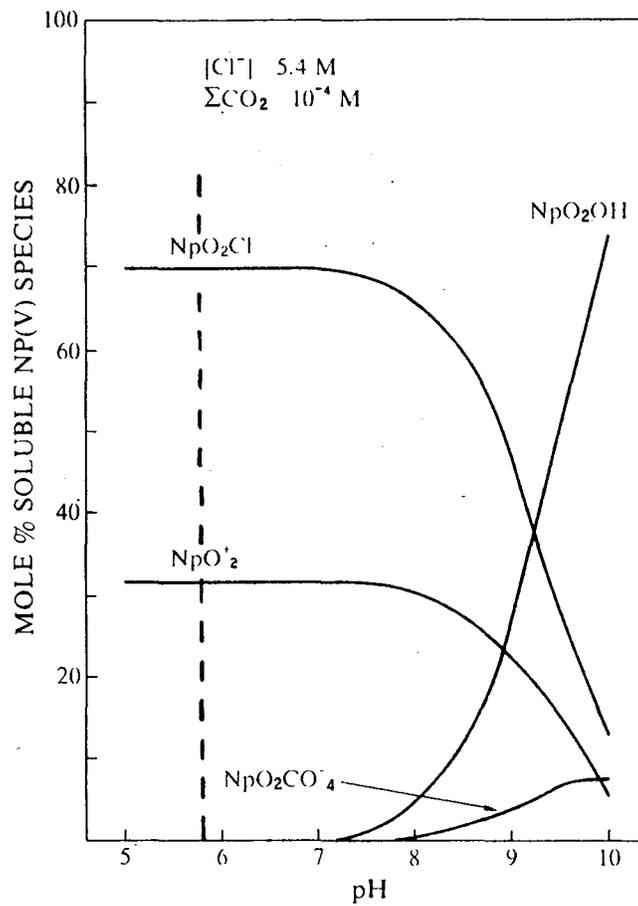


Figure 6 : partitioning of Np(V) soluble species in a saturated brine solution

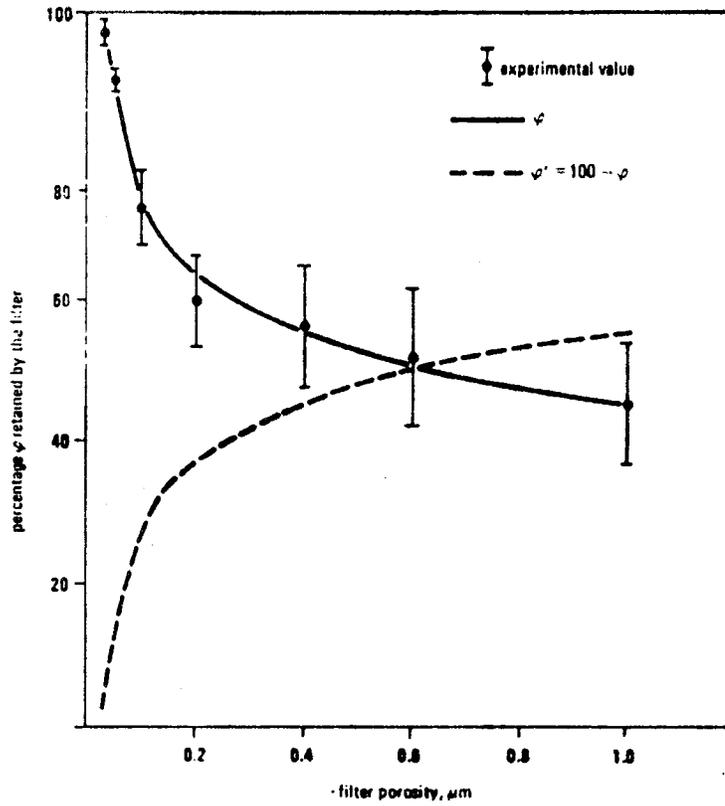


Figure 7 : retention of leached Americium versus filter porosity

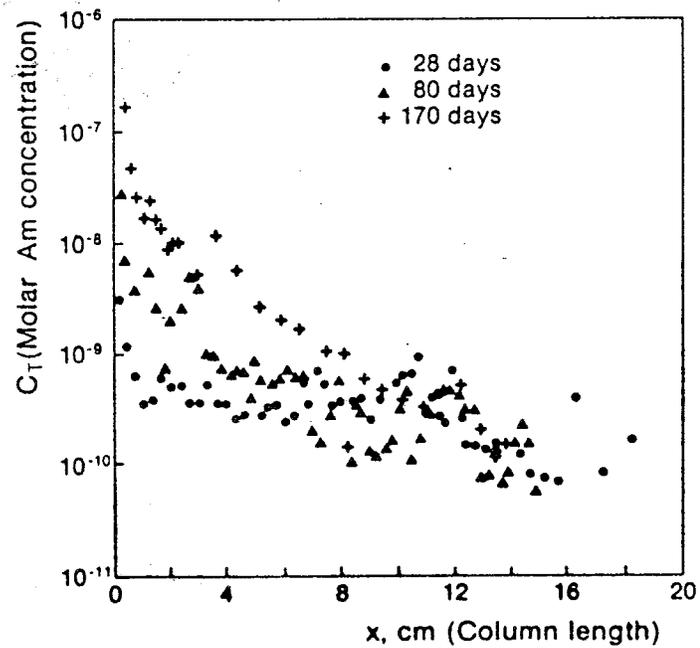


Figure 8 : Americium column profile for three percolation experiments of different length

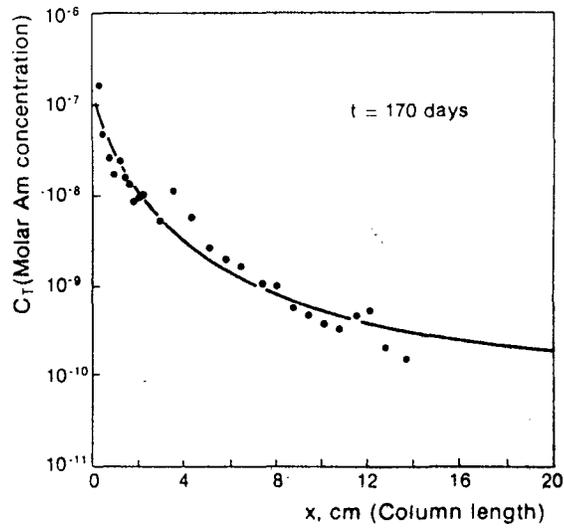


Figure 9 : Americium filtration pattern, comparison between experimental and theoretical data

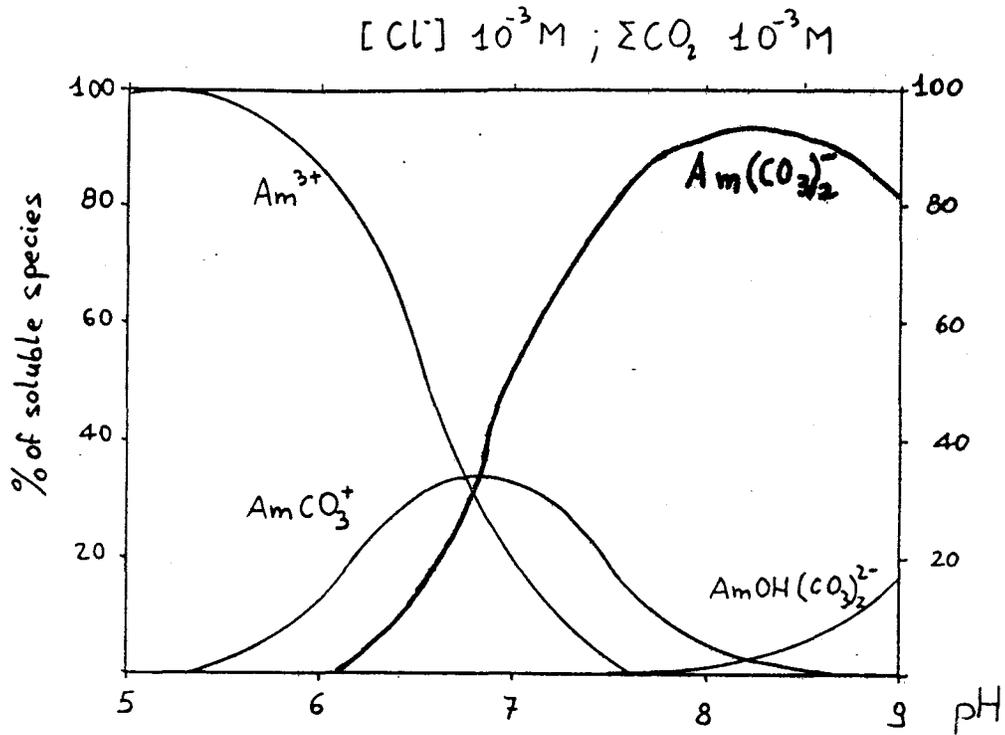


Figure 10 : Distribution of Am soluble species as a function of pH for a chemical environment typical of a clay aquifer

LABORATORY EXPERIMENTS DESIGNED TO PROVIDE LIMITS ON THE
RADIONUCLIDE SOURCE TERM FOR THE NNWSI PROJECT

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ABSTRACT

The Nevada Nuclear Waste Storage Investigations Project is investigating the suitability of the tuffaceous rocks at Yucca Mountain Nevada for potential use as a high level nuclear waste repository. The horizon under investigation lies above the water table, and therefore offers a setting that differs substantially from other potential repository sites. The unsaturated zone environment allows a simple, but effective, waste package design. The source term for radionuclide release from the waste package will be based on laboratory experiments that determine the corrosion rates and mechanisms for the metal container and the dissolution rate of the waste form under expected long term conditions. This paper describes the present status of laboratory results and outlines the approach to be used in combining the data to develop a realistic source term for release of radionuclides from the waste package.

RÉSUMÉ

"The Nevada Nuclear Waste Storage Investigations Project" est en train d'étudier la pertinence des rochers en tuf dans la montagne Yucca en Nevada pour son utilisation possible pour le stockage définitif des déchets radioactives. Le terrain, sous investigation, se situe au-dessus de la nappe aquifère et offre donc un emplacement qui diffère notablement d'autres lieux de stockages possibles. Cette zone d'environnement non-saturé nous permettrait de désigner un conteneur simple et à la fois effectif. La "source term" pour l'émission de radionucléides du conteneur des déchets se sera basée sur des expériences de laboratoire qui détermineront le taux de corrosion et les mécanismes nécessaires au conteneur métallique, ainsi que le taux de dissolution des déchets dans des conditions prévisibles à long termes. Ce papier décrit le statut présent des résultats de laboratoire, et décrit l'approche qu'on utilisera en combinant toutes les données pour développer une "source term" réaliste aux fins de minimiser la relâche de radionucléides du conteneur des déchets.

INTRODUCTION

The Nevada Nuclear Waste Storage Investigations Project is studying the tuffaceous rock formations at Yucca Mountain, Nevada, to determine the suitability of these rocks for construction of a high level nuclear waste repository. The horizon that is under investigation is the Topopah Spring Member of the Paintbrush Tuff, a welded, devitrified ash flow tuff. At Yucca Mountain, this unit lies in the unsaturated zone. The water table is approximately 150 m below the potential repository horizon in the center of the repository exploration block.

The unsaturated setting results in several conditions that are different from the more familiar circumstances for a repository designed for siting below the water table. Some of the important design considerations for the unsaturated zone include:

- (1) The waste package will not be in contact with standing water under anticipated conditions;
- (2) The waste package will not be subjected to lithostatic or hydrostatic load;
- (3) The maximum temperature of liquid water that can contact the waste package is determined by the unconfined boiling point of water at the appropriate elevation (95°C at Yucca Mt.);
- (4) Water influx will be limited to that available through downward infiltration (rainfall minus evapotranspiration);
- (5) The waste packages will be in contact with air;
- (6) Container and waste form degradation will occur in air-steam and dripping water environments.

WASTE PACKAGE ENVIRONMENT and WASTE PACKAGE DESIGN

The welded, devitrified sections of the Topopah Spring tuff consist of a fine grained intergrowth of quartz, cristobalite, and alkali feldspar, with a small proportion of phenocrysts. Phenocryst minerals are quartz, alkali feldspar, plagioclase, and biotite [1]. Samples of water have not been obtained yet from the unsaturated zone tuff at the repository level; these samples will be obtained during the construction of the exploratory shaft. Pending availability of unsaturated zone water samples, the water from Well J-13, which is located several miles to the east of Yucca Mt., has been adopted as the reference ground water for NNWSI experimental work. The well is at a lower elevation than Yucca Mt. and the Topopah Spring tuff, which is below the water table at this elevation, is the major producing horizon for the well.

Experiments have been conducted to determine the potential changes in water chemistry due to interaction of the rock with J-13 water at elevated temperatures [2]. The expected upper limit temperature for liquid water in macroscopic openings at Yucca Mt. is 95°C; however, the capillary forces in pores may allow rock and water to equilibrate at somewhat higher temperatures. To account for this possibility, the rock-water experiments have been conducted at temperatures of 90, 120, and 150°C. A summary of the predicted steady-state water chemistry as a function of temperature is given in Table I. The bicarbonate content of J-13 water is approximately 140 ppm. Carbonate/bicarbonate following reaction with the rock depends on the partial pressure of carbon dioxide and the pH. The other anion components are those originally present in J-13 water: F = 2 mg/l, Cl = 7 mg/l, NO₃ = 9 mg/l,

and $\text{SO}_4 = 18 \text{ mg/l}$. There is no significant source of these anions in the rock, so concentrations are independent of temperature.

TABLE I: Estimate of Steady State Water Chemistry for Topopah Spring Tuff and J-13 Water as a Function of Temperature

Element	Concentration in mg/l at			
	25°C	90°C	120°C	150°C
Al	0.01	0.4	1.2	1
B	0.13	0.1	0.1	0.1
Si	27	49	81	122
Ca	12.5	8	3.5	3
Mg	1.9	0.2	0.1	0.1
K	5.1	9	9	9
Na	44	40	45	40

The maximum amount of water that can contact a waste package in a fixed time interval is a function of the infiltration rate and the area of repository rock that channels water flow past the waste package. For vertical emplacement of waste packages in boreholes in the floor of drifts, the maximum water drainage can be reasonably estimated by considering a unit cell of the drift to be associated with each waste package. For a drift width of 6.1 m and package borehole spacing along the drift floor of 5 to 8 m, the average drift area per package would be 40 sq.m. The water influx to that area would be 40 l per year for an infiltration rate of 1 mm/y, the expected upper limit under normal conditions at Yucca Mt.[3]. By contrast, if only the water that flows directly downward onto the top of a borehole can enter that emplacement hole, the 1 mm/y infiltration rate would deliver only 0.5 l of water to the borehole. In order to investigate the effects of higher infiltration rates, we will use 1, 2, and 8 mm/y as cases for release rate scenario analysis.

Analysis of the waste package environment described above has led to the following reference waste package design for NNWSI. The design for spent fuel consists of a 70 cm. OD container fabricated from austenitic stainless steel [4]. The container thickness is 1 cm. An internal space frame will be used to separate intact fuel assemblies or consolidated bundles of fuel pins. The reference emplacement conditions are vertical emplacement in boreholes drilled in the floor of emplacement drifts. No backfill or packing material is used around the waste packages. Reprocessed borosilicate glass waste forms from West Valley or from the Defense Waste Processing Facility would be placed in an overpack that would be similar to the spent fuel outer container. These reprocessed waste forms contain lower amounts of heat-producing radionuclides than spent fuel and are expected to be less complicated than spent fuel from the point of view of developing a waste package source term. The remainder of this paper will consider only the source term for spent fuel.

The reference waste package design for spent fuel assumes that the fuel is 10 years out of reactor and had an average burnup for PWR fuel of 33,000 MWd/MTHM. Figure 1 shows the thermal history for a waste package containing consolidated fuel pins from six PWR assemblies with a total thermal output of 3.3 kW. The emplacement conditions used in the calculation were vertical emplacement with 5 m package pitch and 47 m drift pitch. This produces an average thermal loading on emplacement of 48.4 kW per acre. The

peak temperature for the spent fuel would be approximately 320°C, while the canister surface experiences a peak temperature of somewhat less than 250°C. The host rock temperature for a distance of more than 1 meter around the borehole remains above 100°C for more than 1000 years under these emplacement conditions. Because the temperature surrounding the borehole is above the boiling point of water, the expected conditions for the waste package during the first 1000 years would be an atmosphere of air saturated with water vapor at the appropriate temperature. After the temperature drops below the local boiling point of water, liquid water might contact the container. For waste packages that contain lower thermal loading or are at the edge of the repository the time of first ingress of liquid water into the borehole would be expected to be earlier than for the conditions used in the example above.

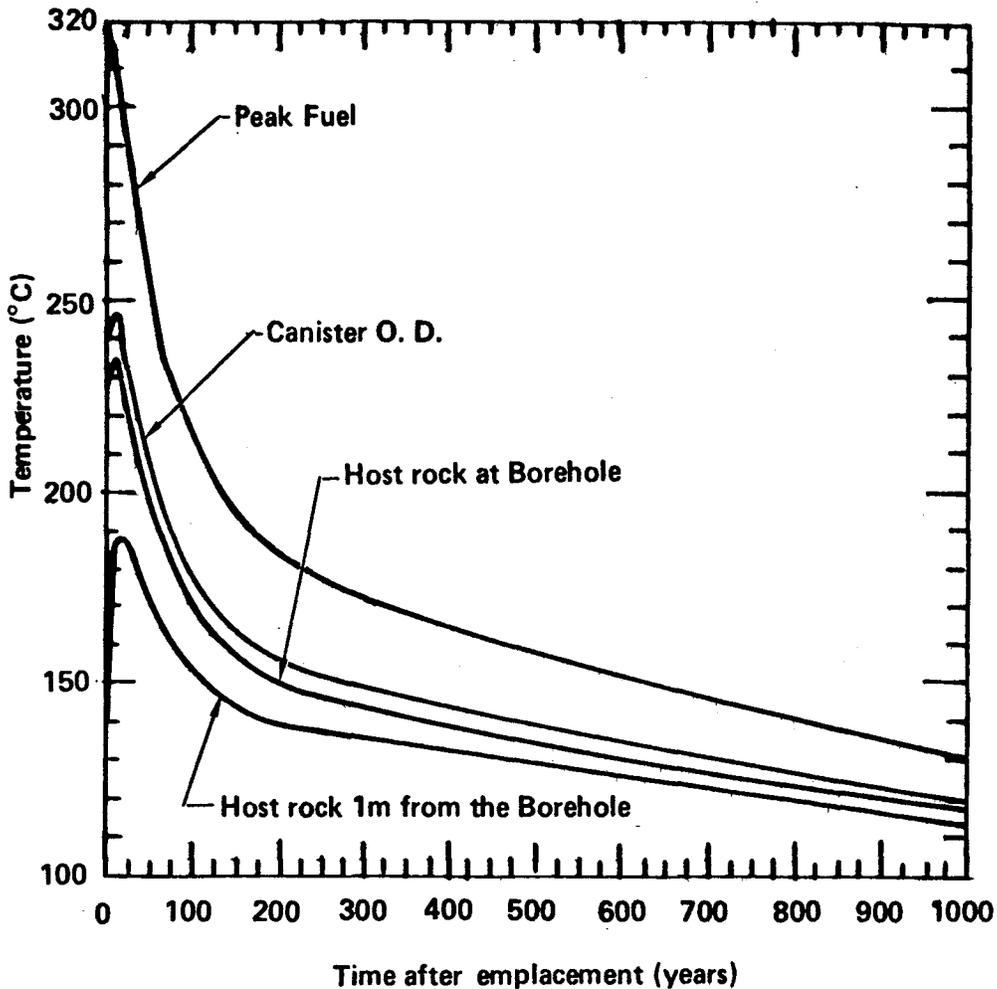


Figure 1: Thermal history for reference waste package.

CONTAINER CORROSION RATES AND MECHANISMS

The reference container material for NNWSI waste packages is austenitic stainless steel. Several grades of stainless steel are under investigation, including 304L, 316L, 317L, 321, 347, and high-nickel stainless alloy 825. Of these materials, the laboratory work has emphasized 304L and

316L. Widespread industrial use of these grades indicates that they perform well in oxidizing conditions and, therefore, they are promising candidate materials for nuclear waste containers in an unsaturated tuff repository. The results of experiments conducted to determine the general corrosion rate of these materials immersed in J-13 water in the 50 to 100°C range indicate that the rate is essentially independent of temperature and the corrosion is uniformly distributed over the exposed surface area [5]. There was no significant difference in corrosion rates measured for 304L, 316L, and 317L in 50, 70, 80, 90 and 100 °C J-13 water at exposure times of 3548 and 5000 hours. The grand average of data gave a corrosion rate of 0.19 +/- 0.04 µm/y. If more recently obtained data for 7500 hours of exposure are included in the average, the rate is 0.15 +/- 0.036 µm/y. The total range of measured corrosion rates in this series of experiments was 0.025 to 0.36 µm/y.

Published [6] and unpublished results of testing of these materials in 100°C saturated steam (7500 exposure hours) gave a range of corrosion rates of 0.037 to 0.31 µm/y and an average of 0.16 +/- 0.03 µm/y. Oxidation rates ranging from 0.001 to 0.008 µm/y have been measured in 150°C unsaturated steam (3800 exposure hours). As expected, the rates under "wet" steam conditions overlap those from the fully immersed conditions, while the rates obtained under "dry" steam conditions are substantially lower. Tests conducted in the presence of gamma radiation give similar results to those without radiation.

As discussed above, the exact temperature history of a waste package depends on its position in the repository layout and on the thermal loading of the package. In fact, these parameters are themselves interdependent. An exact description of the layout and package thermal loadings is not possible until the operations stage of repository development when shipping information from waste producers is available. To allow for the uncertainties in these parameters, we have chosen to use the 100°C air/steam data to represent the corrosion rate for higher temperatures. Since these data are comparable to the data for immersed conditions, we will use the grand average of the immersed corrosion data to estimate the waste package lifetime under the assumption that uniform corrosion is the service limiting degradation mode.

The only indications of localized corrosion that have been observed to date for 304L, 316L, and 317L occurred at 100°C and consisted of enhanced corrosion at the site of artificially induced crevices that were created underneath Teflon washers. The highest rate of preferential attack was about 0.3 µm/yr after 7500 hours of exposure. No preferential attack was observed at 90°C and lower temperatures for these materials.

The other corrosion mechanism of concern for waste packages is intergranular stress corrosion cracking (IGSCC). Occurrence of IGSCC requires attainment of three concomitant conditions: (1) development of a continuously sensitized (Cr depleted) microstructure along grain boundaries; (2) the presence of a sufficiently aggressive corrosion environment to attack the Cr-depleted regions and initiate a crack; and (3) a stress level above a critical threshold to propagate the crack. This level is usually on the order of 70% of the yield strength. While waste package designs and container fabrication process specifications will ensure that the operating and residual stress levels are kept well below this threshold, it is instructive to determine whether the container alloy could become sensitized under the long term thermal conditions in the repository.

Figure 2 shows the temperature history for a waste package containing consolidated rods from BWR assemblies plotted as time vs $1/T$ (thermal data from [7]). The line for 304L sensitization was obtained by extrapolation of data obtained at higher temperatures (450-750°C). This particular material had a carbon content (0.028%) near the top of the permitted range and was heavily cold-worked [8]. Both of these conditions enhance susceptibility to sensitization. The offset of the waste package cooling curve from the sensitization line suggests that long-term, low-temperature sensitization of even heavily cold-worked material should not be of concern. Additional conservatism can be incorporated into the container material selection, however, as illustrated by the line for non cold-worked 316LN stainless steel [9]. Additions of nitrogen and molybdenum in the 316LN retard the diffusion of carbon in austenitic structures and therefore reduce the susceptibility to sensitization. Figure 2 further illustrates that experiments can be performed at 250 to 400°C for one to a few years in duration to confirm the predictions on sensitization made from the higher temperature extrapolations discussed above.

The data available on corrosion in the environment anticipated at Yucca Mt. indicate that uniform corrosion is the most likely mechanism for container degradation. Extrapolation of the data for the average uniform corrosion rate (0.15 $\mu\text{m}/\text{yr}$) to obtain the time necessary to corrode through 1 cm of metal gives a predicted package lifetime of 67,000 years. Crevice corrosion under saturated steam conditions at 100°C would reduce this lifetime somewhat. The duration of experiments is presently limited to under one year (7500 h = 312.5 days) and more data is required to determine that increased corrosion rates do not occur following prolonged exposure. Present results, however, indicate that failure of the metal container in times less than 10,000 years will be an unlikely event. Potential causes of premature breach of the metal container could include defective closure welds that are not detected during weld inspection and portions of the container being highly stressed due to some off-normal fabrication condition. These are considered to be low probability conditions; however, the consequences of these conditions are being evaluated as part of the metal corrosion testing program.

SPENT FUEL DEGRADATION RATE

Light water reactor fuel generally consists of UO_2 pellets contained in Zircaloy cladding. A small percentage of fuel is clad in stainless steel. For simplicity, we will confine discussion to Zircaloy clad fuel. A similar treatment will apply to stainless steel clad fuel.

At the end of its useful life, most spent fuel cladding is intact; a small percentage of cladding will have developed a breach during reactor service. Fuel designs and reactor operating conditions used during the 1960's led to development of pin hole or crack defects in several percent of the pins. More recent designs and operating conditions result in far fewer defects in the cladding. The defect population for fuel presently in use has been estimated to be about 0.1% or less [10].

We are investigating the corrosion rates and mechanisms for Zircaloy under expected disposal conditions for a repository in tuff. Preliminary analysis indicates that the dominant corrosion mechanism will be stress corrosion cracking. Degradation by uniform corrosion or pitting corrosion is expected to be minor [11]. Experiments are currently under way to measure the

rate of uniform and non-uniform corrosion of irradiated Zircaloy. Results of these experiments will be used to determine the rate of defect generation in the spent fuel cladding population. Experiments are also being conducted on spent fuel oxidation rates since fuel oxidation through small cladding defects might result in an increased rate of cladding degradation.

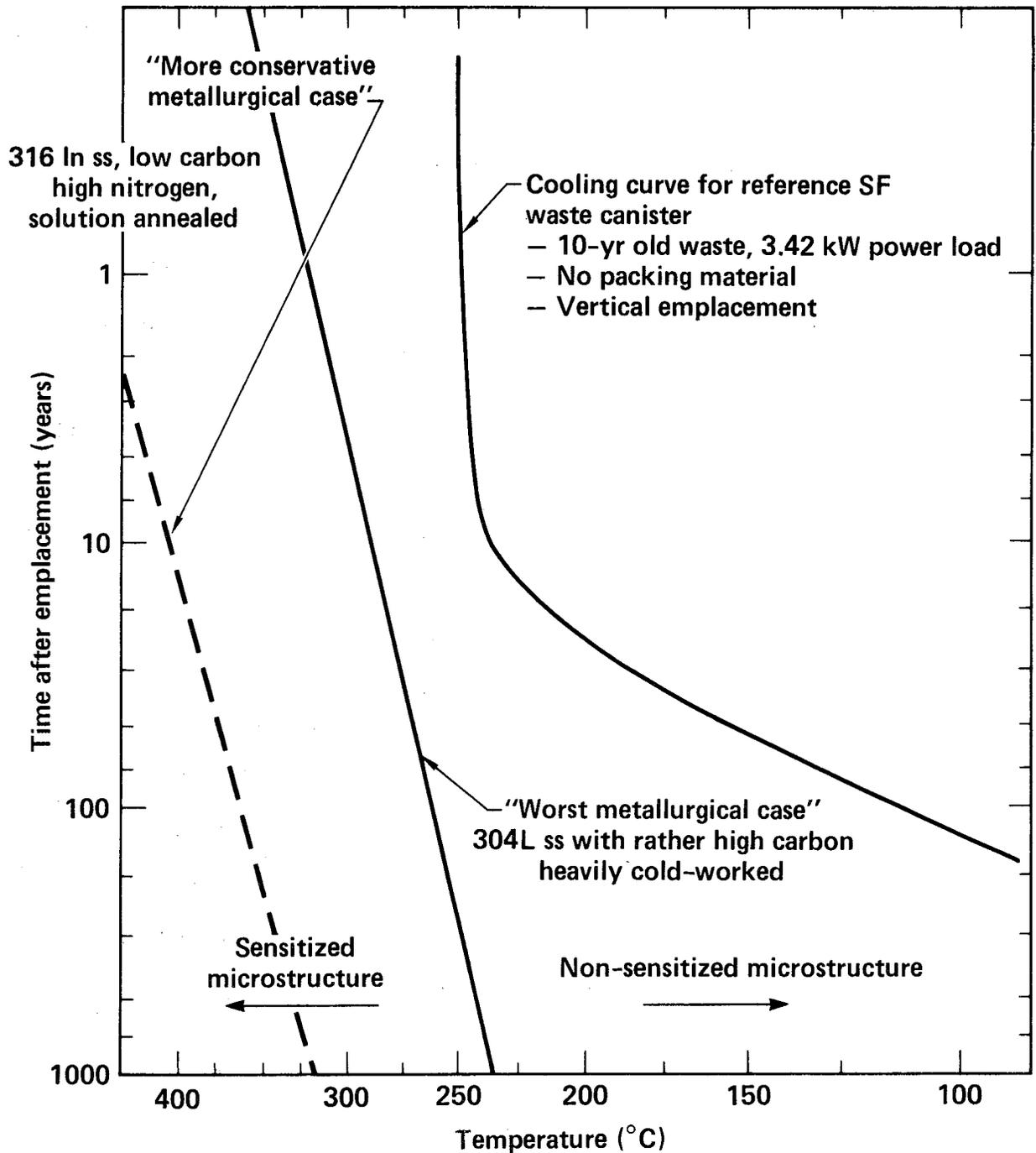


Figure 2: Relationship between thermal history of emplaced nuclear waste container and long-term sensitization in austenitic stainless steels.

Leaching of radionuclides from spent fuel can occur only after the cladding is breached and water or air can contact the fuel. In most cases, contact of fuel with water will occur through small defects in the cladding. In some cases, the cladding may split and expose the fuel pellets directly to water. To cover the possible geometric configurations for fuel-water contact, we are conducting spent fuel dissolution studies that use four fuel conditions: (1) bare fuel plus the cladding from which the fuel was removed, (2) a fuel segment approximately five inches long, end capped with water tight fittings, and no defects induced in the cladding, (3) specimen similar to number 2, but with a laser drilled hole in the cladding, and (4) specimen similar to number 2, but with a slit machined in the cladding. Specimen 2 provides an indication of the surface contamination of the cladding. Such contamination may occur during reactor service, pool storage at the reactor, or during preparation of the specimens for testing. Details of the experimental procedure are given in reference [12].

The first series of spent fuel tests were conducted in deionized water at ambient hot cell temperatures and used Turkey Point PWR fuel. Solution samples (generally 10 ml) were taken periodically and fresh deionized water added to the test vessel to return the volume to 250 ml. The test was run for approximately 9 months, temporarily terminated to allow transfer of the fuel test specimens to new reaction vessels, and then restarted in fresh deionized water. Results for uranium in solution samples for the first sixty days of the first cycle of the test are shown in Figure 3, along with results for a similar series of tests using J-13 water and H.B. Robinson PWR spent fuel. The solution concentration that would be produced if one part in 10^5 of the inventory present in the test were dissolved is shown for reference for each test. Details of results for the deionized water tests are contained in reference [13] and for the J-13 water tests in reference [14].

The bare fuel sample in deionized water showed an initial pulse of U release followed by a rapid decrease of U in the solution. Subsequent testing showed that the U was not in true solution, but was contained in particles larger than $0.4 \mu\text{m}$ in size. The concentration of other elements in the solutions, such as Pu, indicated that the initial pulse of release was due to suspension of very fine particles of fuel that rapidly settled out and plated out onto the reaction vessel surface. Analysis of acid rinse solutions of the test vessels after initial termination of the test gave compositions that indicated plate-out of material with an inventory of elements that would be expected in bulk spent fuel. When the tests were restarted with fresh deionized water, another pulse of release was observed, but it was substantially smaller than the first pulse. Release from specimens with induced cladding defects did not show an initial pulse of release, and resulted in solution concentrations that were one or two orders of magnitude lower than for the bare fuel. Eventually the particulate U settled out and final solution concentrations were similar to those found for the intact control sample. Settling time for the initial test was over 8 months, while in the restarted test settling occurred after only 4 months. The amount of uranium present in true solution or in particles smaller than $0.4 \mu\text{m}$ was only a few ppb in all tests in deionized water.

Results for testing of bare fuel in J-13 water also show an initial pulse of release that is similar in magnitude to that observed in deionized water. In this case, the uranium becomes complexed with carbonate in the solutions and is present as a true solution species. The uranium

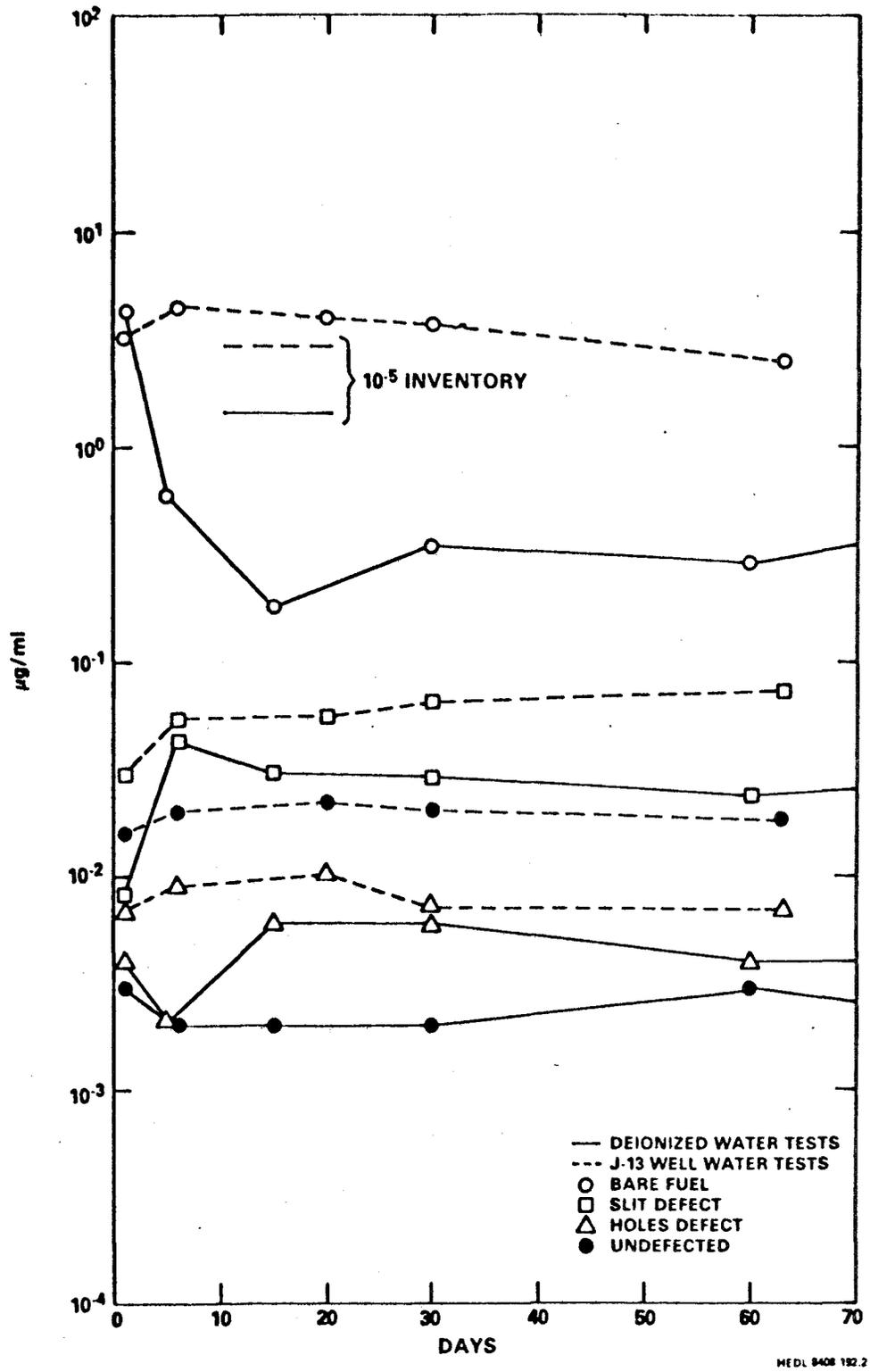


Figure 3: Uranium in unfiltered solutions from testing of PWR spent fuel. See text for details.

concentration decreases slowly as the test progresses. This may be due to removal of some of the initial "pulse" material as analytical samples are taken that is not replaced by further spent fuel reaction. The control sample (marked undefected) shows U at levels between that of the laser hole and slit defect samples. This indicates a small amount of residual contamination on the control sample, amounting to about 5 micrograms of U. The J-13 water tests are still in progress and will follow a test plan similar to that for the deionized water tests. A second series of tests using Turkey Point fuel in J-13 water is also in progress. Tests using H. B. Robinson fuel and J-13 water under higher temperature conditions are planned.

Some radioactive species in spent fuel are concentrated in the gap between the pellet and cladding and/or on the grain boundaries of the fuel. These species became segregated during reactor operation and lie in regions that allow them to be released to solution at a rate faster than the matrix fuel dissolves. Cesium, iodine, and possibly technetium, show an initial release rate that is high compared to the U release and that correlates with the content of fission gas in the pellet-cladding gap [13,15]. The amount of cesium and similar species that is contained in the highly mobile fraction is usually less than 1% of the inventory in the pin [10]; the remainder is dispersed through the fuel matrix and should be released at the same rate as the matrix dissolves. For the tests discussed above, Cs release from bare fuel was essentially instantaneous and corresponded to about 0.2% in the Turkey Point tests in either solution and about 0.6% in the H. B. Robinson tests. In the deionized water tests the release of Cs from slit and hole defects was slower but eventually reached the same levels as the bare fuel initial release. On restarting the deionized water tests, an additional rapid release was seen; however, the amount of release was smaller than for the first contact with water.

A third source of radioactivity in spent fuel exists in the metal components of the fuel assembly. Neutron activation products are formed in the fuel cladding and in the metal assembly spacers and grids. For steel components, the corrosion rates will probably be similar to those determined as part of the container corrosion testing. This will be checked by a limited series of experiments on fuel assembly parts. The main long-lived radionuclides contained in the steel components will be nickel isotopes.

The most significant radionuclide present in the cladding is C-14. It is formed by the reaction $N-14(n,p)C-14$. Experiments conducted at temperatures of about 275°C have shown that approximately 0.2% of the inventory of C-14 from a fuel assembly can be released into an air atmosphere within about one month [16]. The process involved in the release is thought to be removal of carbon from the oxidized skin of the Zircaloy cladding by reaction of the oxygen in the atmosphere with the carbon in the cladding oxidation layer to release CO_2 . The proposed mechanism will be checked by experiments conducted under controlled conditions using defueled cladding. Further release of C-14 from the Zircaloy is much slower than the initial release from the oxidized layer, and will probably be controlled by the rate of oxidation of the Zircaloy. Since this rate is very low at low temperatures, release of C-14 will probably be slow after the initial oxide layer carbon has been removed.

The experiments described above result in a source term for spent fuel that will be composed of at least four components that are released at

different rates. The parts will consist of

- (1) Elements whose release is controlled by matrix dissolution;
- (2) Elements present in part in the pellet-cladding gap;
- (3) Elements contained in stainless steel spacers and grids;
- (4) Elements contained in the fuel cladding.

A separate dissolution/degradation rate will be determined for each of these components of the source term.

WASTE PACKAGE SOURCE TERM DEVELOPMENT

Data from the experiments described above will be used to develop the model for release rate of radionuclides from the waste package as a function of time. A distribution function will be developed for container breach that includes both expected conditions and off-normal conditions. Data presently available suggest that breach of a container earlier than 50,000 years after disposal would not occur under anticipated conditions.

The container breach-time distribution will give the starting point for radionuclide release from the waste package. The first radionuclide released would be C-14 from the oxidized outer layer of the Zircaloy cladding. This release does not require contact of water with the fuel. Following container breach, water might enter the container. The geometric description of the breached container and the expected water flow rate will be used to determine the appropriate water to fuel ratio to be used in modelling the breached container. Present data indicate that infiltration rates of 0.1 to 8 mm/y should cover the range of likely conditions.

A waste package with one or more cracks is the most likely form of a breached container. Depending on the location of the cracks, infiltrating water might collect to some depth in the container. For the purposes of initial source term modelling, we will assume that two cracks exist with both cracks near the top of the container. The volume of a container is less than 1800 l, while the weight of spent fuel in the container is about 3100 kg. More than half of the volume will be occupied by the fuel, so the maximum water to fuel ratio would be about 0.3 l/kg. The spent fuel dissolution studies described above use water to fuel ratios of 3 to 10 l/kg. It is unlikely that we will be able to conduct experiments at a water/fuel ratio as low as 0.3; however, we will establish dissolution rates over a range of water/fuel ratios so that extrapolation to the appropriate value can be made.

The source term will include an estimate of the rate of degradation of the Zircaloy cladding. Spreading the breach of cladding over a range of time has a large effect on the release rate of elements contained in the pellet-cladding gap. If the cladding fails at a uniform rate over 2000 years, a rapid release of 1% of the iodine on breach of cladding would become a population release rate of 0.5 parts in 10^5 of the iodine inventory due to that mechanism. The total release rate of iodine would then be found by summing the parts due to the rapid release fraction and that due to matrix dissolution.

The Zircaloy, stainless steel, and spent fuel dissolution and degradation rates will then be used to determine the concentrations of radionuclides in the water contained within a breached waste package. This information, when combined with the water infiltration rate, will then provide the volume of water containing radionuclides that is displaced from the breached container annually, and the radioactive inventory contained in that

water. This calculation will provide the source term for radioactive release from the waste package.

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THE POTENTIAL EFFECTS OF RADIATION ON THE SOURCE TERM IN A SALT REPOSITORY

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ABSTRACT

The escape of radionuclides from a salt repository depends upon release from the engineered barrier system (source term) and upon an accident scenario which allows exit from the salt media. Several factors can affect the source term. These factors include the interactive effects of waste package materials, the particular accident scenario, and radiolysis effects. The current discussion will focus upon radiolysis effects.

Gamma radiolysis can have its main effect by enhancing metallic hard barrier corrosion and by generating sodium metal colloids within the surrounding crystalline salt. When the irradiated salt is then exposed to brine, local basic pH excursions can occur. This can have significant impact upon the source term by causing changes in both leach rates and solubilities.

At longer times, after breaching the hard barriers, alpha radiolysis of the brine can occur. Alpha radiolysis can cause high gaseous pressures, very oxidizing conditions in the brine, and low pH values. Both the highly oxidizing brine (high Eh) and low pH can result in as much as three orders of magnitude increase in actinide solubilities.

Recent research is described on the effects of gamma radiolysis on crystalline salt core samples and the subsequent effects of reacting the irradiated salt with brine. Alpha radiolysis effects on saturated brines and upon actinide solubility are also discussed.

(Abstract only available)

THE CHEMISTRY OF NUCLEAR FUEL (UO₂) DISSOLUTION
UNDER WASTE DISPOSAL VAULT CONDITIONS

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ABSTRACT

The basic chemistry of UO₂ dissolution is considered under conditions typical of a nuclear fuel waste disposal vault, with particular emphasis on redox conditions and the effect of groundwater constituents, oxidizing agents and water radiolysis. The anodic processes that occur during the oxidative dissolution of UO₂ have been established on the basis of electrochemical and X-ray photoelectron spectroscopic experiments. Using similar techniques, the kinetic effects of potential groundwater species, such as bicarbonate/carbonate, phosphate, and chloride, have been studied.

The effect of potential oxidizing agents is not so well characterized. A number of interrelated reactions with UO₂, involving dissolved oxygen, hydrogen peroxide, and the products of water radiolysis, have been identified and discussed. The directions in which our studies are being extended are discussed.

RESUME

La dissolution du UO₂ a été examinée du point de vue chimique, en payant une attention particulière aux conditions oxido-réductrices, à l'effet des constituants des eaux souterraines, aux agents oxydants et à la radiolyse de l'eau. Les processus anodiques survenant lors de la dissolution oxydative du UO₂ ont été établis en se basant sur des expériences électrochimiques et sur la spectroscopie photoélectronique au rayons-x. En utilisant des techniques similaires, l'effet cinétique des espèces présentes dans les eaux souterraines, tel que les ions carbonate/bicarbonate, phosphate et chlorure, a été étudié.

L'effet d'agents oxydants n'est pas si bien caractérisé. Un nombre de réactions étroitement imbriquées, impliquant l'oxygène dissout, le peroxyde d'hydrogène et les produits de la radiolyse de l'eau a été identifié. La direction future de ces études est discutée.

1. INTRODUCTION

The development of a model to predict the rate of release of radionuclides from irradiated nuclear fuel under waste disposal vault conditions is a task requiring a detailed knowledge of the chemistry of the host matrix (UO_2), and how it is affected by irradiation and the various groundwater conditions to which it may be exposed. To achieve such an understanding, an integrated experimental approach involving thermodynamic, kinetic and leaching studies is being followed. Some of the details of this approach have been reviewed recently [1].

The physical and chemical properties of irradiated fuel depend on its irradiation history. Physical changes that occur during irradiation include grain growth, cracking, and the production of open and closed porosity due to the formation of fission gas bubbles at grain boundaries. These factors combine to produce an inhomogeneous distribution of radionuclides throughout the fuel. Radionuclides have been identified in a number of specific sites, e.g., in void spaces, such as the fuel/sheath gap, cracks in the fuel pellets, and inter-pellet gaps; at UO_2 grain boundaries; and within UO_2 grains.

The rate of release of the various radionuclides from these locations has been the subject of many leaching studies [2-8]. However, since over 90% of the radionuclide inventory is located within the UO_2 grains, the chemistry of dissolution of the UO_2 matrix is of major importance in the development of any radionuclide release model. Some of the factors that will exert a major influence on the chemistry of UO_2 include redox conditions [9-13], groundwater composition [11,13], radiation effects, temperature, physical effects such as fuel pellet erosion and break-up [4], and fuel/container interactions [14].

In this paper we review some of our basic studies on UO_2 dissolution, with particular emphasis on redox conditions and the effect of groundwater constituents, oxidizing agents and water radiolysis. Since the control of redox conditions is essential to any study of the dissolution of UO_2 , we have used a variety of electrochemical methods and X-ray photoelectron spectroscopy (XPS) to characterize the surface films formed on UO_2 under a variety of redox conditions.

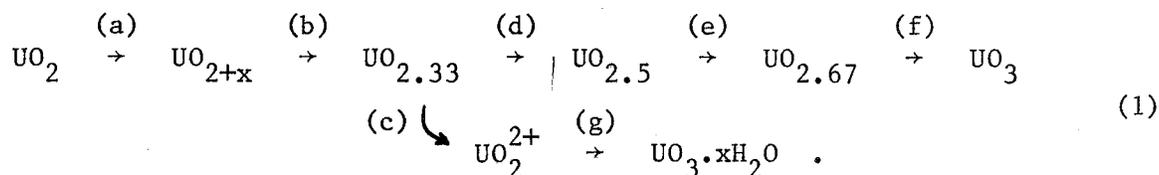
2. EXPERIMENTAL

All of our experiments have been performed on a UO_2 electrode fabricated from an unirradiated fuel pellet, as previously described [4]. The details of our electrochemical and XPS procedures and analyses have been published previously [4,15-17]. The cell used in our α -radiolysis experiments has also been described previously [18].

3. RESULTS AND DISCUSSION

3.1 Redox Conditions

On the basis of an extensive series of electrochemical and XPS experiments [4,15-17,19], we have established the following reaction scheme for the oxidative dissolution of UO_2 :



The film growth process (a) is limited to a few atomic layers [16,20], the film being thicker the higher the pH. No major crystallographic rearrangement is required to convert UO_{2+x} to $\text{UO}_{2.33}$ ((b) in scheme (1)). Film growth probably occurs via O^{2-} insertion at interstitial sites in the fluorite lattice, and proceeds to thicknesses of about 4 to 8 nm [16,20].

The dissolution process (c) (to yield UO_2^{2+} , almost certainly complexed or hydrolyzed) appears to start once a surface composition of $\text{UO}_{2.33}$ is achieved, irrespective of solution composition [20], or whether oxidation is promoted electrochemically [16], or by dissolved oxidants [21]. In step (d), the onset of dissolution is accompanied by a slow surface recrystallization process, from $\text{UO}_{2.33}$ with a fluorite lattice, through $\text{UO}_{2.5}$, to $\text{UO}_{2.67}$ with an orthorhombic lattice. This second, slower stage of oxidation, and the dissolution process, are envisaged as proceeding via a common intermediate (uranyl-type species) produced by the oxidative dissolution of $\text{UO}_{2.33}$.

The final step, (f), to UO_3 , is only observed in alkaline solutions [19]. The phase $\text{UO}_3 \cdot x\text{H}_2\text{O}$ is formed by the precipitation of dissolved UO_2^{2+} from locally supersaturated solutions, and is generally only observed at very anodic potentials ($\lambda +300$ mV vs SCE) [16], or after extensive dissolution at lower potentials [4].

From the waste management point of view, these results show that a degree of oxidation can be tolerated prior to the onset of dissolution of the UO_2 matrix. We have attempted to determine the minimum electrode potential for the onset of oxidative dissolution. A value in the region 0 to +50 mV (vs SCE) was obtained from coulometric experiments [17]. This could be taken as a minimum redox condition, below which UO_2 should be a stable host matrix for radionuclides.

3.2 Groundwater Composition

Although the relative importance of the dissolution/film formation reactions changes slightly, our electrochemical results show that the mechanism of oxidative dissolution of UO_2 remains essentially unchanged in the pH range $5 < \text{pH} < 10$, the range expected in groundwaters. These results are in agreement with those of Nicol and Needes [22], who showed that the pH had no effect on the steady-state current vs potential curves for the anodic dissolution of UO_2 in this pH range.

However, the effect of potential groundwater anions, such as carbonate and phosphate, is more complicated. The early stages of UO_2 oxidation, when no dissolution is occurring (scheme (1), steps (a) and (b)), are unaffected by the presence of complexing anions [20,23]. Our coulometric experiments, aimed at determining the redox potential at which dissolution first occurs, suggest that carbonate does not affect this potential. At more anodic potentials, our electrochemical experiments show a substantial effect for the complexing anion, in qualitative agreement with the earlier results of

Nicol and Needes [24]. Our inability to observe an effect due to carbonate at low anodic potentials may be due, in part, to the presence of dissolved atmospheric CO_2 in our supposedly carbonate-free solution. Consequently, a redox potential of 0 to +50 mV (vs SCE) appears to represent a genuine, minimum, redox condition for the onset of oxidative dissolution, even in the presence of strong uranyl ion complexing agents such as carbonate.

At more anodic potentials, dissolution proceeds through a surface intermediate, UO_2CO_3 in the case of carbonate, and through an unidentified uranyl phosphate (possibly UO_2HPO_4) in the case of phosphate. For carbonate solutions, an acceleration of the dissolution reaction is observed for $[\text{CO}_3]_{\text{total}} \approx 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, and the chemical dissolution of the UO_2CO_3 layer tends to partially control the dissolution kinetics for $[\text{CO}_3]_{\text{total}} > 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$. For phosphate, only a small effect on the dissolution rate is observed unless $[\text{PO}_4]_{\text{total}} > 5 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$. The uranyl phosphate film is much less soluble than the corresponding carbonate film and completely controls the dissolution kinetics under sufficiently oxidizing conditions (> 325 mV vs SCE).

On the basis of these and similar experiments for other anions, we can define the following conditions under which we would expect various anions to affect the dissolution rate of UO_2 :

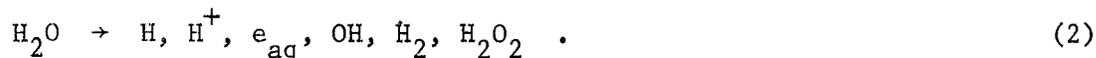
- (1) Carbonate/bicarbonate will accelerate the oxidative dissolution of UO_2 for $[\text{CO}_3]_{\text{total}} \approx 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$. Since concentrations in the range 10^{-3} to $10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ are expected in groundwaters in the Canadian Shield [13], carbonate is likely to affect the chemistry of UO_2 in a waste vault.
- (2) Since phosphate concentrations less than $10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ are expected in groundwater [13] and concentrations $> 5 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ are required to affect the dissolution reaction, phosphate is not expected to have a significant effect on the oxidative dissolution of UO_2 .
- (3) No effect of chloride ion up to $10^{-1} \text{ mol}\cdot\text{dm}^{-3}$ has been observed, suggesting that the saline groundwaters sometimes encountered in the Canadian Shield [13] pose no extra threat to UO_2 fuel stability, unless radiolysis of chloride solutions produces oxidizing species.

3.3 Effect of Oxidizing Agents

The electrochemical studies described above are limited to the anodic reactions occurring on UO_2 , the cathodic reaction being relegated to a subsidiary electrode elsewhere in the experimental system. To determine the kinetics of the corrosion of UO_2 , we also need to know the mechanism of the cathodic reaction. A number of cathodic reactions are possible, since oxidizing agents may be introduced to the waste vault either by transport in groundwater, or by radiolytic decomposition of water within the vault.

We have chosen to study UO_2 corrosion in solutions containing dissolved oxygen as an example of an oxidizing reagent that may be transported into the waste vault, though it is possible to envisage many scavenging mechanisms for the removal of dissolved oxygen, such as preferential reactions with components of the buffer material and with the metal containers [14].

Oxidizing conditions at the fuel surface could also be produced by the radiolytic decomposition of water, viz.,



Consequently, we have been studying the effect of H_2O_2 and the actual α -radiolysis of water on UO_2 corrosion [18].

(a) Dissolved Oxygen

Figure 1 shows the UO_2 corrosion potential recorded in oxygen-saturated $0.1 \text{ mol}\cdot\text{dm}^{-3}$ NaClO_4 ($\text{pH} = 9.5$). The data points are from 13 separate experiments, showing good reproducibility. The potential rises rapidly ($\lesssim 1$ min) to ~ -400 mV from -2000 mV, the potential at which the electrode was cathodically cleaned. Over the next 6 to 8 hours, the corrosion potential rises to $\sim +30$ mV and a thin film is observed (by cathodic stripping voltammetry) to grow on the UO_2 . A limiting thickness of 6 ± 1 nm is achieved. For longer times, the corrosion potential slowly drifts to $\sim +90$ mV, but no further film thickening is observed.

It appears that, as in the electrochemical case, an initial surface oxidation occurs, followed by dissolution from a UO_{2+x} surface film. It is tempting to assume that oxidation to the $\text{UO}_{2.33}$ stage (step (b), scheme (1)) has occurred and that dissolution is proceeding by the oxidative dissolution of this layer. However, this hypothesis requires confirmation by XPS and dissolution rate measurements.

The reduction of oxygen on the UO_2 surface (the accompanying cathodic reaction), via the overall reaction



appears to be first order in oxygen, indicating no oxygen dissociation on the UO_2 surface prior to electron transfer. On the basis of the electrochemically determined Tafel slopes and the pH dependence of the reduction currents, Needes and Nicol [25] have proposed that the first electron transfer reaction is rate-determining. This reaction is then followed by a sequence of three further electron transfer reactions to produce OH^- .

A major feature of this mechanism is that the reduction does not appear to proceed via a peroxide intermediate, unlike O_2 reduction at many other metal surfaces [26]. This suggests that there will be fundamentally different mechanisms for the reactions of UO_2 with O_2 and with H_2O_2 (produced by water radiolysis). We are presently studying the corrosion of UO_2 over a wider range of pH, temperature and solution composition.

(b) Hydrogen Peroxide

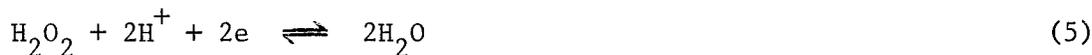
Figure 2 shows the corrosion potential of UO_2 as a function of time after the addition of H_2O_2 . The two concentrations employed are close to those of dissolved O_2 in air-saturated ($[\text{O}_2] = 2.66 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$) and oxygen-saturated ($[\text{O}_2] = 1.27 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$) solutions. A surface oxidation of UO_2 occurs, similar to that observed in dissolved oxygen. However, the rate of oxidation is much faster in H_2O_2 than in O_2 , which may be due to a

reaction involving OH radicals, as discussed below. Thus, the corrosion potential achieves a value of +85 mV (vs SCE) in ~ 5 min in a solution containing 10^{-3} mol \cdot dm $^{-3}$ of H₂O₂ compared with ~ 24 h for a similar concentration of dissolved O₂.

Figure 3 shows the UO₂ corrosion potential as a function of H₂O₂ concentration, as well as the potential achieved at a Pt surface in the same solutions. For the UO₂ electrode, the potential is effectively independent of the H₂O₂ concentration for concentrations $\lesssim 10^{-2}$ mol \cdot dm $^{-3}$, whereas for the Pt electrode, the potential is constant over the concentration range $5 \times 10^{-3} < [\text{H}_2\text{O}_2] < 2 \times 10^{-1}$ mol \cdot dm $^{-3}$. It is well known that Pt catalyzes the decomposition of H₂O₂ [27] according to the overall reaction



The near invariance of the potential with H₂O₂ concentrations $< 10^{-2}$ mol \cdot dm $^{-3}$ suggests the decomposition reaction (4) is occurring at both the Pt and UO₂ electrodes. Examination of the two half-cell reactions involved in the peroxide decomposition reaction,



shows that, provided the reaction mechanism does not change, the shift in potential with H₂O₂ concentration for the two half-cell reactions will be equal but of opposite sign. Consequently, the mixed potential would not be expected to change, as observed in Figure 3. That H₂O₂ decomposition does occur on UO₂ in this potential region is confirmed by the rotating ring-disk experiments of Needes and Nicol [25].

For $[\text{H}_2\text{O}_2] > 10^{-2}$ mol \cdot dm $^{-3}$, the shift of the UO₂ electrode potential to more anodic potentials suggests that further oxidation of the UO₂ is occurring. Our XPS results [21] show that the UO₂ surface is predominantly UO_{2.33} at low concentrations of H₂O₂, the phases UO_{2.5} and UO_{2.67} being formed at the more anodic potentials achieved in the higher concentration region. These observations agree with our electrochemical results described above, and are consistent with the rotating ring-disk results of Needes and Nicol [25], which show that the formation of surface phases on the UO₂ leads to a switch from predominantly peroxide decomposition, reaction (4), to the oxidative dissolution of UO₂, as the electrode potential is decreased.

A comparison of these results with those obtained in dissolved O₂ shows that two distinctly different reaction pathways are possible, depending on the peroxide concentration. At low concentrations, H₂O₂ decomposition will lead to O₂ formation, and the subsequent rate of UO₂ dissolution by reaction with oxygen would be expected to be slow. At higher concentrations, direct reaction of H₂O₂ with UO₂ will occur and dissolution is expected to be accelerated. Our results suggest that there is a threshold concentration of H₂O₂ ($\sim 5 \times 10^{-2}$ mol \cdot dm $^{-3}$) above which UO₂ dissolution is enhanced. Hence, for H₂O₂ produced by water radiolysis, we might expect a dose-rate threshold for enhanced UO₂ dissolution (and radionuclide release), since the H₂O₂ concentration is determined by the dose rate. So far our work has been confined to the pH range 9 to 10.

(c) Alpha radiolysis

Figure 4 shows the corrosion potential of a UO_2 electrode as a function of time in argon-degassed solutions with the electrode in close proximity ($\sim 30 \mu\text{m}$) to α -particle sources of various strengths. In the presence of weak α sources, the potential increases quickly from -2000 to -1000 mV and then slowly drifts to about -200 mV. This behaviour is similar to that obtained in the absence of an α source and can be considered to represent "nominally reducing" conditions, the small amount of UO_2 oxidation being attributable to residual traces of dissolved oxygen. In the presence of the $686 \mu\text{Ci}^*$ α source, the change in potential from "nominally reducing" (up to 2 h) to oxidizing (> 10 h) reflects the buildup of α radiolysis products as a function of time. The change in potential is slow compared with the changes observed in H_2O_2 (Figure 4) and oxygen-saturated (Figure 3) solutions. The potential of $+70$ to $+75$ mV (vs SCE) is similar to that achieved in H_2O_2 and O_2 -containing solutions, demonstrating that oxidizing conditions are achieved at the UO_2 surface as a consequence of water radiolysis. The surface composition has yet to be established by XPS.

Up to ~ 30 h (at which time the experiment was terminated), the UO_2 potential remains in the region of $\sim +70$ mV (vs SCE). This suggests that the H_2O_2 concentration in the small volume of solution between the electrode and the α source does not build up to concentrations $\gtrsim 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$, where we would expect an anodic shift in potential (see Figure 3) and an extensive attack on the UO_2 . At a potential of $+70$ mV (vs SCE), we would expect H_2O_2 decomposition via reaction (4). It is also possible that radical reactions occur at the UO_2 surface, although no evidence for such reactions presently exists. Experiments in which the volume of solution between the electrode and the α source, and hence the concentration of radiolysis products, are varied [18] support these conclusions.

If H_2O_2 decomposition occurs on UO_2 , then the main mechanism of UO_2 oxidation and dissolution will be via reaction with O_2 . As shown above, this reaction is significantly slower than the reaction of UO_2 with H_2O_2 , and would not be expected to lead to as severe an attack. The relative importance of the decomposition of H_2O_2 to UO_2 dissolution remains to be determined.

So far our experiments have been confined to durations of $\lesssim 70$ h. For this time period, the two weaker α sources ($4.7 \mu\text{Ci}$ and $100 \mu\text{Ci}$), which produce α fluxes close to those expected to occur at the surface of irradiated fuel after 500-a storage, showed no tendency to oxidize the UO_2 surface. It is tempting to interpret this switch in behaviour from "nominally reducing" to oxidizing, as the strength of the α source increases, as a dose-rate effect. However, it is most likely due to the cell design [18], which allows the transport of radiolysis products out of the solution volume between the UO_2 electrode and the α source. At the low dose rates obtained with the two weaker α sources, these transport losses will be more significant in determining the concentration of radiolysis products at the UO_2 surface.

We are presently developing a model to calculate the expected yields of radiolysis products, using published models for the α radiolysis of water,

*1 Ci = 376 Bq

and taking into account the transport losses of radiolysis products. Also, in experiments now in progress, we are attempting to use the gold-plated surface of the α source as an electrode, in the hope of analyzing the yield of radiolysis products by electrochemical techniques. By comparing the measured values with those calculated using the model, we hope to be able to measure the effect of dose rate.

Finally, all the data presented in this section on oxidizing agents are for pH 9 to 10. Our preliminary experiments at other pH values suggest a much more aggressive attack on UO_2 at lower pH values, especially in H_2O_2 solutions. Obviously, this effect of pH, plus the effect of radiation on solution species such as chloride and carbonate, must be studied in detail before a more complete picture of UO_2 dissolution under oxidizing conditions will be possible.

4. CONCLUSIONS

The anodic processes occurring on UO_2 under electrochemical conditions, and in the presence of oxidants such as dissolved O_2 and H_2O_2 have been elucidated.

The corrosion potential of UO_2 has been measured in solutions containing dissolved O_2 , H_2O_2 , and in the presence of an α source. In all cases oxidizing conditions are achieved at the UO_2 surface, but the rate of oxidation is much faster in H_2O_2 solutions than in solutions containing dissolved O_2 . In the presence of H_2O_2 , or the α radiolysis products of water, H_2O_2 decomposition and UO_2 dissolution occur simultaneously at the UO_2 surface, the relative importance of each reaction being determined by the H_2O_2 concentration.

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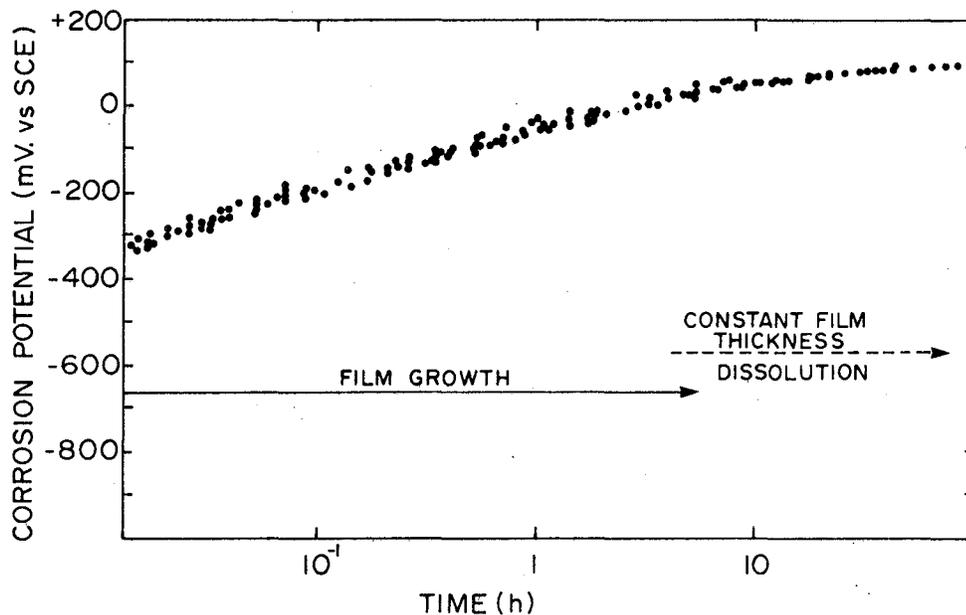


Figure 1. Corrosion potential of a UO_2 electrode in an oxygen-saturated solution ($[\text{O}_2] = 1.27 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) containing $0.1 \text{ mol} \cdot \text{dm}^{-3}$ NaClO_4 ($\text{pH} = 9.5$). Data points are from 13 individual experiments. Electrode potential = -2000 mV at $t = 0$.

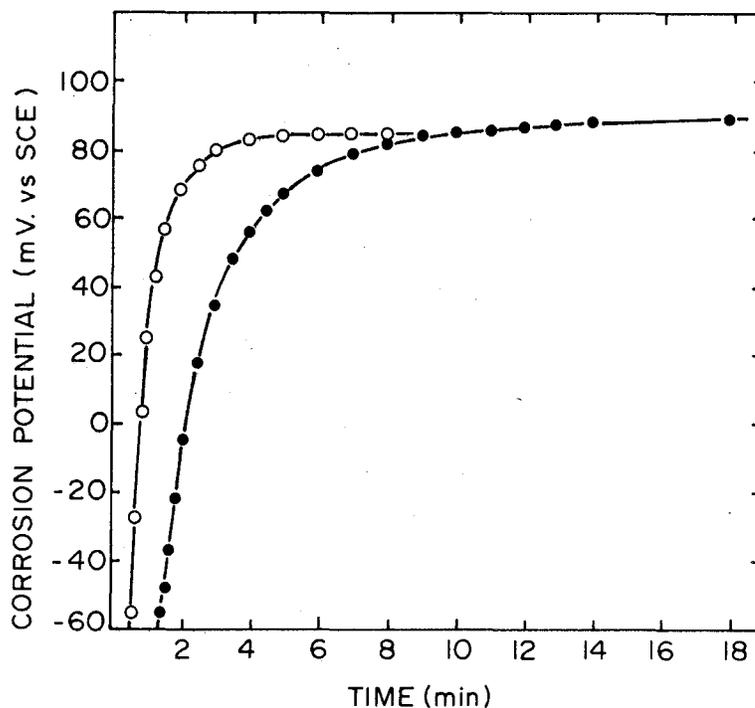


Figure 2. Corrosion potential of a UO_2 electrode in a N_2 -degassed $0.1 \text{ mol} \cdot \text{dm}^{-3}$ NaClO_4 solution ($\text{pH} = 9.5$) containing hydrogen peroxide. ($\text{---}\bullet\text{---}$) $[\text{H}_2\text{O}_2] = 2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$; ($\text{---}\circ\text{---}$) $[\text{H}_2\text{O}_2] = 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$. Electrode potential = -2000 mV at $t = 0$.

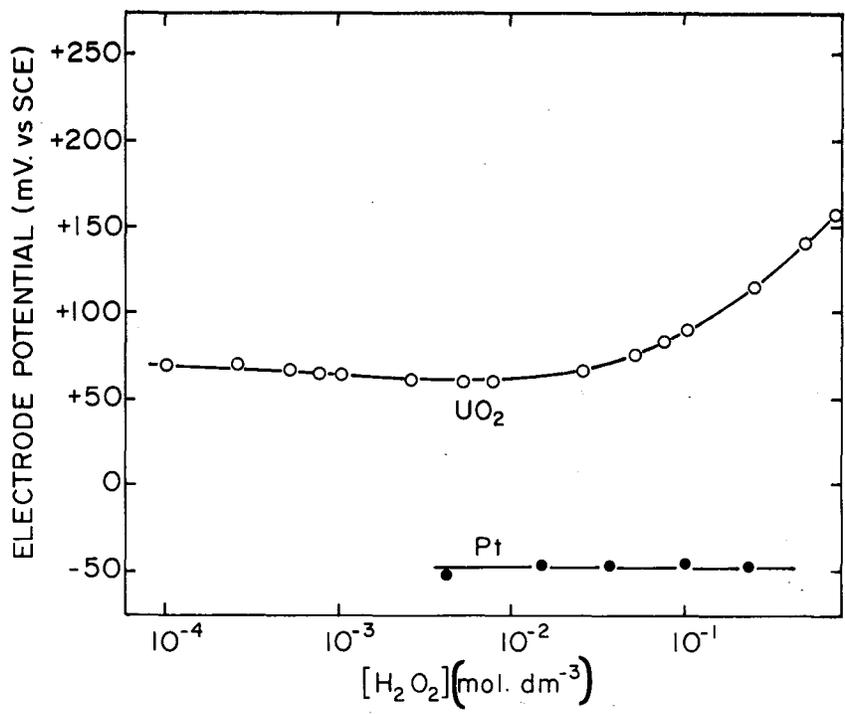


Figure 3. Steady-state corrosion potential of a UO₂ electrode (---○---), and the potential at a Pt electrode (---●---), as a function of H₂O₂ concentration, in 0.1 mol·dm⁻³ NaClO₄ solution (pH = 9.5).

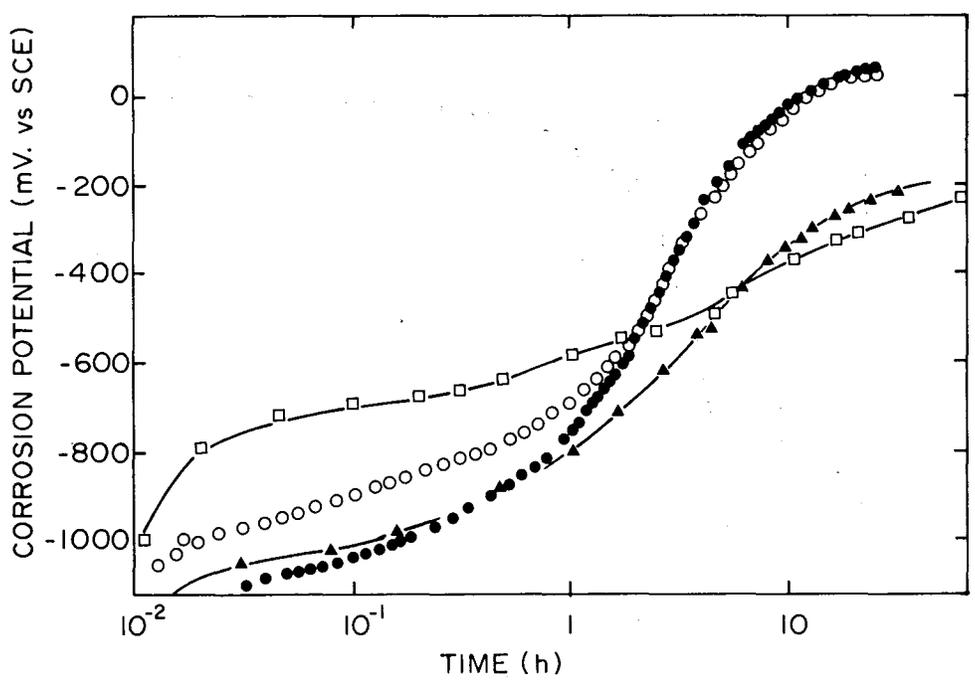


Figure 4. Corrosion potential of a UO₂ electrode in an Ar-degassed 0.1 mol·dm⁻³ NaClO₄ solution (pH = 9.5) (---□---) UO₂ electrode ~ 30 μm from a 4.7 μCi ²⁴¹Am α source; (---▲---) ~ 30 μm from a 100 μCi ²⁴¹Am α source; (○) ~ 30 μm from a 686 μCi ²¹⁰Po α source; (●) repeat experiment with 686 μCi α source.

WORKSHOP SUMMARY AND CONCLUSIONS

This workshop provided a unique opportunity to examine the role and underlying technical basis for the source terms used in calculating the long-term performance of nuclear waste repositories. It allowed a brief, but extremely revealing, exchange of information on modeling approaches, fundamental mechanisms, and experimental results by the participants. The representation of programs from many different countries allowed the development of an international perspective on the role of source terms. While in many cases there are different approaches and emphases in the various countries, numerous similarities and common understandings were revealed in the presentations and discussions.

The workshop first concentrated on the appropriate role of source terms in radionuclide isolation and on the need for definition and restrictions on the performance of the source term. In all cases, the knowledge of source-term performance clearly provides (1) a measure of the integrity of the waste form (high-level waste or spent nuclear fuel) in the repository environment and (2) definition of the rates of radionuclide release into the groundwater system. Different requirements are apparent in the programs represented by workshop participants. In the U.S., the regulatory agencies have stated specific performance objectives for the lifetime of the engineered barriers that provide containment of radioactivity and for the rate of release, as a function of the inventory present at 1000 years, from the engineered systems into the groundwater. The requirements in other countries are based largely on minimizing radionuclide release into the biosphere, but engineered systems that virtually guarantee containment for tens of thousands of years are proposed in many countries.

The spatial location of the source term received considerable attention. No common definition or specification was agreed upon. It was clear that different repository configuration and modeling approaches will require different definitions of the source term. However, it was believed that the definition is determined by the modeling method used and that it will in most cases be the interface where waste package modeling stops and transport calculations begin.

The description of the source term and the conditions that determine its characteristics are directly tied to the assumptions about the prevailing geohydrologic conditions in the repository. Conditions resulting from unlikely, disruptive events considered credible over extremely long times will also influence the source-term descriptions. These descriptions are generally presented in terms of scenarios for groundwater flow and waste package degradation. A wide range of scenarios was presented. Hard rock repositories (granite, basalt, tuff, etc.) are generally characterized as having small fluxes of water traveling either in the rock matrix or in fractures. Additional differences in defining scenarios are introduced by considering saturated or unsaturated repository conditions. A repository in

salt provides different mechanisms for source-term determination. The potential for thermally induced migration of in situ brine is being considered. The creep deformation of the rock has the potential not only to seal passageways and prevent waste-water contact but also to provide a mechanism for moving brine, initially present because of flooding of the underground cavities, to overlying aquifers. Finally, the inherent solubility of salt provides the means for various degrees of contact of brine with the waste form if unsaturated brine sources are available near the repository.

In all cases, the mechanisms that primarily determine the characteristics of the source term can be placed into four categories: the first deals with the amount of groundwater available to interact with the waste package and the geochemical condition of that water after modification by the thermal and radiation conditions in the vicinity of the waste. In the second category, the controlling mechanisms are those that determine the time and extent of degradation of the engineered barriers protecting the waste form. A third category of mechanisms deals with the dissolution of the waste form, including the selective degradation of various constituents and the speciation and quantity of individual radionuclides that are released. The last category deals with the host rock near the waste package, where the dominant mechanisms determining the source term involve the transport of radionuclides along the flow path and the competing processes for retarding or stimulating movement with respect to the groundwater flux.

While the source term modeling and experimental studies generally fit into these broad categories, a number of specific mechanisms were revealed that warrant additional evaluation. These include (1) the potential for alpha radiolysis of local groundwater that might create a "redox front," consisting of an oxidizing region that moves with the radionuclides in the groundwater system, (2) the quality and effects of gas produced from radiolysis and corrosion, (3) corrosion and failure mechanisms for canister materials that allow for water entry into the waste packages and the subsequent exit of solutions containing radionuclides, (4) the potential for formation of colloids and the chemical and physical mechanisms for their retardation in the groundwater system, and (5) the synergistic effect of each of these phenomena acting together over long periods of time.

Finally, the experimental basis for parameters defining the source term was examined. The evolution of repository concepts for specific host rock appears sufficiently advanced to allow an emphasis on experimental simulations of geochemical and hydrologic environments that would be present in a specific medium. It was believed such experiments should be encouraged. Further, the modeling of repository performance has also developed to the point that specific parameter needs and ranges can be specified. Thus, it is appropriate that interaction between experimentalists and modelers be encouraged and increased beyond that currently evident in most programs.

The process of combining the conceptual framework used by the modelers, the environmental conditions and controlling mechanism being defined by analysts, and the existing data base and experimental capabilities of the experimentalist was initiated by this workshop. It is hoped that additional interaction will provide elaboration on specific individual effects and further integration of these fundamental approaches into a comprehensive basis for modeling repository performance.

NEA WORKSHOP ON
THE SOURCE TERM FOR RADIONUCLIDE MIGRATION

Albuquerque, New Mexico
November 13-15, 1984

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