Title
On the Disposition of Graphite Containing TRISO Particles and the Aqueous Transport of Radionuclides via Heterogeneous Geological Formations

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On the Disposition of Graphite Containing TRISO Particles and the Aqueous Transport of Radionuclides via Heterogeneous Geological Formations

By

Bret Patrick van den Akker

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Engineering – Nuclear Engineering

in the

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of the

University of California, Berkeley

Committee in charge:

Professor Joonhong Ahn, Chair
Professor Eric B. Norman
Professor Per-Olof Persson

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Abstract

On the Disposition of Graphite Containing TRISO Particles and the Aqueous Transport of Radionuclides via Heterogeneous Geological Formations

by

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Doctor of Philosophy in Nuclear Engineering

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Deep Burn Modular High Temperature Reactors (DBMHR) have been proposed as a means to reuse the transuranic (TRU) content of commercial spent nuclear fuel (CSNF). By fissioning greater than 60% of the initial TRU load DBMHR’s transmute much of the fuel inventory into shorter-lived fission products. This use of a DBMHR to recycle CSNF offers remarkable benefits including the extraction of additional electricity without the need for additional raw fuel materials, added proliferation resistance by utilizing up to 99% of the $^{239}\text{Pu}$ content in the initial load, and a reduction of the radiotoxicity of the subsequent spent fuel. Two central features of the DBMHR design are the TRISO fuel particles and the all graphite core. This is important from a repository perspective because pure graphite is reported to be “one of the most chemically inert materials” known, and offers the potential to serve as an ultra-durable matrix for the sequestration of radionuclides (over geologic time periods) generated as a result of the nuclear fuel cycle.

In this study we evaluate the performance of DBMHR spent fuel (DBSF) for final geological disposition. The Yucca Mountain geological repository (YMR) is used as the environment for this study because of the completeness of the data sets necessary to conduct this investigation and because the regulations associated with the YMR provide a clear basis for evaluating the performance of the DBSF. A study of DBMHR fuel cycles shows a radiotoxicity benefit from the recycling CSNF in a DBMHR. Additionally, models developed to evaluate the release and transport of radionuclides from TRISO fuel particles and DBSF in a geological repository environment, including a novel model for the transport of an arbitrary length decay chain through an arbitrary combination of fractured and porous transport segments, demonstrate the efficacy of the DBMHR fuel cycle in reducing the environmental impact from the geological disposition of DBSF relative to CSNF. Calculations of the far-field transport of radionuclides released from DBSF are made by the newly developed TTBX computer code (a multi-region extension to the to the existing single region TTB computer code) which implements a numerical inversion of the Laplace-transformed analytical solutions to the radionuclide transport equation. This is done to evaluate the exposure of the target population. Results indicate
compliance of the fuel form with regulatory standards related to exposure via groundwater for all cases studied by many orders of magnitude.

In our studies of the repository behavior of DBSF we have seen here that graphite is an extremely robust material that has the potential to serve as a highly durable matrix for the sequestration of high level nuclear materials. The long lifetime of the graphite matrix (3 x 10^6 years at a minimum) allows many of the short-lived fission products to decay away before they are transported to the biosphere. Additionally, lifetime estimates for the graphite matrix greatly exceed the projected lifetime of many other matrices currently being considered such as UO2 or borosilicate glass. We have seen that in the YMR the long graphite lifetime assures that radionuclides are released congruently with the oxidation of the graphite (which oxidizes extremely slowly). This removes uncertainties associated with the solubilities of the radionuclides and assures that radionuclides will always be present at levels which are at or below their solubility limit. The remarkable performance of graphite in a geological repository highlights its utility to serve as a matrix for the disposition of nuclear material and the need for further detailed material studies of the performance of graphite in repository environments.
Chapter 1  Introduction

1.1 Introduction

High Temperature Reactors have been proposed to incinerate transuranics (TRUs), including plutonium, americium, neptunium (and possibly curium) derived from light water reactor (LWR) spent fuel. This concept is referred to as deep-burn because fissioning of TRU elements above 60% of the initial load can be attained in a single pass of the fuel through the reactor [1]. This use of a Deep Burn Modular High Temperature Reactor (DBMHR) to recycle commercial spent nuclear fuel (CSNF) offers remarkable benefits including the extraction of additional electricity, added proliferation resistance, and a reduction of the radiotoxicity of the spent fuel [1] [2] [3] [4]. Two central features of the DBMHR design are the TRISO fuel particles and the all graphite core.

Typical DBMHR designs utilize prismatic fuel elements (Figure 1.1) [1]. These are hexagonal graphite blocks (fuel elements) penetrated by holes arranged in a hexagonal lattice, some of which are filled with fuel or burnable poisons and others which are used for the coolant flow. The fuel is made of TRISO particles, which contain the fissile material. The TRISO particles are small multi-structural spheres with a kernel of fissile material, (Figure 1.2). The outer layer of the TRISO particle is comprised of pyrolytic carbon (PyC), the next layer, the main structural component of the particle, is made of silicon carbide (SiC) and, this is followed by a second layer of PyC, and finally surrounding the fuel kernel is a layer of porous carbon. These particles are dispersed in a graphite matrix that forms the cylindrical fuel compacts. The compacts are inserted into the fuel channels (Figure 1.3). The fuel elements are configured in a hexagonal array, within the reactor, on multiple levels to form the active region of the core (containing approximately 1,000 fuel elements and on the order of $10^{10}$ TRISO particles) [2] [5]. This all graphite core design of the DBMHR is reported to be highly attractive from a repository perspective because of the extremely slow corrosion of graphite in both air and water [6] [7] [8].

![Figure 1.1 Cross-section of hexagonal fuel element](image)

Figure 1.1 Cross-section of hexagonal fuel element [5].
Figure 1.2 Scanning electron microscopy image of TRISO particle showing fuel kernel, porous carbon buffer layer, IPyC layer, SiC layer, and OPyC layers [2].

Figure 1.3 TRISO particle, fuel compacts, and hexagonal fuel element [2].

Subsequent to discharge the spent fuel from the DBMHR (DBSF) will need to either be recycled in some fashion or sent to some location for final disposition. Geological disposal represents one of the best options for the long term containment of nuclear materials. If we assume a DBMHR has an effective operational lifetime of thirty
years, this means that there will be on the order of ten thousand hexagonal fuel elements to be disposed of per reactor over its operational lifetime. This is a non-trivial amount of spent nuclear fuel and highlights the need for a systematic study of the performance of the DBSF in a geological repository.

Once in the repository, one of the main pathways for the radionuclides contained in the DBSF to reach the biosphere is via aqueous transport through fracture networks in the geological media in which the DBSF is to be stored [9] [10]. Groundwater will infiltrate the tunnel drifts in which the nuclear materials are housed and corrode the multi-purpose containers (MPC’s) which hold the DBSF. Once water comes into contact with the DBSF radionuclides will begin to be leached into the groundwater. This radionuclide laden water will then flow through fracture networks to some down gradient location where individuals may be exposed to this contaminated water.

1.2 State of the Art

A literature review has revealed a number of studies which are relevant to the investigation of the geological disposal of DBSF. Studies conducted by Gray [6], and Fachinger, et al. [7] probed the material performance of graphite and silicon carbide (SiC) in aqueous environments. Both studies found graphite and SiC to be extremely resilient to aqueous water corrosion. However, it should be noted that in Gray’s 1982 study (which many studies on the repository performance of DBSF/TRISO particles reference) the graphite and SiC were only in contact with water for between 1 – 3 days, while Fachinger’s 2006 study was conducted over a period of more than two years. Although the results of the studies are in good agreement (order of magnitude) the results of Fachinger’s study are considered more reliable (because of the length of the experiment and variety of conditions studied) and are used throughout the remainder of this work.

Many studies on the repository behavior of DBSF have focused on the TRISO particles and their role in preventing the release of radionuclides into the surrounding environment [1] [2] [3] [11] [12]. A 2005 study at Argonne National Laboratory [11] investigated the role of the TRISO coatings in protecting the fuel kernels from exposure to groundwater. This study made use of a simplified representation of the waste package failure rate as a function of time and assumed either that the TRISO layers provided no protection for the fuel kernels (in this case the fuel kernels were assumed to be protected by the graphitic fuel compact) or that the kernels were protected exclusively by the TRISO layers. In both cases it was estimated that the fuel kernels could be protected from groundwater exposure for millions of years. However, this study did not take into account any other possible failure mechanism for the TRISO layers other than a simple dissolution mechanism and did not address the issue of radionuclide release from the TRISO kernels, nor any subsequent transport of these materials.

In other studies, it is suggested that the main mechanism for failure of the TRISO particles is over pressurization of the particle resulting from fission gas accumulation during reactor operation and α-decay subsequent to discharge coupled with a thinning of the SiC layer from groundwater contact [1] [3] [12]. These studies suggest that the TRISO particle be treated as a miniature pressure vessel with the SiC layer acting as the main structural component. Lifetime estimates of the SiC layer are on the order of hundreds of thousands of years [12], and are in good agreement with some of the estimates made in this study.
Investigations into the effect of the transmutation of TRU’s on the subsequent spent fuel from the Deep-Burn fuel cycle were made by a number of researchers [1] [2] [3] [5]. The utilization of up to 99% of the $^{239}\text{Pu}$ content of the fresh TRISO fuel can be achieved via the DBMHR fuel cycle [2]. Additionally, analyses of the DBSF have shown the potential for a modest a reduction in the radiotoxicity of the spent fuel. [1] [2] [3]. However, these studies fall short of discussing actual repository impacts such as radionuclide release or transport.

### 1.3 Purpose and Scope of this Dissertation

An extensive literature review on the geological disposition of DBSF has identified a number of studies relevant to an investigation in this area. The pertinent studies have mainly focused on the performance of the materials which constitute DBSF under repository conditions [6] [7] [8], radiotoxicity assessments of the spent fuel form [1] [4] [5], studies of failure mechanisms and rates for the TRISO particles [11] [12], and DBSF lifetime estimates [1] [8]. While these studies are relevant to the repository performance of the spent fuel, they do not constitute a performance assessment of the spent fuel form. Which is to say that no studies have been identified which characterize the release and transport of materials from DBSF stored in a geological repository, nor the potential health hazard posed to the public from such disposal in terms of an annual dose delivered to a representative individual.

A survey of available literature reveals that no comprehensive model for radionuclide release from TRISO fuel particles or DBSF in a geological repository environment has been developed, and no calculation of the far-field transport has been made for the released radionuclides in order to establish a basis on which to evaluate the exposure of the target population, and thus the compliance of the fuel form with regulatory standards. The objective of this study, therefore, is to evaluate the performance of DBMHR spent fuel (DBSF) for final geological disposition and to develop such models which are necessary to make this evaluation. The Yucca Mountain geological repository (YMR) has been chosen as the environment for this study based on the completeness of the data sets necessary to conduct this study and because the regulations associated with the YMR provide a clear basis for evaluating the performance of the spent fuel. A further goal of this is to assure that the models used and developed in this study for radionuclide transport in the near and far fields are sufficiently generic, so that they will allow for a comparison across a wide range of repository environments, given specified performance standards.

To implement this study we begin in Chapter 2 with an assessment of two potential DBMHR fuel cycles based on the recycling of CSNF. In this chapter, because of the availability of datasets and because of the practicalities of the study, only the TRU content of the CSNF and the subsequent DBSF is considered. In Chapter 3, motivated by the results in Chapter 2, which demonstrate a modest reduction in the radiotoxicity of the DBSF relative to CSNF, and which hint at the benefits of the longevity of the graphite waste form, we develop a detailed source term for the release of radionuclides from the DBSF, including detailed analysis of the lifetime of the graphite waste matrix, and a probabilistic analysis of the failure of the TRISO fuel particles in a repository environment. In Chapter 4, realizing that the product from the oxidation of graphite, CO$_2$, has an important effect on the solubilities of actinides and TRU’s we investigate the
solubilities of these radionuclides released from the DBSF in the YMR environment. The results from the studies in Chapter 3 and Chapter 4 are implemented in Chapter 5 in which the performance of the DBSF in the YMR is assessed by evaluating the annual dose received by the reasonably maximally exposed individual (RMEI) from radionuclides released and transported from the DBSF. Because of the important effects of fission products in aqueous transport analysis on the far-field dose, in Chapter 5 we make use of MOCUP burnup data for a third proposed fuel cycle. The data from the burnup calculations contains comprehensive information on the radionuclide inventory of the spent fuel, including actinide, TRU, fission, and activation product content, thereby providing the detailed information necessary for implementation in our comprehensive radionuclide transport analysis and performance assessment models. Finally, in Chapter 6 we develop a model and computer code for the calculation of the transport of radionuclides through heterogeneous geological formations. Comparison of the results with a lower fidelity model demonstrate that increasing model fidelity, in this case, results in a lower calculated dose to the RMEI, demonstrating the importance of high-fidelity, flexible models which maintain significant conservatism in their implementation.
Chapter 2  Analysis of Deep Burn Fuel Cycle Options, Radiotoxicity Assessment of Graphite Containing TRISO Particles, and Initial Radionuclide Release Estimates

2.1 Introduction
This chapter establishes the physical description of the DBSF. Two deep burn fuel cycle options are examined for the effects of transmutation on the reduction of radiotoxicity of the subsequent spent fuel and initial estimates of the release rates of radionuclides from DBSF into the near field environment are made. Commercial Spent Nuclear Fuel (CSNF) is used as a basis for comparison of the fuel cycles presented and only the contribution of the TRU’s and their decay daughters to the radiotoxicity of the spent fuel or released materials are considered. Because of the long half-lives associated with TRU’s and the low maximum permissible concentrations, these elements represent the majority of the long-term radiotoxicity of the spent fuel forms and will be sufficient for this portion of the study.

2.2 Description of Graphite/TRISO Waste Form
Typical DBMHR designs utilize prismatic fuel elements. These hexagonal graphite blocks are penetrated by 324 holes arranged in a hexagonal lattice, 216 of which are filled with fuel and 108 are used for the coolant flow. The fuel is made of TRISO particles, which contain the fissile material. The TRISO particles are small multi-structural spheres with a kernel of fissile material, 200μm in diameter, at its center. The outer layer of the TRISO particle is comprised of pyrolytic carbon (PyC), 40μm in thickness, the next layer, the main structural component of the particle, is made of silicon carbide (SiC) and is 35μm thick, this is followed by a second 35μm layer of PyC, and finally surrounding the fuel kernel is a layer of porous carbon 120μm thick. These particles are dispersed in a graphite matrix that forms cylindrical compacts 4.928 cm long and 1.245 cm in diameter. The compacts are inserted into the fuel channels (3,126 compacts per fuel element). The fuel elements, 79.3 cm tall and 36 cm wide flat-to-flat, are configured in a hexagonal array on multiple levels to form the active region of the core.

2.3 Fuel Cycle Options and Spent Fuel Inventory
In order to begin a discussion about the repository behavior of DBSF, we have evaluated the composition of the DBSF. As is mentioned above, the DBSF is comprised of hexagonal fuel elements loaded with cylindrical fuel compacts containing the TRISO particle. It is the TRISO particles that contain the fissile material necessary to generate the heat for operating the DBMHR. There are a number of different fuel cycles and fuel compositions that have been proposed for the Deep Burn process. In the following analysis, we make use of the proposed fuel loading scheme and fuel cycles found in [2] (Figure 2.1 and Figure 2.2). The first fuel cycle is based on the recycling of CSNF. The fresh deep burn fuel spends a three-year residence time in the DBMHR and in the second fuel cycle we allow for a further recycling of the DBSF. In the second fuel cycle, after removing the fission products from the spent TRISO fuel, the TRU’s are combined with the Am and Cm from the CSNF and the resulting fuel spends three more years in the DBMHR, after which it is transferred to an accelerator driven sub-critical reactor for four
additional years. The first fuel cycle will only consider a once through fuel cycle based on a Np/Pu oxide fuel (with the Am and Cm from the CSNF is destined for long-term storage) and a single three year burn in the DBMHR reactor. The second fuel cycle will utilize the Am and Cm from the CSNF in the second pass through the reactor.

Figure 2.1 Mass flow for a once through Deep Burn fuel cycle [2].

Figure 2.2 Mass flow for a twice through Deep Burn fuel cycle [2].
2.4 Radiotoxicity of DBSF

One method of assessing the potential radiological impact of spent nuclear fuel is to calculate its radiotoxicity. Radiotoxicity is measured in terms of the amount of water necessary to dilute the radioactive material of interest to the highest allowable concentration given a specified set of regulatory standards. The radiotoxicity of a given amount of spent fuel is a material-specific quantity, and will be invariant under differing disposal conditions. Given a fuel inventory, the computer code ORIGEN2 can calculate the radiotoxicity as a function of time in the repository [13]. The radiotoxicity of a material is given as

\[
\text{Toxicity} (m^3 \text{water}) = \sum_i \frac{\lambda_i N_i}{C_i},
\]

where the numerator is the activity of the \(i\)th radionuclide (in Bq or Ci) and the denominator, \(C_i\), is its maximum permissible concentration (in terms of Bq/(m\(^3\) water) or Ci/(m\(^3\) water)). Because of their long half-lives and low maximum permissible concentrations, TRU’s represent the largest and longest lasting contributors to the overall radiotoxicity of a spent fuel form [14]. By making an analysis of the content of the fuel at various stages in the fuel cycle we can draw conclusions on the effectiveness of the DBMHR in reducing the radiotoxicity burden in a geological repository.

Table 2.1 shows the radionuclide inventory of the CSNF and the DBSF fuel forms which were used to make the following radiotoxicity calculations [2]. Figure 2.3 shows the results of the radiotoxicity analysis of the one-pass fuel cycle. The fresh TRISO fuel is composed of the Np and Pu from the CSNF. The Am and Cm are not considered here to be part of the TRISO fuel; therefore in order to make a fair comparison, their contribution to the overall radiotoxicity are included in the analysis of both the CSNF and the spent TRISO fuel from the one-pass fuel cycle (Figure 2.1).

<table>
<thead>
<tr>
<th>Radionuclide Inventory</th>
<th>LWR TRU</th>
<th>Fresh TRISO</th>
<th>Spent TRISO</th>
<th>Transmuted TRISO</th>
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<td>2.07</td>
</tr>
<tr>
<td>241Pu</td>
<td>7.47</td>
<td>0.747</td>
<td>8.3</td>
<td>0.747</td>
</tr>
<tr>
<td>242Pu</td>
<td>4.5</td>
<td>0.45</td>
<td>5</td>
<td>0.45</td>
</tr>
<tr>
<td>241Am</td>
<td>8.18</td>
<td>0.818</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>242mAm</td>
<td>0.03</td>
<td>0.003</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>243Am</td>
<td>1.48</td>
<td>0.148</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>244Cm</td>
<td>0.29</td>
<td>0.029</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>245Cm</td>
<td>0.02</td>
<td>0.002</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>10</td>
<td>100</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 2.1 LWR TRU Waste and TRISO Inventory from 1000kg CSNF [2].
An initial analysis of the radiotoxicity of the two fuel forms shows that the spent TRISO fuel is more toxic than the CSNF. However, it should be noted that the composition of the fuel has changed, and that the main constituents of the spent TRISO are now $^{244}\text{Cm}$ and $^{242}\text{Pu}$. $^{244}\text{Cm}$ has a relatively short half-life of about 18 years and should cease to contribute to the overall toxicity rapidly. Even when we include the Am and Cm from the CSNF we can still see a marked difference in the fuel forms. Additionally, we see that overall, the TRU content of the CSNF is reduced by 60%. However, a time dependent analysis of the behavior of the CSNF and spent TRISO is necessary in order to see if there is any radiotoxicity benefit of the once through Deep Burn fuel cycle (Figure 2.1).

Figure 2.4 shows the results of the twice through fuel cycle option (Figure 2.2). In this comparison we see that the TRU content of the transmuted TRISO fuel has a slightly greater radiotoxicity than the CSNF while the remaining TRU mass has been reduced by an order of magnitude (by the fissioning of 90% of the original TRU content of the CSNF, including greater than 99% utilization of the $^{239}\text{Pu}$ content). It can also be seen that the constituents of the fuel has changed dramatically, and that the main constituent of the transmuted TRISO in terms of its radiotoxicity is now $^{244}\text{Cm}$ which has a half-life of about 18 years. Because of the short-lived nature of this portion of the fuel, if we make an analysis of the radiotoxicity as a function of time we should expect to see a rapid reduction in the radiotoxicity of the TRISO fuel form.

![Figure 2.3 Radiotoxicity of CSNF TRU content and fresh and spent TRISO fuel forms from the once through fuel cycle (Figure 2.1).](image-url)
The time-dependent radiotoxicity of the TRU’s from the CSNF and the DBSF from both fuel cycles was calculated with the ORIGEN2 computer code. The input data is given in Table 2.1. In our analysis, we will consider the fact that the fissile material making up the TRISO fuel has been utilized multiple times. That is, we have been able to extract more energy out of the same amount of material without the need for additional raw materials. In this light, it is a fair analysis to judge the fuel forms on a GWd basis (i.e. (m³ water)/GWd). Using a burnup of 50GWd/MTHM, a capacity factor of 0.8, and a thermal efficiency of 0.325 for the CSNF and a burnup of 600 GWd/MTHM, a capacity factor of 0.8, and a thermal efficiency of 0.5 for the Deep Burn TRISO we are able to generate the results below (Figure 2.5). We see, using this normalization, that the spent TRISO fuel is less toxic from the moment of discharge from the DBMHR, and remains that way through the million-year time frame studied. Although it is the case for the once through fuel cycle that in the very early times (< 10 years) and very long times (> 10⁵ years) the radiotoxicity of the spent fuel form is nearly equal to the CSNF (on a GWd basis). Based on these results we can conclude that the one-recycle Deep Burn fuel cycle is an effective way of extracting extra energy from the CSNF while modestly reducing the radiotoxicity burden that the subsequent spent fuel will pose. Further, as can be seen in Table 2.1, the overall plutonium inventory has been substantially reduced, thus illustrating the efficacy of the one-recycle Deep Burn fuel cycle as a means to mitigate the proliferation of weapons grade material. We see similar, although more marked, results for the twice through fuel cycle. This issue requires further study, however, as the fate of the reprocessing byproducts and the fission products and decay daughters generated during residence in the DBMHR have not been accounted for.
Figure 2.5 Radiotoxicity of CSNF, spent TRISO (once-through cycle) and transmuted TRISO (twice through cycle) normalized to total GWde produced over lifetime of the fuel.

Figure 2.6 shows a breakdown of the radiotoxicities of the TRU constituents of the CSNF. We see that the main contributors to the overall radiotoxicity are initially $^{241}\text{Am}$, $^{240}\text{Pu}$, and $^{239}\text{Pu}$ (until approximately 100,000yrs) while the later behavior is dominated by $^{237}\text{Np}$ and $^{242}\text{Pu}$. Figure 2.7 shows a breakdown of the radiotoxicity of the once through spent TRISO fuel form (Figure 2.1). We see that the early behavior of the once through DBSF (plus the Am and Cm from the recycling of the CSNF) is again dominated by $^{241}\text{Am}$ and $^{240}\text{Pu}$, however the $^{239}\text{Pu}$ contribution (and inventory) has been reduced by a substantial amount (close to two orders of magnitude). The later behavior of the fuel form is dominated by $^{239}\text{Pu}$, $^{237}\text{Np}$, and $^{242}\text{Pu}$. Finally, in Figure 2.8, we examine the behavior of the twice through cycle (Figure 2.2). We can see that the main contributors to the overall radiotoxicity change rapidly with time. The earliest contributors to the overall toxicity are $^{244}\text{Cm}$ and $^{238}\text{Pu}$, however, their contribution rapidly reduces and are negligible by 1,000 and 10,000 years respectively. For the time frame of between roughly 500 to 100,000 years the main contributors are $^{241}\text{Am}$, $^{243}\text{Am}$, and $^{240}\text{Pu}$. The long-term behavior is dominated by $^{237}\text{Np}$ and $^{242}\text{Pu}$. 
Radiotoxicity from 1000kg CSNF

Figure 2.6 Total radiotoxicity of TRU's from 1000kg of CSNF.

Radiotoxicity of Spent TRISO (+ Am & Cm from CSNF recycling) from 1000kg CSNF

Figure 2.7 Radiotoxicity of spent TRISO fuel with Am and Cm from CSNF (once-through fuel cycle).
2.5 Preliminary Release Model

A model has previously been developed within the Waste Management Research Group at U.C. Berkeley that is well adapted to use in the determination of the release rate of radionuclides from a failed waste package (or the simultaneous release from multiple failed waste packages) in a geological repository [14]. The radiotoxicity of the released radionuclides is used as a measure of the environmental impact of storing spent nuclear fuel in a geological repository. Radionuclides that are released from a failed package are considered to have an environmental impact even though some of the released material could still be contained within the engineered barriers or in the near-field host rock. In this manner we can elucidate whether DBSF may be acceptable for disposal in a geologic repository, and we can use the previous study on the disposal of CSNF as a basis for comparison [14].

Although this model was developed to determine the release rates of nuclides from failed waste packages containing CSNF and defense waste, with careful interpretation it can also be applied to the case of failed waste packages containing DBSF. The main difficulty in adapting this model to DBSF stems from the disparate nature of DBSF with respect to CSNF. While CSNF was idealized as a base matrix material (UO$_2$ in the case of CSNF) with its radionuclide inventory homogenously spread throughout, DBSF is of a different nature entirely. It is the graphite waste matrix of the DBSF fuel elements and the TRISO particles that makes the DBSF so different. Rather than having the inventory of radionuclides spread evenly throughout the matrix material, the TRISO particles contain the spent fuel in discreet locations within the graphite matrix.

![Radiotoxicity of Transmuted TRISO from 1000kg CSNF](image)

Figure 2.8 Total radiotoxicity of transmuted TRISO fuel (twice-through fuel cycle).
(the fuel compact and fuel element). The protective PyC and SiC coatings of the TRISO particles prevent the release of radionuclides within the matrix material until they are compromised and the fuel kernel is exposed to the corroding environment. Additionally, the rate at which the various layers of the TRISO particle corrode (with respect to the graphite fuel compact and graphite fuel element) may play a role in the rate of radionuclide release. However, if it is assumed that the graphite corrodes much slower than either the PyC or SiC layers of the TRISO particle (which is currently indicated by experimental studies) [6] [7], and that the TRISO particles are distributed homogeneously throughout the graphite matrix of the DBSF, then the model described previously can be applied with only minor adaptations.

2.5.1 Physical Processes

When the graphite matrix of DBSF comes into contact with groundwater, the matrix begins to oxidize and radionuclides are released (assuming homogeneous distribution of radionuclides in the matrix as discussed previously). If the solubility of an individual radionuclide is sufficiently high, then that nuclide will be released congruently with the waste matrix. That is, the fractional release rate of the radionuclide will be equal to the fractional dissolution rate of the waste matrix. However, if the solubility of an individual radionuclide is relatively low with respect to the waste matrix, then a low solubility precipitate of that radionuclide will form and the precipitate will dissolve at a rate governed by the mass transfer of the radionuclide into the pores of the surrounding host rock, with the concentration of the nuclide in the water adjacent to the surface of the waste form given by its solubility [14]. Solubility limits for a number of important radionuclides are already well established for certain repository conditions in the case of CSNF in the YMR [14]. These solubilities will be used in this present study, although it should be mentioned that the corrosion product of the oxidation of graphite is CO₂. This will likely have an impact on the geochemistry of the corroding groundwater, and may have an important effect on the solubilities of radionuclides released from the DBSF.

2.5.2 Mathematical Formulation

Presented in this section is an outline of the mathematical model that is used to calculate the release rate of radionuclides from failed waste packages. For a detailed discussion of the model, the reader is referenced to [14].

Consider that a waste package is placed into a repository at time \( t = 0 \) and that it subsequently fails at a time \( t = T_f \). During this time no radionuclides are released into the environment (the mass of waste in the environment \( W_i(t) \) is equal to zero here). However, because of the process of nuclear decay, the overall inventory of the package will change. During this time the mass \( M_i(t) \) of the \( i \)th nuclide is determined by,

\[
\frac{dM_i(t)}{dt} = -\lambda_i M_i(t) + \lambda_{i-1} M_{i-1}(t),
\]

\[
0 < t \leq T_f, \quad i = 1, 2, \ldots, \lambda_0 = 0,
\]  

subject to
The solution of which is the well-known Bateman equation \[15\]. After \( t = T_f \) the waste package is considered to fail and is immediately flooded with water which begins to corrode the waste form. After the package fails the governing equations become,

\[
\frac{dM_i(t)}{dt} = -\lambda_i M_i(t) + \lambda_{i-1} M_{i-1}(t) - F_i(t),
\]

\[ t > T_f, \quad i = 1, 2, \ldots, \lambda_0 = 0, \]

(2.3)

for the mass in the package, subject to the value of \( M_i(T_f) \) obtained by the solution to (2.1) as the initial condition, and

\[
\frac{dW_i(t)}{dt} = -\lambda_i W_i(t) + \lambda_{i-1} W_{i-1}(t) - NF_i(t),
\]

\[ t > T_f, \quad i = 1, 2, \ldots, \lambda_0 = 0, \]

(2.4)

subject to

\[ W_i(T_f) = 0, \quad i = 1, 2, \ldots, \]

(2.5)

for the mass of the \( i \)th nuclide in the environment from \( N \) failed waste packages. Both (2.3) and (2.4) contain the term \( F_i(t) \) which is the release rate of the \( i \)th nuclide from the failed waste package.

The release of radionuclides is considered to occur in two modes in this model: in a congruent release mode or in a solubility limited release mode. In the case of congruent release the fractional release rate of the nuclide is equal to the fractional dissolution rate of the waste matrix. If the solubility of an individual radionuclide is low, then a precipitate of the nuclide will form. The precipitate slowly dissolves at a rate given by the rate of mass transfer into the water in the pores in the surrounding medium, with the concentration of the nuclide in the water adjacent to the surface of the waste form given by its solubility. For the case of a graphite waste matrix, the dissolution rate is taken to be \( 1.3 \times 10^{-6} \text{ g/m}^2\text{/day} \) in the case of fast graphite oxidation and \( 7.4 \times 10^{-8} \text{ g/m}^2\text{/day} \) in the case of slow graphite oxidation, which is within the ranges in \[7\]. The full solution to the above model is available in \[14\].

2.5.3 Input Data

Below, Tables 2.2 to Table 2.5 provide a summary of the input data necessary for the release model described in the previous section.
### Table 2.2 TRISO Fuel, Compact, Element, and Waste Package Data.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel type</td>
<td>TRUO2</td>
<td>Mass of graphite per element (kg)</td>
<td>Number of Element/Assemblies</td>
</tr>
<tr>
<td>Kernel (diameter, mm / density in g/cm$^3$)</td>
<td>200 / 10.0</td>
<td>Dimensions (length in mm / across flats of hexagon in mm)</td>
<td>Waste Packages Parameters Used in the Analysis</td>
</tr>
<tr>
<td>Buffer layer (thickness, mm / density in g/cm$^3$)</td>
<td>120 / 1.05</td>
<td>Volume (m$^3$)</td>
<td>Radius (m)</td>
</tr>
<tr>
<td>IPyC layer (thickness, mm / density in g/cm$^3$)</td>
<td>35 / 1.9</td>
<td>Number of compacts per element</td>
<td>Length (m)</td>
</tr>
<tr>
<td>SiC layer (thickness, mm / density in g/cm$^3$)</td>
<td>35 / 3.18</td>
<td>Mass of carbon in an average fuel element including compacts (excluding TRISO coatings, kg / including TRISO coatings, kg)</td>
<td>Waste Matrix</td>
</tr>
<tr>
<td>OPyC layer (diameter, mm / density in g/cm$^3$)</td>
<td>40 / 1.9</td>
<td>Total mass of an average fuel element (kg)</td>
<td></td>
</tr>
<tr>
<td>Radius (cm)</td>
<td>0.6225</td>
<td></td>
<td>DBSF</td>
</tr>
<tr>
<td>Length (cm)</td>
<td>5.114</td>
<td></td>
<td>0.481 (whole element)</td>
</tr>
<tr>
<td>Matrix (density in g/cm$^3$)</td>
<td>1.7</td>
<td></td>
<td>0.225 (compact only)</td>
</tr>
<tr>
<td>Packing fraction (%)</td>
<td>24</td>
<td></td>
<td>5.144</td>
</tr>
<tr>
<td>Number of TRISO particle per avg. compact</td>
<td>10753</td>
<td></td>
<td>Graphite</td>
</tr>
<tr>
<td>Mass of fuel compact (g)</td>
<td>11.79</td>
<td></td>
<td>CSNF</td>
</tr>
<tr>
<td>Number of graphite per element (kg)</td>
<td>90</td>
<td></td>
<td>42 graphite fuel elements</td>
</tr>
<tr>
<td>Mass of graphite per element (kg)</td>
<td>90</td>
<td></td>
<td>0.792</td>
</tr>
<tr>
<td>Dimensions (length in mm / across flats of hexagon in mm)</td>
<td>794 / 360</td>
<td></td>
<td>5.165</td>
</tr>
<tr>
<td>Volume (m$^3$)</td>
<td>0.0889</td>
<td></td>
<td>UO2</td>
</tr>
<tr>
<td>Number of compacts per element</td>
<td>3126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass of carbon in an average fuel element including compacts (excluding TRISO coatings, kg / including TRISO coatings, kg)</td>
<td>115.1 / 123</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total mass of an average fuel element (kg)</td>
<td>126.9</td>
<td></td>
<td></td>
</tr>
</tbody>
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### Table 2.3 Waste Package Parameters (adapted from [14]).

<table>
<thead>
<tr>
<th>Waste Package Design</th>
<th>Number of Element/Assemblies</th>
<th>Waste Packages Parameters Used in the Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBSF</td>
<td>42 graphite fuel elements</td>
<td>0.481 (whole element)</td>
</tr>
<tr>
<td>Multi-Purpose Canister</td>
<td></td>
<td>0.225 (compact only)</td>
</tr>
<tr>
<td>CSNF</td>
<td>21-PWR 21 PWR fuel assemblies</td>
<td>0.792</td>
</tr>
<tr>
<td></td>
<td>12-PWR 12 PWR fuel assemblies,</td>
<td>5.165</td>
</tr>
<tr>
<td></td>
<td>44-BWR 44 BWR fuel assemblies</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24-BWR 24 BWR fuel assemblies</td>
<td></td>
</tr>
</tbody>
</table>
### Table 2.4 Solubility Data for Radionuclide Inventory [14].

<table>
<thead>
<tr>
<th>Elements</th>
<th>Minimum (mol/m$^3$)</th>
<th>Maximum (mol/m$^3$)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl, H, Sr, Te, Rh, Ru</td>
<td>1.00E+03</td>
<td></td>
<td>These were assumed to be released congruently with the waste matrix.</td>
</tr>
<tr>
<td>Cd, Sb, I, Cs, Pm, Eu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>1.00E+01 9.40E-03</td>
<td>1.00E+02 9.40E-01</td>
<td>These values have been taken from TSPA-VA.</td>
</tr>
<tr>
<td>Pd</td>
<td>6.80E-07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>1.00E-04</td>
<td></td>
<td>For these elements, in TSPA-SR, fixed values were given.</td>
</tr>
<tr>
<td>Nb</td>
<td>5.01E-05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>1.00E-02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>2.30E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>2.00E-05 1.92E+02</td>
<td></td>
<td>For these elements, in TSPA-SR ranges are as shown.</td>
</tr>
<tr>
<td>Ni</td>
<td>1.40E-03 3.10E+03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pu</td>
<td>1.00E-07 2.00E-01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pa</td>
<td>1.00E-07 1.00E-02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>1.00E-07 1.00E-02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cm</td>
<td>2.00E-05 1.90E+02</td>
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<td></td>
</tr>
<tr>
<td>U</td>
<td>5.01E-04 3.98E-01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Am</td>
<td>2.00E-05 1.90E+02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np</td>
<td>2.00E-03 1.58E+01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ac</td>
<td>2.00E-05 1.90E+02</td>
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</tr>
</tbody>
</table>

### Table 2.5 Inventory of CSNF and DBSF (adapted from [14], [2]).

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-Life (yr)</th>
<th>MPC(Ci/m$^3$)</th>
<th>Inventory per Package at Emplacement (mol/package)</th>
<th>Inventory per Package at Package Failure (75,000 yrs) (mol/package)</th>
<th>CSNF</th>
<th>DBSF</th>
<th>CSNF</th>
<th>DBSF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{243}$Cm</td>
<td>8.50E+03</td>
<td>2.00E-08</td>
<td>9.02E-02</td>
<td>1.07E-01</td>
<td>1.99E-04</td>
<td>2.35E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{244}$Cm</td>
<td>1.80E+01</td>
<td>3.00E-08</td>
<td>1.29E+00</td>
<td>1.45E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td>7.40E+03</td>
<td>2.00E-08</td>
<td>6.18E+00</td>
<td>6.59E+00</td>
<td>5.50E-03</td>
<td>5.86E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{242m}$Am</td>
<td>1.40E+02</td>
<td>2.00E-08</td>
<td>4.45E-02</td>
<td>1.29E-01</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>4.30E+02</td>
<td>2.00E-08</td>
<td>2.71E+01</td>
<td>1.84E+01</td>
<td>1.06E-05</td>
<td>1.26E-05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>3.80E+05</td>
<td>2.00E-04</td>
<td>2.55E+01</td>
<td>1.71E+01</td>
<td>2.23E+01</td>
<td>1.49E+01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>1.40E+01</td>
<td>1.00E-06</td>
<td>2.32E+01</td>
<td>1.36E+01</td>
<td>3.28E-07</td>
<td>3.88E-07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>6.50E+03</td>
<td>2.00E-08</td>
<td>3.54E+02</td>
<td>1.81E+00</td>
<td>1.19E-01</td>
<td>1.09E-03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>2.40E+04</td>
<td>2.00E-08</td>
<td>1.86E+02</td>
<td>2.10E+00</td>
<td>2.23E+01</td>
<td>1.32E+00</td>
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</tr>
<tr>
<td>$^{238}$Pu</td>
<td>8.80E+01</td>
<td>2.00E-08</td>
<td>7.10E+00</td>
<td>3.95E+00</td>
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<td>5.08E+00</td>
<td>7.06E+01</td>
<td>3.63E+01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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2.5.4 Numerical Results

Discussed in this section are the numerical results of applying the computer code for the release of radionuclides into the environment discussed in the previous sections. For all of the cases considered the package failure time was taken to be 75,000 years [14]. The cases of high and low solubility for graphite are explored using the results of leaching experiments presented in [7]. The performance of the graphite waste matrix is compared to that of CSNF (UO$_2$) as a means to gauge the durability of the graphite waste form. In this analysis, it is assumed that the protective TRISO coatings are not present, and that the radionuclide inventory is spread homogeneously throughout the graphite fuel element, or fuel compact (whole element disposal and compact disposal, respectively). In the case of whole element disposal, it is considered that the entire fuel element is placed in the waste package, while in the case of compact disposal it is assumed that the fuel compacts have been removed from the fuel elements and subsequently placed into the waste package. In both cases each waste package contains the same radionuclide inventory; the difference is the smaller amount of graphite matrix in the case of compact disposal.

Figure 2.9 shows the fraction of remaining waste matrix in the waste package as a function of time. As can be seen in both cases the graphite fuel element and fuel compact perform surprisingly well. Even in the high solubility case, more than 90% of the waste matrix (and thus the radionuclide inventory because of the homogenization assumption discussed above) remains in the waste package for more than 10 million years. The results are even more remarkable when compared to that of CSNF. CSNF is seen to degrade completely before the 500,000-year mark. Not shown in the figure is the result for the low solubility CSNF case. This instance very closely mirrored the fast oxidation regime for the compact only disposal condition with a lifetime of approximately $3 \times 10^8$ years.

In Figure 2.10 we see the results of comparing the release rates of CSNF to that of DBSF (both once-through cycle and the twice-through option). For this calculation we considered that 63,000MT of commercial spent fuel (the amount that is proposed for YMR) was processed and the relevant material was separated and converted into TRISO pellets destined for a Deep Burn reactor and the radiotoxicity subsequently released into the environment from failed waste packages was normalized to the total amount of energy generated over the lifetime of the fuel form. Further, we assumed the low value for the solubility of the CSNF waste matrix (UO$_2$) given in [14] and a high value for the constant dissolution rate of the graphite waste matrix ($1.3 \times 10^{-6}$ g/m$^2$/day). The results for the spent TRISO were generated assuming that the Am and Cm from the CSNF that was not included in the once-through fuel, was packaged into a graphite matrix in a similar manner to the DBSF. The number of waste packages is 7886 for the CSNF, 12,073 for the once through DBSF, and 4829 for the once-recycled DBSF (transmuted TRISO). We can clearly see in these results that if the post-irradiated graphite does indeed perform as robustly as assumed that there is a clear benefit in terms of radiotoxicity released into the environment as well as in extra energy production.
Lifetime Comparison of CSNF and DBSF Across Disposal Conditions

Figure 2.9 Fraction of waste matrix remaining in waste package after failure.

Figure 2.10 Radiotoxicity released from CSNF, Spent TRISO and Transmuted TRISO normalized to total electrical power production over lifetime of the fuel.
2.6 Summary

Based on these results we can conclude that the once through Deep Burn fuel cycle is an effective way of extracting extra energy from the CSNF while simultaneously reducing the radiotoxicity burden that the subsequent spent fuel will pose. This issue requires further study, however, as the fate of the reprocessing byproducts (fission products, and decay daughters) has not been accounted for. Additionally, per ton of CSNF we are able to generate an additional 2.16GWd electricity (for a once through fuel cycle) and up to 3.12GWd electricity (for the transmutation option, without accounting for losses from the accelerator driven portion of the fuel cycle), without the need for any additional raw fuel materials. This reduces our overall annual natural uranium requirement by between 0.57MT and 1.23MT (for once-through and twice-through respectively) per 1000 kg of CSNF. This represents a savings of between 7.7% to 16.6% on the raw materials and an additional 16.6% to 24% electrical power generation. Further, the $^{239}$Pu inventory has been substantially reduced, thus illustrating the efficacy of the Deep Burn process as a means to mitigate the proliferation of weapons grade material.

From the results of the preliminary analysis of radionuclide release, graphite appears to be an extremely robust waste form with very low radionuclide release rates. However, a number of assumptions and simplifications were made that may affect the reliability of this study. First, the radionuclide inventory was taken to be homogeneous throughout the graphite waste matrix while it is in fact contained in concentrated kernels spread heterogeneously through the matrix. The release of radionuclides from failed TRISO particles could cause a deviation from the above results. Second, the experiments that provided the dissolution rates for graphite that were used in the analysis above, were not carried out on post-irradiated graphite. In order to provide an accurate estimate of the release rates of radionuclides from DBSF it is important that experiments be carried out to verify the dissolution rates that have previously been reported, or (if the material properties with respect to leaching behavior are different for post-irradiated graphite) to provide accurate estimates of corrosion behavior. Third, the solubilities used to calculate the release rates from the DBSF are those which are strictly valid for CSNF. The oxidation of graphite that takes place when the DBSF comes into contact with the groundwater will introduce CO$_2$ into the groundwater system and thereby alter the groundwater geochemistry. It is unknown at this time what effects this may have; subsequent studies will investigate this matter. Finally, no sorption processes of radionuclides with the graphite matrix were included. Given all of the above uncertainties in the analysis performed, it cannot be concluded with certainty that the results represent a conservative point of view. This analysis should serve as a starting point for further studies in which the above uncertainties and assumptions can be addressed.
Chapter 3  Source Term Development for Implementation in Radionuclide Transport Calculations

3.1 Introduction

Previous assessments of the performance of DBSF in a geological repository indicate that graphite may be a superior matrix for the disposal of high level nuclear wastes. However, a number of assumptions were made which were not supported. One example is the neglecting of the TRISO layers as a barrier against the release of radionuclides, and another is the use of incomplete radionuclide inventory datasets to calculate the radiological impact of the DBSF from the TRU content only. In order to make a rigorous performance assessment of DBSF in a geological repository a detailed assessment of DBSF must be made from the standpoint of developing a source term for subsequent radionuclide transport calculations. This chapter establishes rigorous lifetime estimates for the graphite waste from and the TRISO particles. From Chapter 3 forward, in order to make the most accurate and consistent assessments, we make use of fuel cycle datasets and fuel loading protocols outlined in [5] along with data from other studies which remain relevant. The results of this source term development will be used throughout the remainder of the study and will support simplifying conservative assumptions used in subsequent transport calculations.

3.2 Graphite Waste Form Lifetime Assessment

For a discussion about the near-field behavior of DBSF, we need to understand the behavior of the elements that comprise the spent fuel form. In the case of DBSF, the two main components are the graphite matrix and the TRISO particles, each of which serves as an engineered barrier against the release of radionuclides from the spent fuel. We begin our discussion with an assessment of the lifetime of the graphite matrix when in contact with groundwater.

The process of oxidation that takes place when graphite comes into contact with liquid water in the presence of air occurs with the dissolved oxygen in the water, and oxygen absorbed on the surface of the graphite, not with the water itself (although the water catalyzes the reaction). This is evidenced by the fact that the oxidation rate is higher in the presence of water and the activation energy is lower [7]. Long-term degradation studies performed on graphite in a brine solution revealed the absence of hydrogen or carbon monoxide in the gas phase composition, which indicates that corrosion is not caused by the interaction of graphite with water. Further, short-term degradation studies performed on graphite in both brine and water solutions under argon, air, and oxygen atmospheres show marked differences in the corrosion rates [6] [7]. The corrosion rates are the fastest when the graphite was under a pure oxygen atmosphere and slowest under an argon atmosphere. Additionally, there was a significant difference between the corrosion rates of graphite samples in brine and water under a pure oxygen atmosphere. The samples in the water/oxygen system corroded much faster than those in the brine/oxygen system. This can be explained by the fact that the solubility of oxygen in NaCl and MgCl₂ solutions (the two brines studied were NaCl and MgCl₂ based) decreases with increasing salt concentration [7]. Therefore, the corrosion rate of graphite in water will be limited not only by the availability of dissolved oxygen in the water, but also by the kinetics of the oxidation process and the solubility limit of the corrosion.
product(s) in the water. Table 3.1 provides graphite corrosion rates in a number of aqueous solutions and under various gaseous atmospheres.

<table>
<thead>
<tr>
<th>Material</th>
<th>Aqueous Solution</th>
<th>Atmosphere</th>
<th>R(g/m²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>Brine</td>
<td>Argon</td>
<td>1.70E-08</td>
</tr>
<tr>
<td>Graphite</td>
<td>Water</td>
<td>Oxygen</td>
<td>1.29E-06</td>
</tr>
<tr>
<td>Graphite (irradiated)</td>
<td>Brine</td>
<td>Argon</td>
<td>1.28E-05</td>
</tr>
<tr>
<td>PyC</td>
<td>Brine</td>
<td>Oxygen</td>
<td>9.30E-08</td>
</tr>
<tr>
<td>PyC</td>
<td>Water</td>
<td>Oxygen</td>
<td>4.70E-07</td>
</tr>
<tr>
<td>PyC (irradiated)</td>
<td>Brine</td>
<td>Argon</td>
<td>2.60E-05</td>
</tr>
<tr>
<td>SiC</td>
<td>Water</td>
<td>Air</td>
<td>2.03E-06</td>
</tr>
<tr>
<td>SiC</td>
<td>Brine</td>
<td>Air</td>
<td>4.09E-05</td>
</tr>
</tbody>
</table>

For the oxidation of the graphite waste matrix, we make the following simplifying assumptions. We first make a geometric transformation of the DBSF from 42 hexagonal fuel elements (in the case of whole element disposal), or a single cylindrical fuel compact (in the case of compact only disposal), into a graphite sphere of equivalent mass. Additionally, we consider that the rate at which the oxidation proceeds remains constant. If we consider a sphere of radius \( r \) (in m) and density \( \rho \) (in kg/m³) degrading at a rate \( R \) (in kg/m²/s), then the rate of change of the radius of the sphere is given as:

\[
\frac{dr}{dt} = \frac{R}{\rho}
\]

(3.1)

and the time it takes to completely degrade the sphere is given as:

\[
t = \frac{r_0 \rho}{R},
\]

(3.2)

where \( r_0 \) is the initial radius of the sphere. Using this formulation we can make a calculation of the lifetime of the graphite waste matrix of the DBSF.

Figure 3.1 shows the proposed multi-purpose canister (MPC) for the disposal of DBSF in the YMR. Each MPC can contain 42 fuel elements. In considering the lifetime of the DBSF, we consider four disposal scenarios; (1) whole-element disposal and (2) compact-only disposal, each in the fast and slow limits of graphite oxidation. The whole-element disposal scenario considers the disposal of 42 fuel elements per MPC; the geometric transformation to a spherical form is made by considering that the entire mass of graphite in the MPC is converted into a monolithic sphere. In the compact-only disposal scenario, we consider that the unit of waste which is being degraded is the single fuel compact. We consider that these four cases will represent the bounding values for the lifetime of the graphite waste matrix in the MPC after it has breached.
Figure 3.2 shows the fractional amounts of graphite remaining in a failed waste package as a function of time after groundwater contact. As can be seen from the figure, the “worst case” among the four cases, i.e., the compact-only disposal (the smallest total graphite mass) coupled with the fast oxidation regime, produces a matrix lifetime of greater than 3,000,000 years. If we consider the scenario of the whole-element disposal in the fast oxidation regime the matrix lifetime is greater than $3 \times 10^8$ years. This long lifetime hints at the possible use of graphite as a highly durable waste form for the disposal of high-level waste, especially under oxidizing conditions, as is the case in the YMR. In light of this robust performance of the waste matrix, it remains to be seen if the TRISO layers significantly contribute as engineered barriers against the release of radionuclides from the spent fuel form.

![Figure 3.1 MPC and waste loading](image1)

**Figure 3.1 MPC and waste loading [1].**

![Figure 3.2 Fractional amount of waste matrix left in MPC after canister failure](image2)

**Figure 3.2 Fractional amount of waste matrix left in MPC after canister failure.**
3.3 TRISO Particle Failure Model

When considering the performance of DBSF in a geological repository as a waste form, we must also consider the behavior of the TRISO particles. Central to the performance of the TRISO particles is the performance of the SiC layer, which is the TRISO particle’s main structural component. The layers of the TRISO particle act as a pressure vessel, containing the remaining actinide elements, fission products, some of which are gases [1] [2] [3] [11]. Helium gas generated from α-decay [1] [3] of actinide isotopes will also build up in the TRISO particle while in the repository. Thus, the pressure in the spent TRISO particle is due to the fission gases generated in a reactor and the helium gas from α-decay while in the repository.

When the tensile stresses in the SiC layer exceed its strength, the SiC layer ruptures and the TRISO particle is considered to have failed. It has been reported [1] [3], that the stress in the SiC layer due to gases within the particle will be given by

\[ \sigma(t) = \frac{p(t) R_{SiC}}{2x_{SiC}(t)}, \]  

(3.3)

where \( p(t) \) is the time-dependent internal pressure in the TRISO particle due to fission gases and helium from α-decay, at time \( t \), \( R_{SiC} \) is the radius to the middle of the SiC layer and \( x_{SiC}(t) \) is the thickness of that layer at time \( t \).

The probability of failure of the particle can be expressed as a Weibull distribution [1] [3],

\[ P_f(t) = 1 - \exp \left[ -\ln 2 \times \left( \frac{\sigma(t)}{\sigma_f} \right)^M \right], \]  

(3.4)

where \( P_f(t) \) is the cumulative probability of failure at time \( t \), \( \sigma(t) \) the hoop stress in the SiC layer at time \( t \), \( \sigma_f \) the mean fracture strength of the SiC layer, and \( M \) the Weibull parameter. In our evaluation of the lifetime, \( \sigma_f \) is assigned the value of 388 MPa and \( M \) is set to 7.9 [3] [16]. The volume available to gases was calculated from the dimensions of the TRISO particle given in Table 3.2 by considering that the void fraction of the porous buffer layer was 0.5 and that the void fraction of the fuel kernel is 0.07 and that the IPyC layer forms the boundary of the available volume [12].

Figure 3.3 shows the relation of the internal pressure in the TRISO particle to the time after discharge from the reactor. The internal pressure is calculated using the ideal gas law at 25°C and by assuming that the only contributors to the pressure are the noble gases generated during burnup and the helium accumulated after discharge by radioactive decay of alpha emitting nuclides. These time-dependent concentrations were calculated by the ORIGEN2 code. By assuming a kernel temperature of 25°C, we have effectively neglected the heat resulting from the decay of the short-lived fission products. In our model this will lead to a lower internal pressure, which will in turn result in a longer overall lifetime for the SiC layer. Effects of assuming a low temperature will be discussed subsequently.
Table 3.2 Fuel Compact and Fuel Element Composition and Dimensions Used in Performance Assessment of DBSF.

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>TRISO Fuel [1] [3] [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRISO Fuel</td>
<td>TRUO$_{1.7}$</td>
</tr>
<tr>
<td>Kernel (diameter, $\mu$m / density in $g/cm^3$)</td>
<td>200/10.0</td>
</tr>
<tr>
<td>Buffer layer (thickness, $\mu$m / density in $g/cm^3$)</td>
<td>120/1.05</td>
</tr>
<tr>
<td>IPyC layer (thickness, $\mu$m / density in $g/cm^3$)</td>
<td>35 / 1.9</td>
</tr>
<tr>
<td>SiC layer (thickness, $\mu$m / density in $g/cm^3$)</td>
<td>35 / 3.18</td>
</tr>
<tr>
<td>OPyC layer (diameter, $\mu$m / density in $g/cm^3$)</td>
<td>40 / 1.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isotopic composition of fresh TRISO kernel (weight percent) [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{237}$Np</td>
</tr>
<tr>
<td>$^{238}$Pu</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
</tr>
<tr>
<td>$^{241}$Pu</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
</tr>
<tr>
<td>$^{241}$Am</td>
</tr>
<tr>
<td>$^{242m}$Am</td>
</tr>
<tr>
<td>$^{243}$Am</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel Compact [1] [3] [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (cm)</td>
</tr>
<tr>
<td>Length (cm)</td>
</tr>
<tr>
<td>Matrix (density in $g/cm^3$)</td>
</tr>
<tr>
<td>Packing fraction (%)</td>
</tr>
<tr>
<td>Number of TRISO particle per avg. compact</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel Element [1] [3] [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of graphite per element (kg)</td>
</tr>
<tr>
<td>Dimensions (length in mm / across flats of hexagon in mm)</td>
</tr>
<tr>
<td>Volume ($m^3$)</td>
</tr>
<tr>
<td>Number of fuel channels</td>
</tr>
<tr>
<td>Number of fuel channels under dowels</td>
</tr>
<tr>
<td>Number of compacts per fuel channel (under dowels / not under dowels)</td>
</tr>
<tr>
<td>Number of compacts per element</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Waste Package (MPC) [3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity (number of elements)</td>
</tr>
<tr>
<td>Outside diameter (m)</td>
</tr>
<tr>
<td>Length (m)</td>
</tr>
</tbody>
</table>
Figure 3.3 TRISO particle internal pressure as a function of time after discharge from the reactor.

After emplacement in the repository, the failure of the TRISO fuel particle is considered to occur during the degradation of the DBSF due to the exposure to groundwater. As the OPyC layer is eroded by contact with groundwater, the SiC layer will be exposed and will subsequently erode. Experimental data is available for the dissolution rates of graphite, SiC, and PyC in several different aqueous solutions and a number of temperatures. The data is summarized in Table 3.1.

We can formulate the time-dependent thickness of the SiC layer as

\[ x_{SiC}(t) = r_{SiCo} - r_{SiCl} - \frac{Rt}{\rho}, \quad (3.5) \]

where \( \rho \) is the density of the SiC layer, \( R \) is the corrosion rate in g/m²/yr, \( r_{SiCo} \) is the initial outer radius of the SiC layer and \( r_{SiCl} \) is the radius of the inner surface of the SiC layer. A calculation of the lifetime of the SiC layer exposed to water corrosion can be made if we make use of the above formula (3.5), the internal pressure data presented from Figure 3.3 and the failure models presented above in Eqs. (3.3) and (3.4). Substituting Eq. (3.5) into Eq. (3.3) yields

\[ \sigma(t) = \frac{p(t)R_{SiC}}{2 \left( r_{SiCo} - r_{SiCl} - \frac{Rt}{\rho} \right)}, \quad (3.6) \]
which upon substitution in Eq. (3.4) results in the formula for the overall probability of failure of the SiC layer in the form of

$$P_f = 1 - \exp\left[-\ln 2 \times \left(\frac{p(t)R_{SiC}}{2(r_{SiCo} - r_{SiCi} - \frac{Rt}{\rho})/\sigma_f}\right)^M\right].$$

The corrosion rates $R$ for the SiC layer are taken to be the high and low rates of corrosion presented in Table 3.1. The material properties and dimensions of the TRISO particle and the SiC layer are given in Table 3.2.

Figure 3.4 shows that the effective lifetime of the SiC layer is sensitively dependent on the corrosion rate and the model used to predict the stress in the SiC layer. The two curves shown in the figure represent the bounding cases for the cumulative failure probability given the available experimental data. We can see that the SiC layers have a lifetime (time to total failure) of between 7,000 to 140,000 years (neglecting the protective effects of the OPyC layer). If we include the protective effects of the OPyC layer by considering a similar dissolution model as given by Equation (3.1), then the lifetime of the TRISO particle is extended to up to a maximum lifetime of 2,000,000 years. This is seen to be much less than the calculated lifetime of the graphite waste matrix ($3 \times 10^6 - 3 \times 10^8$ years in the fast graphite oxidation regime).

![Figure 3.4 Cumulative probability of SiC layer failure as a function of time exposed to groundwater.](image-url)
3.4 Summary

We have seen here that graphite is an extremely robust material, and has the potential to serve as a highly durable waste matrix for the disposal of HLW. The lifetime of the graphite waste matrix is observed to be in excess of $3 \times 10^6$ years at a minimum. Lifetime estimates for the graphite waste matrix greatly exceed the projected lifetime estimates of the SiC layer of the TRISO particles. Because of this significant difference between the lifetimes of graphite and TRISO and because of the large number of TRISO particles embedded in graphite matrix, in the remainder of our discussion, we assume that the TRISO layers do not serve as a barrier that delays the release of radionuclides from failed waste packages, and that the radionuclides in the TRISO particle are homogeneously dispersed in the graphite matrix. Thus, the radionuclides are assumed to be released by degradation of the graphite matrix. Note that for the TRISO particle lifetime the temperature of 25 °C has been assumed, which resulted in overestimation of the particle lifetime. Thus, if we take into account elevated kernel temperatures, or additional gases, this simplification assumption would still be further supported.
Chapter 4  Solubility of Radionuclides Released from Graphite Waste in a Welded Tuff Environment

4.1 Introduction

Of primary importance when considering the performance of DBSF in a geological repository is the performance of the graphite waste form. While graphite exhibits a resistance to oxidation by groundwater, it does corrode slowly over time, meaning that eventually radionuclides will be released from the waste form. The corrosion product from the oxidation of graphite is carbon dioxide, which will alter the chemistry of the groundwater in contact with the waste form, and potentially change the solubilities of the radionuclides in porewaters after being released from the waste form. If the advection of the groundwater at the surface of the waste form is sufficiently slow, then the mass transfer of the corrosion product away from the waste form surface is governed by molecular diffusion.

The objective of this study is to evaluate dissolved concentration limits of certain elements with radioactive isotopes in the environments expected in the repository for the use in radionuclide transportation modeling. Dissolved concentration limits of U, Np, Am, Th, Ra, and Pu are presented as tabulated functions of environmental conditions (specifically pH and carbon dioxide fugacity, fCO2). The two prerequisites for solubility evaluation based on geochemical modeling are a thermodynamic database (with a compatible modeling tool) and the environmental conditions for which the solubility will be evaluated. In this assessment, we report on the solubilities of the above radionuclides evaluated using the PHREEQC geochemical modeling program, and two separate thermodynamic databases [17] [18] [19].

4.2 Graphite and TRISO Particle Degradation Under Repository Conditions

Previous studies [6] [7] have demonstrated the robust nature of graphite with respect to groundwater leaching. However, according to both studies, the leaching (or more appropriately the oxidation) of graphite in water does not occur as a result of the interaction of the graphite with the water itself, but rather with the oxygen dissolved in the water - the lack of hydrogen and carbon monoxide as corrosion products is evidence of this fact [6] [20]. Also, it was shown [7] that the rate of oxidation of the graphite in brine solutions was substantially reduced – this was interpreted as further proof of the interaction mechanism, as brines display a reduced capacity to hold dissolved oxygen relative to pure water. It is noted that [7] the oxidation rate of graphite in water is substantially higher than in air, so that while the water is not a reactant, it is a catalyst in the reaction. In both of the water/graphite oxidation studies, carbon dioxide is used as the metric to determine the rate of the reaction of oxygen with the graphite. It should be noted, however, that in both studies, the graphite that was studied was not post-irradiated graphite, and the results regarding the performance of the graphite in contact with water could be substantially changed if the experiments were carried out with post-irradiated materials.

To date, a study of the relevant literature has been unable to identify the detailed mechanisms of the interaction of oxygen with graphite in an aqueous environment at repository temperatures, or to elucidate exactly how water may act as a catalyst in the overall reaction in the anticipated repository environment. Without an understanding of mechanisms for the interaction of graphite and oxygen in an aqueous environment, we
are unable to develop detailed mechanistic simulation of graphite degradation in repository conditions. However, with the forward reaction rate and the oxidation product reported in [7], we can identify the rate controlling mechanism by applying the mass-transfer theory.

Following [21], if we consider a spherical waste form surrounded by a porous medium containing groundwater with pore velocity slow enough that the mass transfer is controlled by molecular diffusion, then the governing equation for the diffusive mass transfer of dissolved carbon dioxide in the porous medium is given as

\[ K \frac{\partial C}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right), \]

subject to

\[ C(r, 0) = 0, \quad r > r_o, \quad t > 0, \quad r > r_o \]

where \( C(r,t) \) is the concentration of the dissolved carbon dioxide in the groundwater, \( K \) is the retardation coefficient, \( D \) is the diffusion coefficient in the water, \( r \) is the radial distance from the waste center, \( r_o \) is the radius of the waste form, and \( t \) is time.

The boundary condition at the solid-liquid interfaces dictates that the diffusive flow of the dissolved species at the outer waste surface equal to the rate of chemical reaction:

\[ -\varepsilon D \frac{\partial C}{\partial r} \bigg|_{r=r_o} = j_o \left[ 1 - \frac{C(r_o,t)}{C_s} \right], \]

\[ t > 0 \]

where \( \varepsilon \) is the porosity of the surrounding medium, \( C_s \) is the saturation concentration of the dissolved species, and \( j_o \) is the reaction rate of that species, per unit external surface area. The remaining boundary condition is assumed to be

\[ C(\infty, t) = 0, \quad t > 0. \]

The solution to these equations yields for the time-dependent concentration in the liquid adjacent to the outer surface of the waste as

\[ \frac{C(r_0, \tau)}{C_s} = \frac{R}{1 + R} \left\{ 1 - e^{r} \text{erfc} \left( \sqrt{\tau} \right) \right\} \]

with

\[ \tau = \frac{(1 + R)^2 D}{K r_0^2} t, \quad \text{and} \quad R = \frac{j_o r_0}{\varepsilon D C_s} \]

\[ \frac{C(r_0, \tau)}{C_s} \]
Here $\tau$ is the dimensionless time and $R$ is the dimensionless flux ratio. And the time dependent dissolution rate $j(r_0, \tau)$ is given as

$$j_0(r_0, \tau) = j_0 \left[ 1 - \frac{C(r_0, \tau)}{C_s} \right] \tag{4.7}$$

At steady state, the concentration and mass transfer rate are very much simplified, and are given as

$$C(r_0, \infty) = \frac{RC_s}{1 + R} \tag{4.8}$$

and

$$j(r_0, \infty) = \frac{j_0}{1 + R} \tag{4.9}$$

The parameter $R$ can be interpreted as the ratio of the reaction rate per unit area to the steady state mass transfer rate, both evaluated at $r = r_0$. By evaluating $R$, we can determine the dominant process in the dissolution of the waste form. If $R >> 1$, then the process is dominated by the chemical reaction, and the molecular diffusion of the corrosion product away from the surface of the waste form in the surrounding porous medium will be the rate limiting process. If $R << 1$, then molecular diffusion dominates, and the chemical reaction is the limiting process. The value of $j_0$ is found to be between $1.5 \times 10^{-10} \text{g/m}^2/\text{s}$ and $1.9 \times 10^{-13} \text{g/m}^2/\text{s}$ [6] [7], in a YMR type environment, $\varepsilon$ typically has a value on the order of 0.1, the saturation concentration, $C_s$, of carbon dioxide in water is $1.4 \times 10^3 \text{g/m}^3$ (at 25°C and 1 atm, or STP) [22] [23], and the molecular diffusion coefficient, $D$, of carbon dioxide in water is $2 \times 10^{-9} \text{m}^2/\text{s}$ at STP. The parameter, $r_o$ can be determined by making a geometric transformation of the graphite waste form. In the case of the whole element disposal, we make a geometric transformation of the hexagonal prism fuel elements in a waste package (42 elements per waste package) by conserving the surface area of the waste form, in the case of compact only disposal we conserve the overall surface are of the compacts disposed in a waste package. In the case of whole element disposal $r_o = 2.2m$ and in the case of compact only disposal $r_o = 4.6m$ are obtained. This gives us a range of $R = 2.5 \times 10^3 - 1.5 \times 10^6$, which indicates that the oxidation of the graphite waste form is the limiting process. In this case, we can simplify our steady state concentration and mass transfer rate at the surface area as:

$$C(r_0, \infty) \approx RC_s = 3.5 \frac{g}{m^3} - 2.1 \times 10^{-3} \frac{g}{m^3} \tag{4.10}$$

$$j(r_0, \infty) \approx j_0 = 1.5 \times 10^{-10} \frac{g}{m^2 s} - 1.9 \times 10^{-13} \frac{g}{m^2 s} \tag{4.11}$$
A gas and a liquid in equilibrium will obey Henry’s Law with \( k = \frac{p}{c} \), where \( k \) is the equilibrium constant, \( p \) is the partial pressure of the gas in equilibrium with the liquid and \( c \) is the concentration of the gas dissolved in the liquid. Using \( k = 29.4 \text{ L/(atm mol)} \) for water and CO\(_2\) at STP, the steady state concentration of CO\(_2\) from the oxidation of the waste form is \( 8 \times 10^{-5} \) to \( 4.5 \times 10^{-8} \) mol/L, this yields a \( \log_{10}(f\text{CO}_2) = -2.63 \) to \(-5.878\). This information will be used as an input into the PHREEQC geochemical simulation code [17], in order to determine the pore water chemistry, and subsequently solubilities of radionuclides of interest in the porewater directly adjacent to the oxidizing waste form.

### 4.3 Geochemical Solubility Modeling

A number of input parameters are necessary to run the PHREEQC computer code. These include the nominal environmental conditions (pH range, \( f\text{CO}_2 \) and \( f\text{O}_2 \) ranges, and temperature), groundwater chemistry, identification of the solubility-controlling mineral, and a thermodynamic database.

#### 4.3.1 Environmental Conditions

The YMR is designed so that the waste is under atmospheric conditions except in isolated situations [24]. Therefore, oxidizing conditions are assumed, and all solubilities are calculated with \( f\text{O}_2 \) at 0.2 bars (atmospheric value). Although the decay heat from spent fuel can cause package temperatures to rise as high as 200°C, for the purposes of solubility in liquid water the relevant temperature range is 25°C to 100°C. It is reported [24] that actinides are retrograde soluble, therefore only concentrations at 25°C are presented. The widest range of pH that is expected is between 3.5 and 10.5 [24]; in this effort, we consider a range of 3 to 11. The atmospheric value of the \( f\text{CO}_2 \) is \( 10^{-3.5} \) bars, and the range of \( f\text{CO}_2 \) expected in YMR is \( 1.75 \times 10^{-2} \) to \( 2.20 \times 10^{-5} \) bars [24]. We consider a range of \( \log(f\text{CO}_2) \) between -1.5 to -5; this range will not only cover the nominal environmental conditions expected, it will also cover the entire range of fugacity expected in the water in contact with the graphite waste form.

#### 4.3.2 J-13 Well Water

Modeling the solubilities of radionuclides requires knowledge of the geochemistry of the water with which the radionuclides will react; we have chosen to use J-13 well water for these purposes. For J-13 well water, we make use of a validated composition, as given in [25]. Justification for this choice is given below.

A major portion of the water (possibly 80%) produced from the J-13 well comes from the Topopah Spring member of the Paintbrush Tuff, which is the same formation as that at Yucca Mountain proposed for the repository. The chemical composition of J-13 water is very similar to the compositions of the other wells that produce from the shallow, aerated, saturated zone in and near Yucca Mountain. Only two constituents, potassium and magnesium, differ significantly, but rock/water interaction studies show that these elements would be of little or no consequence in the near-field during the hot thermal period of the nuclear waste [26].

Four types of experiments have been examined with respect to their use of J-13 water: metal corrosion, waste-form leaching, hydrothermal rock/water interactions, and radionuclide migration. In general, the most important parameters of the water in affecting the results of these experiments are pH, concentration of bicarbonate ion, and except for the rock/water interactions, the concentration of oxygen and Eh. However,
these are the chemical parameters in which there is the greatest confidence that J-13 water would be representative of the unsaturated-zone waters of Yucca Mountain [24]. Therefore, the use of J-13 well water as a representative sample of YMR groundwater is justified.

When modeling solubilities with PHREEQC, we assign to the J-13 well water a wide range of pH and tCO₂ values, which differ from the validated values [26]. This causes the modeled solution to become electrically unbalanced. To preserve charge balance, a balancing anion was added. According to [24], a major force in lowering pH is the oxidation of Carbon Steel Type A516 which contains sulfur, therefore, SO₄²⁻ was specified as the ion to balance the solutions; the use of SO₄²⁻ as a charge balancing ion was restricted to cases when SO₄²⁻ would be added to the solution.

4.3.3 Solubility Limiting Solid Phase

In this report, elemental solubility is defined with respect to a solid phase. To evaluate solubility, the controlling solid(s) must be identified. Generally, laboratory experiments and natural analogues provide the basis for choosing the controlling phase. Thermodynamic data on actinide solids are derived from laboratory solubility measurements and from direct thermochemical measurements, such as calorimetry. For some elements, however, the identification of controlling solids for the repository environment by experiments is yet to be reported, or is not well established. In these cases, it is considered a conservative approach to choose an amorphous solid as the controlling phase. The Ostwald step rule is the main reason for this decision. The rule states that unstable (or metastable) minerals will form first, followed by progressively more stable minerals. Thus, during the process of waste form degradation more stable minerals are prevented from precipitating because less stable minerals are kinetically favored.

The solubility controlling minerals were selected based on evidence provided in [24]. They are schoepite, NpO₂, AmOHCO₃, ThO₂, and PuO₂; for U, Np, Am, Th, and Pu, respectively. Because of a lack of thermodynamic data for Ra, Ba is used as a chemical analog to calculate the Ra solubility, and BaO₂ is used as the solubility-controlling mineral. However, because Ba is not retrograde soluble, T=100 °C is used as the temperature for all evaluations of Ba solubility.

4.3.4 Thermodynamic Databases

This solubility modeling effort makes use of two separate thermodynamic databases in calculating the maximum concentration of the radionuclides of interest. The first database is the LLNL.dat database that is included in the PHREEQC software distribution. It is essentially a PHREEQC version of the EQ3/6 thermodynamic database that was used for the Total System Performance Assessment for Yucca Mountain (TSPA) radionuclide solubility modeling [24]. This database was only modified in the case of Th and Pu. In the case of Th carbonate reactions with Th were as per [24], as these reactions were not included in the original LLNL.dat database, and are important for the overall solubility of Th. In the cases of both Th and Pu, the reactions for the solubility-controlling mineral were supplied from the OECD database [19] [18]. The second thermodynamic database that was used was a hybrid database which was constructed by first removing from the LLNL.dat database all of the actinide reactions, and then
replacing them with the reactions for the actinides of interest from the OECD database (called hybrid OECD database hereafter).

The purpose of using the two databases is two-fold. First, by using the LLNL.dat (EQ3/6) database under these environmental parameters, we can use previous studies as a check on our results as part of a confidence building effort. Second, by using the hybrid OECD database, we can see if there is good agreement across these thermodynamic libraries, and what if any significant differences exist between the results generated by these two databases. Any significant differences could indicate an area in which further study is required.

4.3.5 Input Parameter Overview

Table 4.1 and Table 4.2 are a list of the essential parameters used in the solubility modeling.

<table>
<thead>
<tr>
<th>Controlling Mineral &amp; Dissociation Reaction</th>
<th>log(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium: Schoepite</td>
<td></td>
</tr>
<tr>
<td>$\text{UO}_3\cdot2\text{H}_2\text{O} + 2\text{H}^+ = \text{UO}_2^{2+} + 3\text{H}_2\text{O}$ LLNL Database</td>
<td>4.83</td>
</tr>
<tr>
<td>$\text{UO}_3\cdot2\text{H}_2\text{O} = \text{UO}_2^{2+} + \text{H}_2\text{O} + \text{OH}^-$ Hybrid OECD Database</td>
<td>-23.19</td>
</tr>
<tr>
<td>Neptunium: $\text{NpO}_2^-$</td>
<td></td>
</tr>
<tr>
<td>$\text{NpO}_2^- + 4\text{H}^+ = \text{Np}^{4+} + 2\text{H}_2\text{O}$ LLNL Database</td>
<td>-7.80</td>
</tr>
<tr>
<td>$\text{NpO}_2^- + 0.25\text{O}_2^- + \text{H}^+ = \text{NpO}_2^{+} + 0.5\text{H}_2\text{O}$ OECD Database</td>
<td>1.53</td>
</tr>
<tr>
<td>Plutonium: $\text{PuO}_2^-$</td>
<td></td>
</tr>
<tr>
<td>$\text{PuO}_2^- + 2\text{H}_2\text{O} = \text{Pu}^{4+} + 4\text{OH}^-$ Hybrid OECD Database</td>
<td>-58.33</td>
</tr>
<tr>
<td>Americium: $\text{AmOHCO}_3^-$</td>
<td></td>
</tr>
<tr>
<td>$\text{AmOHCO}_3^- + 2\text{H}^+ = \text{Am}^{3+} + \text{H}_2\text{O} + \text{HCO}_3^-$ LLNL Database</td>
<td>3.15</td>
</tr>
<tr>
<td>$\text{AmOHCO}_3^- = \text{Am}^{3+} + \text{CO}_3^{2-} + \text{OH}^-$ Hybrid OECD Database</td>
<td>-20.20</td>
</tr>
<tr>
<td>Thorium: $\text{ThO}_2$</td>
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</tr>
<tr>
<td>$\text{ThO}_2^- + 4\text{H}^+ = \text{Th}^{4+} + 2\text{H}_2\text{O}$ Hybrid OECD Database</td>
<td>7.31</td>
</tr>
<tr>
<td>Barium: Barite (surrogate for Ra)</td>
<td></td>
</tr>
<tr>
<td>$\text{BaSO}_4 = \text{Ba}^{2+} + \text{SO}_4^{2-}$ LLNL Database</td>
<td>-9.97</td>
</tr>
</tbody>
</table>
### Table 4.2 PHREEQC Inputs.

<table>
<thead>
<tr>
<th>Environmental Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.0 to 11.0 in steps of 0.25 pH</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C (except for Ba)</td>
</tr>
<tr>
<td>log(fCO₂) (bars)</td>
<td>-1.5 to -5.0 in steps of 0.5</td>
</tr>
<tr>
<td>log(fO₂) (bars)</td>
<td>held constant at -0.7 (except for Pu)</td>
</tr>
<tr>
<td>SO₄²⁻ concentration</td>
<td>adjusted to maintain solution charge neutrality</td>
</tr>
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</table>

### J-13 Well Water Composition [25]

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<th>Constituent</th>
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<tr>
<td>Ca</td>
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<tr>
<td>K</td>
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</tr>
<tr>
<td>Mg</td>
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<tr>
<td>F⁻</td>
<td>2.18</td>
</tr>
<tr>
<td>Cl⁻</td>
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</tr>
<tr>
<td>NO₃⁻</td>
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</tr>
<tr>
<td>SO₄²⁻</td>
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</tr>
<tr>
<td>HCO₃⁻</td>
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</table>

#### 4.3.6 Simulation Results

With the exception of Pu, the solubilities of all radionuclides calculated in this study using the LLNL.dat agreed well with previously reported results [24]. As such, Table 4.3 through Table 4.8 represent selected results generated using the hybrid OECD database. Pu solubilities are reported for both databases, as the results generated by the databases were not in exact agreement with previous results, this was a result of strong fluoride species formation which was not seen in previous studies. Blank spaces in tabulated data indicate failed convergence of the PHREEQC simulation under those environmental conditions. Table 4.9 represents a table of recommended solubilities for use in transport calculations. Because of the high uncertainty associated with the solubilities of radionuclides in the YMR environment we have taken a conservative approach in developing this table. These values were selected by considering the maximum of the extrema of the solubilities of each element across both database results.
Table 4.3 Uranium Solubility (mol/kg) Calculated Using Hybrid OECD Thermodynamic Database.

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<thead>
<tr>
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<th>log(fCO₂)</th>
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Table 4.4 Neptunium Solubility (mol/kg) Calculated Using Hybrid OECD Thermodynamic Database.

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<td>1.54E-10</td>
<td>8.14E-11</td>
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<td>9</td>
<td>8.20E-11</td>
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<td>9.5</td>
<td>8.90E-11</td>
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</table>
Table 4.7 Plutonium Solubility (mol/kg) Calculated Using LLNL.dat (EQ3/6) Thermodynamic Database.

<table>
<thead>
<tr>
<th>pH</th>
<th>log(fCO2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-1.5</td>
</tr>
<tr>
<td>3</td>
<td>5.09E-05</td>
</tr>
<tr>
<td>3.5</td>
<td>3.16E-05</td>
</tr>
<tr>
<td>4</td>
<td>1.98E-05</td>
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<td>4.5</td>
<td>8.22E-06</td>
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<tr>
<td>5</td>
<td>1.59E-06</td>
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<tr>
<td>5.5</td>
<td>1.94E-07</td>
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<tr>
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<td>2.51E-08</td>
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<td>3.86E-09</td>
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<tr>
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<td>8.5</td>
<td>3.03E-11</td>
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<td>1.02E-11</td>
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<td>9.5</td>
<td>1.16E-11</td>
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<td>10</td>
<td>8.73E-11</td>
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<tr>
<td>10.5</td>
<td>2.05E-09</td>
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<tr>
<td>11</td>
<td>2.74E-08</td>
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</table>

Table 4.8 Plutonium Solubility (mol/kg) Calculated Using Hybrid OECD Thermodynamic Database.

<table>
<thead>
<tr>
<th>pH</th>
<th>log(fCO2)</th>
</tr>
</thead>
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<tr>
<td></td>
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<td>4.5</td>
<td>6.75E-05</td>
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<td>1.419E-05</td>
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<td>5.5</td>
<td>6.595E-06</td>
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<td>6</td>
<td>5.489E-06</td>
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<td>6.5</td>
<td>1.76E-07</td>
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<td>9.37E-08</td>
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<td>7.5</td>
<td>8.9E-08</td>
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<td>2.93E-07</td>
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<td>8.5</td>
<td>4.389E-08</td>
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<td>8.75</td>
<td>9.564E-09</td>
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<td>1.051E-08</td>
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<td>9.5</td>
<td>3.656E-08</td>
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</tbody>
</table>
Table 4.9 Recommended Values for Element Solubility for Use in Transport Evaluations.

<table>
<thead>
<tr>
<th>Element</th>
<th>Solubility (mol/kg)</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>3.54E-06</td>
<td>9.69E-02</td>
<td></td>
</tr>
<tr>
<td>Np</td>
<td>2.66E-07</td>
<td>1.65E-01</td>
<td></td>
</tr>
<tr>
<td>Pu</td>
<td>9.56E-09</td>
<td>4.23E-01</td>
<td></td>
</tr>
<tr>
<td>Am</td>
<td>1.73E-06</td>
<td>8.88E-01</td>
<td></td>
</tr>
<tr>
<td>Th</td>
<td>2.09E-09</td>
<td>2.61E-02</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>5.37E-07</td>
<td>3.09E-01</td>
<td></td>
</tr>
</tbody>
</table>

4.4 Discussion

4.4.1 Uranium Solubility

As mentioned previously, schoepite is selected as the solubility-controlling mineral for U dissolution based on evidence provided in [24]. In the U solubility modeling effort, the results obtained with using the LLNL.dat thermodynamic database agreed well with previous results generated for the TSPA-LA, therefore these results are not presented. Significant differences in both the overall solubility of U, as well as in the speciation of U were seen between the results generated using the LLNL.dat and the hybrid OECD database.

The trend of increasing U solubility with increasing fCO₂ is preserved while implementing the hybrid OECD database and good agreement with previous results is seen over all fCO₂ values studied in the pH range below 6. At pH values greater than 6 the solutions diverge, with the hybrid OECD database predicting a lower total solubility by as much as an order in magnitude in the concentration of dissolved U (Figure 4.1). This difference can be traced to a difference in the equilibrium constant for the following reaction:

\[ 2\text{H}_2\text{O} + \text{UO}_2^{2+} = 2\text{H}^+ + \text{UO}_2(\text{OH})_2 \]  (4.12)

For both databases, in the range of environmental conditions considered, UO₂(OH)₂ concentration remains constant, and provides a floor to the lowest level of total dissolved U. The LLNL.dat database gives the equilibrium constant as \( \log(K) = -10.32 \) while the OECD database gives a value of \( \log(K) = -12.15 \). This amounts to more than an order of magnitude difference in the concentration of products with respect to the reactants in equation (4.12). When the OECD value is changed to the LLNL value, good agreement is observed in the total dissolved U concentration between the two databases.

Another significant difference between the results generated using the two different databases is the speciation of dissolved U (Figure 4.2). Specifically, the OECD database includes a silicon-U complex that is not present in the LLNL.dat database and which contributes significantly to the total dissolved U at lower pH ranges.
Figure 4.1 Comparison of total solubility for Uranium using LLNL.dat and hybrid OECD databases at log(fCO$_2$) = -1.5, -3.5, and -5.0.

Figure 4.2 Speciation of U determined using hybrid OECD database at log(fCO$_2$) = -3.5.
4.4.2 Plutonium Solubility

The results obtained for Pu solubility by using both the LLNL.dat and hybrid OECD databases differed noticeably from results that were generated for the YMR TSPA-LA [24], in terms of both total dissolved Pu, and the composition of the aqueous species. The results generated by the LLNL.dat and hybrid OECD databases provide lower and upper bounds to the results generated for the TSPA-LA, respectively.

The results generated for the TSPA-LA indicate a tendency for Pu to form sulfur complexes in the low pH range, a tendency to form PuO$_2^+$ in the intermediate pH ranges, and a strong tendency to form carbonate complexes in the high pH range. As seen in Figure 4.3, the speciation of Pu calculated with the hybrid OECD database does follow the general trend of speciation outlined above, although with a reduced tendency to form PuO$_2^+$ in favor of PuO$_2$F$^+$. Aside from an increased overall solubility, the hybrid OECD database trends well with the results generated for the TSPA-LA.

![Figure 4.3 Speciation of Pu determined using hybrid OECD database at log(fCO$_2$)= -3.0.](image)

Surprisingly, however, the results generated using the LLNL.dat (EQ3/6) database differ significantly from previous results. Not only is the overall solubility significantly reduced, but as can be seen in Figure 4.4, a trend towards complexing with fluorine at lower pH’s has usurped the former trend to complex with sulfur. This could result in a sensitivity of the solubility of Pu to fluorine concentrations, or this could be a result of a database error in the Pu/fluorine reaction equations.
4.4.3 Neptunium Solubility

As can be seen in Figure 4.5, the Np solubility was calculated with the hybrid OECD database trends well with the solubility calculated with the LLNL.dat database (which in turn is in good agreement with the results generated for the TSPA-LA). An examination of the speciation of Np reveals that over a wide range of pH values (from low to high), the overall solubility is governed by the concentration NpO$_2^+$, which gives way to carbonate-Np complexes at high pH values. The discrepancy between the overall solubility for Np is dominated by the difference in NpO$_2^+$ solubilities calculated using the different databases; these results differ uniformly by approximately order of magnitude over all environmental conditions considered.
4.4.4 Americium Solubility

As is the case for all of the elements studied, with the exception of Pu, the solubility results generated for Am agreed well with previous results both in terms of the overall solubility and speciation trends. The results generated using the hybrid OECD database yield results for the overall solubility, which are higher by about an order of magnitude over the entire range of environmental conditions considered. However, as can be seen in Figure 4.6 the main contributor to the concentration of dissolved Am, as calculated by the hybrid OECD database is a silicon-Am complex. This type of chemical species is entirely absent from the LLNL.dat database. This opens the door to the question of Am sensitivity to silica levels in Yucca Mountain groundwater.

Additionally, it is interesting to note that while all other actinides exhibit an increase in solubility with increasing $\text{fCO}_2$ values, Am trends oppositely. This is likely due to the fact that the controlling mineral for Am is $\text{AmOHCO}_3$ with a dissolution reaction:

$$\text{AmOHCO}_3 = \text{Am}^{3+} + \text{CO}_3^{2-} + \text{OH}^-$$

Therefore, at equilibrium, with decreasing concentrations of carbonates in the solution (i.e. at low fugacities) we would expect the above reaction to be more favorable.
4.4.5 Thorium Solubility

While the overall solubility of Th calculated using the hybrid OECD database trends fairly well with the solubility calculated with the LLNL.dat database, there are some differences in both the overall magnitude of dissolved Th, and its speciation (Figure 4.7). As was the case with Pu (for the LLNL.dat database), we see in Th an increased tendency to form fluoride complexes in favor of carbon complexes. This tendency points to the possibility of sensitivity of actinide solubility to fluoride concentrations in Yucca Mountain groundwater. This could contribute to the overall uncertainty associated with these calculations.
Figure 4.7 Speciation of Th determined using the hybrid OECD database at $\log(f\text{CO}_2) = -3.0$.

4.4.6 Barium Solubility
As discussed above, Ba is used as a chemical analogue to Ra in order to calculate Ra solubility in the absence of a well-developed thermodynamic data set for Ra. No OECD data for Ba was readily available for this study, and the calculations carried out using the LLNL.dat database reproduced reliably, previous results [24].

4.5 Summary
As can be seen from this study, the results of a geochemical simulation effort will vary greatly depending on the choice of the thermodynamic database. While the LLNL.dat and hybrid OECD databases produce results that agree to within an order of magnitude, in most cases, this is a large degree of uncertainty to be associated with a physical parameter (it should be noted, however, that if a given waste matrix were robust enough that all radionuclides were released congruently with the waste matrix the uncertainty associated with this parameter would disappear as all of the nuclides would be present at levels at or below their solubility limit). Two important questions have been raised by this study. First, what is the importance of silicon-actinide complexes in repository performance; the silicon-Am complex played an important role in the Am solubility calculated with the hybrid OECD database. And second, how sensitive are the solubilities of the actinides to the fluorine concentration? While, previous studies have indicated a relative insensitivity of actinide solubility to fluorine concentration in Yucca
Mountain groundwater [24], however this previous study did not exhibit the strong formation of fluorine complexes that was seen here.

Overall, the solubility ranges generated by this study are within the range of uncertainties associated with simulated solubility limits. Table 4.9 provides recommended values for concentrations, based on this study, of the six elements studied. These values were selected by considering the maximum of the extrema of the solubilities of each element across both database results. These values will be used, along with results from the TSPA-LA, as inputs into a transport model for the release and transport of radionuclides from DBSF in a geological repository in order to determine hazard posed by storing this fuel in a Yucca Mountain type repository.
Chapter 5  Performance Assessment of Graphite Waste Containing TRISO Particles in a Welded Tuff Environment Using TTB

5.1 Introduction

The objective of this portion of the current study is to evaluate the performance of DBMHR spent fuel (DBSF) for final geological disposition. To this end we have chosen the Yucca Mountain geological repository (YMR) as the environment for our study. This is based on the completeness of the data sets necessary to conduct this study and because the regulations associated with the YMR provide a clear basis for evaluating the performance of the spent fuel.

A performance assessment of DBSF can only be made relative to predetermined standards for evaluation. In the case of the YMR, the Environmental Protection Agency (EPA) issued radiation protection standards for the potential spent nuclear fuel and high-level radioactive waste disposal system in Yucca Mountain, Nevada. These standards are found in Part 197 of Title 40 of the Code of Federal Regulations (40CFR197). The standards are 15 mrem ($1.5 \times 10^{-4}$ Sv) annual committed effective dose equivalent (CEDE) to the reasonably maximally exposed individual (RMEI) for 10,000 years after repository closure and 100 mrem ($1.0 \times 10^{-3}$ Sv) CEDE to the RMEI for between 10,000 and 1,000,000 years after repository closure. No regulatory limits are set for times greater than one million years after repository closure. Because there are no subsystem performance requirements [27], the performance assessment of the DBSF needs to be extended to the point of evaluation of the annual dose to the RMEI.

The main efforts of this study, therefore, are to determine the relevant physical processes and parameters necessary to evaluate the performance of the DBSF in the YMR and to calculate the annual dose delivered to the RMEI as a result of the disposal of DBSF. From this perspective, we divide the performance evaluation for DBSF into two regions: the near field (source term) and the far field (dose evaluation).

The near-field evaluation includes physical models for the processes involving the constituent materials of the DBSF and of other engineered barriers, and the diffusive transport of radionuclides released from the DBSF as it degrades. It is should be noted that the role of this region is primarily confinement of radioactive materials, and that the fidelity of the models in this region can be improved as scientific understanding of the processes improves. In this study, while recognizing this, due to lack of extensive experimental studies, we have applied simplified models.

The far-field dose evaluation includes models for radionuclide transport in geological formations and for annual-dose evaluation to the RMEI. In contrast to the near-field region, the primary role of this region is dispersion of radioactive materials by hydrological processes, in addition to radioactive decay loss during the transport between the time of leakage from the near field to the time of intake by RMEI. This part of the evaluation inevitably contains significant, irreducible uncertainties and model hypotheses, particularly for the models in the biosphere. Therefore, for the present investigation, we have decided to use the stylized and abstracted model for radionuclide transport developed in the Department of Nuclear Engineering at the University of California at Berkeley called “Transfer to Biosphere” or TTB [9]. With this model, the mass release rates of radionuclides at a point 18 km down gradient from the repository are calculated, consistent with the definition of the RMEI.
The annual dose to the RMEI is determined by applying the biosphere model presented in the license application for the YMR (TSPA-LA) for exposure via groundwater contamination under the current climatic conditions. Among the 31 important radionuclides considered for this study, 26 are tracked and transported. The five radionuclides that are not tracked and transported are $^{245}$Cm, $^{241}$Pu, $^{227}$Ac, $^{228}$Ra, and $^{210}$Pb. In the TSPA-LA, doses from $^{227}$Ac, $^{228}$Ra, and $^{210}$Pb are calculated by assuming they are in secular equilibrium with $^{231}$Pa, $^{232}$Th, and $^{226}$Ra, respectively, because their half-lives are short. Doses from $^{245}$Cm and $^{241}$Pu are not calculated in the TSPA-LA because they are only important for their decay effects on the inventory of $^{241}$Am and $^{237}$Np, as stated in Table 7-1 of reference [28].

It should be noted here that the models used in this study for radionuclide transport in the near and far fields are generic, so that they will allow for a comparison across a wide range of repository environments, given specified performance standards.

5.2 Fuel Cycle and Spent Fuel Characteristics

In order to begin a discussion about the near-field behavior of DBSF in the YMR, we have evaluated the composition of the DBSF. As is mentioned in previous chapters, the DBSF is comprised of hexagonal fuel elements loaded with cylindrical fuel compacts containing the TRISO particles. It is the TRISO particles that contain the fissile material necessary to generate the heat for operating the DBMHR. The DBMHR fuel and TRISO geometry and physical characteristics are assumed to be those shown in Table 3.2.

For our present study we consider a third DBMHR fuel cycle [5]. The radionuclide inventory in the DBSF is determined by the recycling scheme for CSNF. We consider CSNF from a pressurized water reactor (PWR) with a burnup of 50 GWD/MTU and a 5-year cooling time. We consider the reprocessing of the CSNF in a UREX-type process with complete removal of U, Cm, and fission products. The Am, Np, and Pu are recovered from the CSNF and fabricated into TRISO fuel. The composition of the fresh DBMHR fuel is shown in Table 5.1. This fresh TRISO fuel is burned one time for 1,052 days in a DBMHR to a burnup of 621 GWD/MTHM (Figure 5.1) [5].

This third fuel cycle is considered because of the importance of the fission product content of the DBSF to the annual dose subsequently delivered to exposed individuals [9] [10]. In the absence of relevant data in the literature on the fission product content of DBSF from any DBMHR fuel cycle, the above fuel cycle was considered and a depletion analysis was used to generate the necessary radionuclide inventory datasets [5]. To evaluate the DBSF composition, a single fuel block with reflective boundary conditions on all sides is considered. Out of the 216 fuel channels in each fuel element, six are modeled as empty because these channels are reserved for burnable poisons. In this model, however, these poisons are not taken into account.
### Table 5.1 Fuel Compact and Fuel Element Composition and Dimensions.

<table>
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<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel type</strong></td>
<td>TRUO₁.₇</td>
<td>0.6225</td>
<td>90</td>
<td>42</td>
</tr>
<tr>
<td><strong>Kernel</strong></td>
<td>200/10.0</td>
<td>4.928</td>
<td>794 / 360</td>
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<tr>
<td><strong>Buffer layer</strong></td>
<td>120/1.05</td>
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<td>0.0889</td>
<td>5.144</td>
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<td></td>
<td>210</td>
<td></td>
</tr>
<tr>
<td><strong>SiC layer</strong></td>
<td>35 / 3.18</td>
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<td>24</td>
<td></td>
</tr>
<tr>
<td><strong>OPyC layer</strong></td>
<td>40 / 1.9</td>
<td></td>
<td>14 / 15</td>
<td></td>
</tr>
<tr>
<td><strong>Isotopic composition of fresh TRISO kernel (weight percent) [5]</strong></td>
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<td></td>
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</tr>
<tr>
<td>$^{237}$Np</td>
<td>6.8</td>
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<tr>
<td>$^{238}$Pu</td>
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<td>$^{239}$Pu</td>
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<td>$^{240}$Pu</td>
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</tr>
<tr>
<td><strong>Length (cm)</strong></td>
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<td></td>
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<tr>
<td><strong>Matrix (density in g/cm$^3$)</strong></td>
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<td></td>
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<tr>
<td><strong>Packing fraction (%)</strong></td>
<td></td>
<td></td>
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<tr>
<td><strong>Number of TRISO particle per avg. compact</strong></td>
<td>5580</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Mass of graphite per element (kg)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Dimensions (length in mm / across flats of hexagon in mm)</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Volume (m$^3$)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Number of fuel channels</strong></td>
<td>210</td>
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<td></td>
</tr>
<tr>
<td><strong>Number of fuel channels under dowels</strong></td>
<td>24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Number of compacts per fuel channel (under dowels / not under dowels)</strong></td>
<td>14 / 15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Number of compacts per element</strong></td>
<td>3126</td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>Capacity (number of elements)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Outside diameter (m)</strong></td>
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<td></td>
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<tr>
<td><strong>Length (m)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The depletion analysis was performed [5] assuming a uniform power across the core using MOCUP [29]. MOCUP—MCNP-ORIGEN Coupled Utility Program—is a set of scripts that couples MCNP [30] and ORIGEN2 to solve time-dependent depletion problems. MCNP provides flux and reaction rates for each of the nuclides to be depleted. These are used to calculate effective one-group cross sections for input in ORIGEN2 along with the initial fuel composition. ORIGEN2 performs the depletion analysis according to the time and power (or flux) provided in the input and output the depleted materials composition at the end of the time step. These updated compositions are transferred back to MCNP to determine a new set of cross sections. The process is iterated for as many time steps as required by the user. The MOCUP version in use at UC Berkeley includes a number of improvements added to the original version. In particular an extra script is used to modify the branching ratio of $^{241}\text{Am} (n,\gamma)$ to $^{242}\text{Am}$ and $^{242m}\text{Am}$ according to the user need and another script determine the power distributions among the depletion zones using MCNP fission rate tallies [31]. The composition of the DBSF, including the fission product content, can be seen in Table 5.2.
Table 5.2 DBSF Radionuclide Inventory.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-Life (years)</th>
<th>DBSF (At Discharge from DBMHR) (mol)</th>
<th>DBSF (At Package Failure, 1000yr) (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{14}$C</td>
<td>5.72E+03</td>
<td>1.06E-06</td>
<td>9.35E-07</td>
</tr>
<tr>
<td>$^{79}$Se</td>
<td>2.95E+05</td>
<td>2.55E-02</td>
<td>2.52E-02</td>
</tr>
<tr>
<td>$^{90}$Sr</td>
<td>2.88E+01</td>
<td>1.43E+00</td>
<td>5.05E-11</td>
</tr>
<tr>
<td>$^{99}$Tc</td>
<td>2.13E+05</td>
<td>4.51E+00</td>
<td>4.50E+00</td>
</tr>
<tr>
<td>$^{126}$Sn</td>
<td>2.50E+05</td>
<td>1.11E-01</td>
<td>1.11E-01</td>
</tr>
<tr>
<td>$^{129}$I</td>
<td>1.57E+07</td>
<td>4.08E-02</td>
<td>4.08E-02</td>
</tr>
<tr>
<td>$^{135}$Cs</td>
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<td>3.09E+00</td>
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</table>

5.3 Assumptions and Physical Processes

5.3.1 Disposal Timeline and Drift Shadow Description

In the proposed YMR, the DBSF will be loaded into multi purpose waste disposal canisters (MPC’s) and placed into tunnel drifts [1] [3]. In the early years after repository closure, the tunnel walls will heat up and dry out from heat generated from the decay of short-lived fission products [10]. After these fission products have decayed away, the temperature in the drift walls will fall and water will reinfiltrate the pores of the
rock that comprises the drift wall. Subsequently, water will begin to infiltrate the drift tunnel and will contact the MPC (neglecting the drip shield). After package failure, water will be able to enter the MPC and will begin degrading the graphite waste matrix and TRISO particles, and eventually the water will begin to dissolve the radionuclides within the MPC. This water, laden with radionuclides, will then exit the MPC and will enter the near field host rock.

The host rock in the region immediately below the tunnel drift is called “drift shadow region [32] [33] [34].” The drift shadow is a region in the unsaturated zone beneath the tunnel drift that is partially sheltered from downward-percolating water, because the capillary action is not strong enough to draw water into the rock immediately below the drift (Figure 5.2). Transport in this region is controlled mainly by diffusive processes, rather than by advection [32] [33] [34]. The radiocuclides will diffuse through this region until they reach a location at which they can be transported by advection through fracture network in the unsaturated zone to the alluvium, at which point they will travel by advection to some down gradient location. The shortest diffusion path to a region of advective trasport will be to consider that the contaminated water is released from an outside edge of the waste canister, and is subsequently diffusively transported laterally to the edge of the tunnel drift (or equivalently to the edge of the drift shadow region), a distance somewhat greater than 2m. In the remainder of the analysis, we consider that the length of diffusive transport in the near field is 2m.

Figure 5.2 Drift shadow concept. [34].
5.3.2 Near-Field Model

For our analysis, we consider a geometric transformation of the DBSF. In the case of the whole-element disposal, we consider the transformation of 42 fuel elements into a single sphere of equivalent mass. In the case of the compact-only disposal we consider the transformation of a single fuel compact into a sphere of equivalent mass. Figure 5.3 shows the geometry of the near-field region. Recalling that the lifetime of the TRISO layers is seen to be substantially less than that of the graphite waste matrix (Chapter 3), we consider that the TRISO layers do not serve as an engineered barrier against the release of radionuclides from the surface of the DBSF, and that the radionuclide inventory is distributed homogeneously throughout the graphite waste matrix, rather than discretely in TRISO particles. The graphite sphere is then considered to be surrounded by a diffusion barrier whose thickness is 2m. This diffusion barrier is considered to be host rock in the drift shadow region. Although there are a number of different rock types in the proposed YMR, the current repository design locates about 70% of the drifts in the tsuw35 hydrogeologic unit [33] [35]. The supporting documentation for the licence application of the YMR provides distributions for the essential physical parameters necessary to make the near-field calculations.

![Diagram of near-field model](image)

**Figure 5.3 Geometry in the near field showing spherical waste form and surrounding diffusion barrier.**

When the graphite matrix comes into contact with groundwater, the matrix begins to dissolve and radionuclides are released. The release of radionuclides can be considered to occur by two modes in this model; congruent release, and solubility limited release [9] [14]. In the case of congruent release, the fractional release rate of the nuclide is equal to the fractional dissolution rate of the waste matrix, or graphite. If the solubility of an individual radionuclide is low, then a precipitate of the nuclide will form. The precipitate slowly dissolves at a rate given by the rate of mass transfer into the water in the pores in the surrounding medium, with the concentration of the nuclide in the water adjacent to the surface of the waste form given by its solubility. Note that the radionuclide release mode is determined not only by its solubility, but also by the rate of matrix dissolution, radionuclide inventory in the waste form, and the rate of diffusive mass transfer at the point of matrix dissolution. The TTB code can determine the release mode by considering the material balance of each nuclide [9]. For the case of a graphite waste matrix, the oxidation rates of the graphite are taken to be the fast and slow limits of graphite
oxidation provided in Table 3.1. The mathematical formulation for the release rate of radionuclides from the surface of the DBSF can be found in [9].

A number of assumptions were made in order to obtain a conservative (over)estimate of the concentration of radionuclides in the diffusion barrier region released from graphite waste form as it degrades. We give no protective credit to the drip shield, or to the MPC, and we assume that canister failure occurs simultaneously at 1,000 years. Because this is a deterministic assessment of the performance of DBSF relative to 40CFR197, we have chosen 1,000 year as the package failure time in order to have a dose to evaluate with respect to the regulatory dose limits in the first 10,000 years. In actuality, less than 1% of all packages are expected to fail in the first 1,000 years [10]. All radionuclides releases are considered in the maximum limit of their respective solubility.

5.3.3 Mathematical Formulation for Near-Field Transport

As outlined above, we consider the geometric transformation of the DBSF into a sphere surrounded by a concentric spherical diffusion barrier. We will consider that the following physical mechanisms will be sufficient to describe the transport of radionuclides within the diffusion barrier region: sorption with the host rock, radioactive decay, and diffusive transport. Given these physical mechanisms, the concentration of radionuclides in the water phase of the diffusion barrier will be given by the following equations;

\[
K_{e(1)} \frac{\partial N_1}{\partial t} + \lambda_1 K_{e(1)} N_1 = D_{e(1)} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial N_1}{\partial t} \right),
\]

\[
K_{e(2)} \frac{\partial N_2}{\partial t} + \lambda_2 K_{e(2)} N_2 = D_{e(2)} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial N_2}{\partial t} \right) + \lambda_1 K_{e(1)} N_1,
\]

\[\vdots\]

\[
K_{e(i)} \frac{\partial N_i}{\partial t} + \lambda_i K_{e(i)} N_i = D_{e(i)} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial N_i}{\partial t} \right) + \lambda_{i-1} K_{e(i-1)} N_{i-1},
\]

where

\[t > 0, r_1 < r < r_2, i = 1, 2, \ldots, I,\]

\[N_d(r,t) = \text{concentration of the } k^{th} \text{ member radionuclide in a decay chain of length } I (\text{mol/m}^3),\]

\[r = \text{distance from the center of the waste form (m)},\]

\[K_{e(k)} = \text{retardation coefficient for element } e, \text{ and}\]

\[\lambda_k = \text{decay constant of radionuclide } k (\text{yr}^{-1})]\n
The retardation coefficient \(K_{e(k)}\) is given as

\[K_{e(k)} = 1 + \frac{D(1 + \varepsilon)}{\varepsilon} K_d^e,\]

where \(\varepsilon\) and \(\rho\) (kg/m\(^3\)) are the porosity and density of the drift shadow region, and \(K_d^e\) (m\(^3\)/kg) is the equilibrium sorption distribution coefficient for element \(e\) in the diffusion barrier. The solution of these governing equations provides the concentration of radionuclides in the diffusion barrier region. We can also determine the mass flux of
radionuclides across the outer boundary of the diffusion barrier. This mass flux will be used as a source term for the input of radionuclides in our far-field transport calculations. A detailed solution of the governing equations is provided in [9].

5.3.4 Far-Field Model and Physical Processes

The drifts in the YMR are situated some 300 m below the ground surface and about 300 m above the water table. Once radionuclides have been released from the waste packages, they must traverse the unsaturated zone in order to reach the saturated zone where they can be transported down gradient through a network of fractures to the alluvium and subsequently to the RMEI, located a total distance of 18 km down gradient from the repository. Transport of radionuclides in the saturated zone occurs, then, in two regions. In the first 13 km down-gradient from the repository, transport occurs via advection in the fractures of fractured volcanic rock. At the 13 km location, the radionuclides enter the alluvial zone, where transport takes place as advection through a porous medium for the next 5 km [10]. Transport time is significantly shorter through the fracture network, than in the alluvium [10], therefore we consider transport to the 18 km location to occur exclusively in the fractured volcanic rock.

The unsaturated zone is comprised of a number of different rock types, with varying physical properties [36] [37]. The transport of radionuclides to the saturated zone occurs mainly by advection through fractures permeating the unsaturated host rock (although also by diffusion through the rock matrix), however, a number of major faults intersect the unsaturated host rock, and act as a fast path from the tunnel drifts to the saturated zone [10] [36] [37]. In order to simplify our model, in all cases we consider instantaneous transport of radionuclides from the outer edge of the diffusion barrier in the unsaturated zone through these major faults to the saturated zone. With the exception of the narrow diffusion barrier, we neglect the role of the unsaturated zone in slowing the transport of radionuclides into the saturated zone.

The geometry of the far-field transport model is shown in Figure 5.4. For transport beyond the diffusion barrier, a fractured volcanic rock matrix with multiple parallel planar fractures is considered. The following physical processes are taken into account: advection in the fractures, longitudinal dispersion, molecular diffusion, sorption, and radioactive decay. The velocity of the water in the fracture and the longitudinal dispersion considered to be constant and uniform. Additionally we assume that the permeability of the rock matrix is low enough that transport within the host rock is primarily by molecular diffusion while transport along the fracture is much faster than transport in the rock.
Finally, the annual dose to the RMEI is calculated by evaluating Equation 5.3 taken from [38] for exposure via contaminated groundwater:

\[ D_T(t) = \sum_{j=1}^{N} BDCF_j \cdot C_j(18km, t), \]

(5.3)

where

- \( D_T(t) \) = total time dependent dose to the RMEI from the \( N \) transported radionuclides to the 18km observation location at time \( t \) (Sv/yr).
- \( BDCF_j \) = biosphere dose conversion factor (BDCF) for radionuclide \( j \) (Sv/yr per Bq/m³).
- \( C_j(18km, t) \) = time dependent concentration of radionuclides in the groundwater at the 18km boundary (Bq/m³).

The BDCF is a means of translating concentration of radionuclides in the groundwater at the observation location into an annual dose received by the RMEI for the exposure pathway through groundwater transport to the observation point. The BDCF for each radionuclide is determined by considering that the RMEI meets a number of criteria, among which are that they drink 2 liters of contaminated water per day, and use contaminated well water at a rate of 3,000 acre-ft/yr (3.7 x 10⁶ m³/yr) for various domestic and agricultural purposes. Therefore, the BDCF considers not only direct exposure from the consumption of contaminated ground water, but also the consumption of contaminated food stuffs (animals and crops grown with the contaminated water), and other exposure pathways (e.g. inhalation, accidental ingestion of contaminated soil, etc.).
associated with the use of contaminated water. Because the BDCF is dependent on a number of factors it is given in the TSPA-LA as a distribution for three distinct climatic conditions. In our study we assume the mean value of the BDCF for each radionuclide in the current climatic conditions. These values are given in Table 5.3.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>BDCF (Sv/yr per Bq/m³)</th>
<th>Nuclide</th>
<th>BDCF (Sv/yr per Bq/m³)</th>
<th>Nuclide</th>
<th>BDCF (Sv/yr per Bq/m³)</th>
</tr>
</thead>
<tbody>
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<td>1.30E-06</td>
<td>238 U</td>
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<tr>
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<td>3.15E-07</td>
<td>237 Np</td>
<td>2.74E-07</td>
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<tr>
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<td>229 Th</td>
<td>2.58E-06</td>
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<td>7.61E-07</td>
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<td>1.08E-06</td>
<td>239 Pu</td>
<td>9.55E-07</td>
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<td>232 Th</td>
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</table>

It is assumed that the entire inventory of Pu, Np and Am included in 63,000 MT of CSNF destined for the YMR is converted into fresh DBMHR fuel. Of the CSNF destined for YMR, 40,200MT is from pressurized water reactors (PWR’s) and 22,800MT is from boiling water reactors (BWR’s) [37]. In Tables A-12 and A-13 of [39], the radionuclide inventories for the representative PWR and BWR spent fuel assemblies are listed, respectively. The total number of DBSF waste packages is calculated to be 23,612 from this inventory; this is based on the complete utilization of the 239Pu inventory in the 63,000MT of CSNF. The transport calculations for the whole element disposal are obtained by considering a single waste package. The annual dose to the RMEI in this case is scaled by the total number of packages and total number of fractures. The transport calculations for the compact only disposal are made by considering the degradation of a single fuel compact and the annual dose to the RMEI is obtained by scaling the dose by the total number of compacts destined for YMR (23,612 packages x 3,126 compacts per fuel element x 42 fuel elements per package).

5.3.5 Mathematical Formulation for Far-Field Transport

With these assumptions, the equations governing the concentration of radionuclides in the fracture \( C_i (z, t) \) and in the pores \( C_i^p (y, t; z) \) are
\[
R_{e(k)} \frac{\partial C_k}{\partial t} + v \frac{\partial C_k}{\partial z} - D^I \frac{\partial^2 C_k}{\partial z^2} - \frac{D^I}{b} \frac{\partial C_k^p}{\partial y} \bigg|_{y=0} \\
+ R_{e(k)} \lambda_k C_k - R_{e(k-1)} \lambda_{k-1} C_{k-1} = 0 \\
t > 0, y > 0.
\] (5.4)

and
\[
\alpha_{e(k)} \frac{\partial C_k^p}{\partial t} = D^I \frac{\partial^2 C_k^p}{\partial y^2} - \alpha_{e(k)} \lambda_k C_k^p + \alpha_{e(k-1)} \lambda_{k-1} C_{k-1}^p \\
t > 0, 0 < y < a, z > 0.
\] (5.5)

The initial and boundary conditions are given as
\[
C_k(z,0) = 0, z > 0
\] (5.6)
\[
C_k^p(y,0;z) = 0, 0 < y < a, z > 0
\] (5.7)
\[
\epsilon_f \left[ vC_k(0,t) - D^I \frac{\partial C_k}{\partial z} \bigg|_{z=0} \right] = \frac{Q_k(t)}{A}, t > 0
\] (5.8)
\[
C_k(\infty,t) = 0, t > 0
\] (5.9)
\[
C_k^p(0,t;z) = C_k(z,t), t > 0, z > 0
\] (5.10)

and
\[
\frac{\partial C_k}{\partial y} \bigg|_{y=0} = 0, t > 0, z > 0
\] (5.11)

The time-dependent quantity \( Q_k(t) \) is the flux of radionuclide \( k \) from the diffusion barrier and the dimensionless factor \( A \) is determined by repository configuration. The Laplace-transformed analytical solutions are presented in [9], which are inverted numerically to obtain the concentrations at a given distance from the used fuel. For a detailed discussion, see [9].

The capacity factor for the radionuclide \( k \) of element \( e \) is given as
\[
\alpha_{e(k)} = \epsilon_p + \rho_p (1-\epsilon_p) K_{dp}^e,
\] (5.12)
where \( \rho_p \) is the density of the host rock and \( K_{dp}^e \) is the sorption distribution coefficient of element \( e \) for the host rock. The retardation coefficient \( R_{e(k)} \) is given as
\[
R_{e(k)} = 1 + \frac{\rho_f (1-\epsilon_f) K_{dp}^e}{\epsilon_f},
\] (5.13)
where \( \rho_f \) and \( \varepsilon_f \) are the density and porosity of the material filling the fractures and the value \( K^e_{df} \) is the sorption distribution coefficient of element \( e \) for the material filling the fractures. With this information we are able to solve for the annual dose to the RMEI at the down gradient observation location.

### 5.3.6 TTB Input Parameters

Table 5.4, Table 5.5, and Table 5.6 describe the input parameters necessary to perform the calculations for the mathematical models described previously using TTB. In this study, we have considered (1) optimistic, (2) nominal, and (3) pessimistic cases. These cases were created by varying the hydro-geological parameters associated with radionuclide transport.

<table>
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<tr>
<th>Element</th>
<th>Solubility ( N^e_m ) (mol/m(^3))</th>
<th>Free Water Diffusion Coefficient ( D_e ) (m(^2)/yr)</th>
<th>( K^e_{df} ) (m(^3)/kg)</th>
<th>( K^e_{dp} ) (m(^3)/kg)</th>
<th>( D^f_e ) (m(^2)/yr)</th>
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<td>-</td>
<td>6.49E-02</td>
<td>2.00E-03</td>
<td>7.28E-01</td>
<td>1.58E-03</td>
</tr>
</tbody>
</table>
Table 5.5 Retardation Factors for the Diffusion Barrier, Fractured Volcanic Rock, and Fracture.

<table>
<thead>
<tr>
<th>Element</th>
<th>In the Diffusion Barrier</th>
<th>In the Fractured Volcanic Rock</th>
<th>In the Fracture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Optimistic</td>
<td>Nominal</td>
<td>Pessimistic</td>
</tr>
<tr>
<td>Americium</td>
<td>1.97E+04</td>
<td>6.07E+03</td>
<td>2.67E+03</td>
</tr>
<tr>
<td>Plutonium</td>
<td>4.92E+03</td>
<td>1.52E+03</td>
<td>6.68E+02</td>
</tr>
<tr>
<td>Uranium</td>
<td>1.08E+01</td>
<td>4.03E+00</td>
<td>2.33E+00</td>
</tr>
<tr>
<td>Neptunium</td>
<td>5.01E+01</td>
<td>1.61E+01</td>
<td>7.66E+00</td>
</tr>
<tr>
<td>Thorium</td>
<td>2.71E+05</td>
<td>8.34E+04</td>
<td>3.67E+04</td>
</tr>
<tr>
<td>Protactinium</td>
<td>2.71E+05</td>
<td>8.34E+04</td>
<td>3.67E+04</td>
</tr>
<tr>
<td>Radium</td>
<td>1.60E+04</td>
<td>4.93E+03</td>
<td>2.17E+03</td>
</tr>
<tr>
<td>Technetium</td>
<td>1.00E+00</td>
<td>1.00E+00</td>
<td>1.00E+00</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.00E+00</td>
<td>1.00E+00</td>
<td>1.00E+00</td>
</tr>
<tr>
<td>Strontium</td>
<td>1.23E+03</td>
<td>3.80E+02</td>
<td>1.68E+02</td>
</tr>
<tr>
<td>Selenium</td>
<td>4.23E+02</td>
<td>1.31E+02</td>
<td>5.83E+01</td>
</tr>
<tr>
<td>Tin</td>
<td>3.49E+04</td>
<td>1.08E+04</td>
<td>4.73E+03</td>
</tr>
<tr>
<td>Iodine</td>
<td>1.00E+00</td>
<td>1.00E+00</td>
<td>1.00E+00</td>
</tr>
<tr>
<td>Cesium</td>
<td>9.94E+01</td>
<td>3.13E+01</td>
<td>1.43E+01</td>
</tr>
</tbody>
</table>

Table 5.6 Assumed Parameters for Use in Optimistic, Nominal, and Pessimistic Transport Calculations.

<table>
<thead>
<tr>
<th>Waste matrix</th>
<th>Optimistic Case</th>
<th>Nominal Case</th>
<th>Pessimistic Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity of the diffusion barrier region, ( \varepsilon ) [42]</td>
<td>0.043</td>
<td>0.12</td>
<td>0.229</td>
</tr>
<tr>
<td>Density of the diffusion barrier region, ( \rho ) (kg/m(^3)) [43]</td>
<td>2210</td>
<td>2068</td>
<td>1980</td>
</tr>
<tr>
<td>Porosity of the fractured volcanic rock, ( \varepsilon_p ) [43]</td>
<td>0.15</td>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>Density of the fractured volcanic rock, ( \rho_p ) (kg/m(^3)) [43]</td>
<td>2770</td>
<td>1880</td>
<td>1770</td>
</tr>
<tr>
<td>Water velocity in the fractures, ( v ) (m/yr) [43]</td>
<td>0.312</td>
<td>2.37</td>
<td>7.50</td>
</tr>
<tr>
<td>Longitudinal dispersion coefficient, ( D_L ) [43]</td>
<td>31.2</td>
<td>237</td>
<td>750</td>
</tr>
<tr>
<td>Tortuosity correction factor for the diffusion barrier, ( \tau )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Fracture hydraulic aperture, ( 2b ) (m)</td>
<td>2.71E-03</td>
<td>1.97E-02</td>
<td>1.45E-01</td>
</tr>
<tr>
<td>Graphite waste-form oxidation rate, ( R ) (g/m(^2)/d), (fast oxidation/slow oxidation) [7]</td>
<td>1.28E-05 / 1.70E-08</td>
<td>1.28E-05 / 1.70E-08</td>
<td>1.28E-05 / 1.70E-08</td>
</tr>
<tr>
<td>Mass of graphite being degraded (whole element / compact only disposal) (g) [1] [5]</td>
<td>4.93E+06 / 8.77E+00</td>
<td>4.93E+06 / 8.77E+00</td>
<td>4.93E+06 / 8.77E+00</td>
</tr>
<tr>
<td>Radius of the equivalent spherical waste, ( r_1 ) (m) (whole element/compact only)</td>
<td>0.905/0.011</td>
<td>0.905/0.011</td>
<td>0.905/0.011</td>
</tr>
<tr>
<td>Radius of the equivalent spherical diffusion barrier region, ( r_2 ) (m) (whole element/compact only)</td>
<td>2.905/2.011</td>
<td>2.905/2.011</td>
<td>2.905/2.011</td>
</tr>
<tr>
<td>Surface area of the waste form, ( S_1 = 4\pi r_1^2 ) (m(^2)) (whole element/compact only)</td>
<td>10.29/0.0015</td>
<td>10.29/0.0015</td>
<td>10.29/0.0015</td>
</tr>
<tr>
<td>Surface area of the diffusion barrier region, ( S_2 = 4\pi r_2^2 ) (m(^2)) (whole element/compact only)</td>
<td>106.1/50.82</td>
<td>106.1/50.82</td>
<td>106.1/50.82</td>
</tr>
<tr>
<td>Distance between two waste forms (m) [1]</td>
<td>5.24</td>
<td>5.24</td>
<td>5.24</td>
</tr>
<tr>
<td>Characteristic Repository Length ( L_r ) (m) [1] [9]</td>
<td>20.6</td>
<td>20.6</td>
<td>20.6</td>
</tr>
<tr>
<td>Flowing Interval Spacing (m) [43]</td>
<td>2.71</td>
<td>19.65</td>
<td>145.08</td>
</tr>
<tr>
<td>Flowing Interval Porosity ( \varepsilon_f ) [43]</td>
<td>1.00E-03</td>
<td>1.00E-03</td>
<td>1.00E-03</td>
</tr>
</tbody>
</table>
The solubilities for radionuclides in the near field are those which were calculated using the PHREEQC geochemical modeling software (Chapter 4) and those presented in [24] as applicable. A detailed discussion of solubility calculations can be found in references [24] and [40]. The solubilities of all of the radionuclides are fixed at the highest values for this environment. The equilibrium sorption coefficients are chosen to be their mean values for the respective host rocks, and the matrix diffusion coefficient in the fractured volcanic rock is chosen to be its mean value, as given in the supporting documentation for the TSPA-LA [44] [43].

The water velocity, \( v \), and longitudinal hydrodynamic dispersion coefficient \( D_L \) are assumed to be constant with time and uniform throughout space. They are also assumed to be the same for all nuclides considered because dispersion is mainly determined by the geometry of the transport path [9]. The values for the water velocity were chosen in accordance with measurements made for the TSPA-LA for the YMR in the fractured volcanic rock in the saturated zone. The mean value for the longitudinal dispersion coefficient, \( \alpha_L \), was chosen and it is assumed that \( D_L \) is given as

\[
D_L = \alpha_L v .
\]  

(5.14)

When considering the input parameters for the near-field transport, we must recall that the host rock in this environment is considered to be Topopah Spring welded tuff in the unsaturated zone (primarily the tsw35 hydrogeologic unit), and that transport occurs by molecular diffusion exclusively. The porosity and density of the near-field host rock are shown in Table 5.6, and are taken at their maximum, mean, and minimum values [42]. As discussed previously this diffusive transport will occur because the water contaminated with the radionuclides initially interfaces with the drift shadow region, a region in which advective transport is negligible [32] [33] [34]. The tortuosity correction factor in this is conservatively set to one. Retardation effects due to sorption of radionuclides with the host rock are considered based on the mean of the distributions provided in the supporting documentation for the TSPA-LA.

When considering the far-field transport of radionuclides, we are concerned with transport in the fractures of the rock, which comprises saturated zone. Transport calculations are particularly sensitive to the size of the fracture aperture. The supporting documentation for the TSPA-LA calculates the hydraulic fracture aperture, \( 2b \), as the product of the flowing interval spacing and the flowing interval porosity. The flowing interval spacing is the distance between two segments in a bore sample that transmit significant amounts of water, and is generally greater than the actual fracture spacing. We chose as our nominal case the mean value for the flowing interval spacing and, based on the distribution provided, set our minimum and maximum spacing two standards below and above the mean, respectively. The value of the flowing interval porosity was fixed at its mean value. The values for the equilibrium sorption distribution coefficients are taken from the supporting documentation for the TSPA-LA for advective transport in the fractured volcanic rock matrix [41].
5.4 Numerical Results

5.4.1 Results for Optimistic Far-Field Conditions

The results for the optimistic far-field environmental conditions provided above are not presented because the annual dose to the RMEI was observed to be too small to show in the ranges used in Figure 5.5 to Figure 5.9 in any of the four conditions studied (whole-element and compact-only disposal in the fast and slow limits of graphite oxidation). Full compliance with 40CFR197 is observed; the annual dose to the RMEI remains below the regulatory threshold for geologic time periods with many orders of margin.

5.4.2 Results for Nominal Far-Field Conditions

Figure 5.5 shows the annual dose received by the RMEI in the nominal case, for compact-only disposal, in the fast graphite oxidation regime. This combination yields the highest dose to the RMEI among the four conditions in the nominal case. We can see that the DBSF meets the regulatory annual dose threshold (40CFR197) in the million-year time frame. The annual dose actually has two peaks, the first of which is almost entirely due to $^{129}$I between $10^7$ and $10^8$ year, and the second which is almost exclusively due to $^{227}$Ac. $^{227}$Ac is a decay daughter of and $^{235}$U (itself a decay daughter of $^{239}$Pu), and the contribution to dose from $^{227}$Ac is the result of ingrowth. The second peak annual dose is seen at $10^9$ years. This peak is not shown because of its extremely large time. The latter peak dose, $6.3 \times 10^{-8}$ Sv/yr, remains well below the annual dose limit of $10^{-3}$ Sv/yr for the term between 10,000 and million years, indicating that under these conditions DBSF may pose negligible health risk even over geologic time periods.

Figure 5.6 shows the total annual dose to the RMEI in the nominal case for the four disposal conditions considered. We consider both the fast and slow oxidation rates of graphite, and we consider the cases of whole-element and compact-only disposal. As seen in Chapter 3, these conditions provide a wide range in the projected lifetimes of waste matrix. The effects of matrix lifetime are clear. By extending the waste matrix lifetime, the annual dose to the RMEI is reduced. This results from the fact that all of the radionuclides, including the main contributor, $^{129}$I, are released from the failed waste package congruently with the graphite matrix dissolution in each of these four conditions. Because of this congruency, given a greater matrix oxidation rate $R$, or a smaller graphite mass, the release rate of iodine increases, resulting in a higher dose rate at the downstream point.

An important retardation mechanism against the release of radionuclides to the biosphere is the diffusion of radionuclides out of the fracture and transport via diffusion into the volcanic rock matrix where the radionuclides are either sorbed onto the host rock, or from which they will slowly diffuse back into the fracture. The effect of matrix diffusion was investigated by varying the matrix diffusion coefficient in the condition of compact-only disposal (low graphite mass), under fast graphite oxidation, in the nominal case given above. The value of the matrix diffusion coefficient was varied by an order of magnitude both above and below the mean value given in the supporting documents for the TSPA-LA. As seen in Figure 5.7, the case of high matrix diffusion reveals a substantially reduced dose to the RMEI, and highlights the importance of matrix diffusion in sequestering radionuclides from public exposure.
Figure 5.5 Annual dose to the RMEI from the disposal of DBSF (nominal case with compact only disposal condition in the fast graphite oxidation regime).

Figure 5.6 Effect of waste matrix lifetime on the annual dose to the RMEI from the disposal of DBSF in the nominal case.
5.4.3 Results for Pessimistic Far-Field Conditions

In all of the disposal conditions considered in the pessimistic case, all of the radionuclides are released congruently with the waste matrix. Figure 5.8 shows the results for the compact-only disposal, in the fast graphite oxidation regime, in the pessimistic case given above. We can see that even under these combinations the annual dose is observed to be less than the threshold set by 40CRF197 by nearly an order of magnitude. The total dose to the RMEI has two distinct peaks contributed to by several radionuclides. The earliest peak is largely due to $^{99}$Tc (half-life $2.1 \times 10^5$ yr), followed by $^{237}$Np (half-life $2.1 \times 10^6$ yr) which is almost entirely responsible for the highest peak. $^{227}$Ac again provides the dose to the RMEI on the longest time frame. The relatively-high annual dose delivered to the RMEI can be attributed to fast transport of radionuclides through large fractures and high solubilities assumed conservatively. The congruent release of radionuclides from the waste matrix implies that radionuclide concentration will remain below their solubility limits for the duration of their release from the waste matrix. This feature of DBSF performance confers a proportionality between the annual dose to the RMEI and the lifetime of the waste matrix. These results highlight the importance of geological, geochemical, and hydrogeological features in determining the potential health risk to the public from the disposal of high-level waste in a geological repository.
Figure 5.8 Annual dose to the RMEI from the disposal of DBSF (pessimistic case with compact only disposal condition in the fast graphite oxidation regime).

Figure 5.9 Effect of waste matrix lifetime on the annual dose to the RMEI from the disposal of DBSF in the pessimistic case.
Figure 5.9 shows the effects of the graphite matrix lifetime, which is controlled by the initial mass of graphite and the corrosion rate, $R$, of graphite. Between the whole-element and the compact-only cases, the initial masses of graphite associated with each case are $4.93 \times 10^3$ kg and $8.77 \times 10^{-3}$ kg, respectively. This difference in mass translates into a proportional factor of about 100 difference in the transformed radii used in the lifetime calculation of the DBSF in the two disposal conditions (whole element and compact only) considered. This factor also appears proportionally as the difference between the dashed and solid curves for the same $R$ value. Similarly, a factor of about 1,000 difference in $R$ appears as difference by the same factor between two solid curves and between two dashed curves, respectively.

5.5 Discussions

For all the combinations studied, significant conservatism has been commonly implemented. It is assumed that radionuclides released from the entire repository are funneled into, confined in, and carried through, the fictitious planar fracture pathway. The value of the solubility of each element in pore water in the diffusion barrier in the near-field region has been set at its upper-bound value in the assumed geochemical environment at YMR. The package failure time has been assumed only 1,000 years, which is factor of 1,000 or more pessimistic than the assumption made in the TSPA-LA for the YMR. The protective roles of the drip shield and the transport time and retardation effects in the unsaturated zone and in the alluvium are all conservatively neglected.

We have considered $2 \times 2 \times 3 + 2 = 14$ combinations. Of these 14 combinations, 4 cases of the graphite-matrix conditions (mass and dissolution rate of graphite) under the optimistic far-field conditions have shown that the DBSF disposal would comply with the regulation with many orders of margin. Similar observations have been made for the cases under the nominal far-field conditions and even under the pessimistic far-field cases; the annual dose to the RMEI has been observed to comply with the regulatory limit in all cases studied. We have seen that compliance of the DBSF disposal in YMR environment could be demonstrated thanks to the superior robustness of graphite and TRISO layers by a deterministic bounding analysis with high conservatism under the groundwater exposure scenario.

The graphite matrix plays an important role in retarding the release of radionuclides and sequestering them from the public. Parametric studies show a one order of magnitude reduction in the dose to the RMEI for every order of magnitude extension in the lifetime of the fuel form. A significant portion of the radionuclide inventory, especially the shorter lived fission products, decays within the graphite matrix before it has had a chance to be released and transported into either the near or far field regions. If the dissolution rate of graphite is on the lower end of the range and the mass of graphite is large then (see source term development in Chapter 3), even in the pessimistic far-field case, DBSF would comply with the regulation with many orders margin.

Long graphite lifetime makes the congruent release rate of radionuclides small, so that radionuclide concentrations at the graphite dissolution location become lower than their solubility limits. As many previous studies indicate, nuclide solubilities in geochemical conditions are greatly uncertain, resulting in significant uncertainty
associated with the total repository performance. Therefore, with a robust waste form, such as graphite, the total system performance can be greatly improved as shown in this study and made more predictable, implying a need for more detailed material-scientific studies on graphite as waste form.

Further, it should be noted that the model presented in this study for the performance of the DBSF, including the TRISO particles, as a waste form is applicable across a variety of repository conditions and geologies within the parameter ranges assumed presently. The models for near and far-field transport of radionuclides are also generic to any repository in which diffusive transport, and advection through fracture networks are expected to be the dominant transport pathways.

5.6 Summary

In the present study, motivated by the observations made in the previous chapters that revealed superior robustness of graphite and TRISO layers in geological repository conditions, a deterministic bounding analysis has been performed to assess the annual dose to the RMEI by taking the Yucca Mountain conditions and to compare the results with the YMR performance standard given in 40 CFR 197.

Models have been developed for evaluating degradation rates of graphite and TRISO layer based on previous experimental studies. Based on the observation from the model evaluation that graphite dissolution is the rate-limiting process (Chapter 3), the radionuclide release model has been developed, and used as the source term for the far-field transport calculation. The existing computer code, TTB, has been utilized to perform actual computation, which utilizes numerical inversion of Laplace transformed analytical solutions for transport of a multi-member decay chain. Radionuclide composition in TRISO particles has been evaluated by MOCUP code. Solubility of actinide elements in the Yucca Mountain environment with modification of carbon dioxide fugacity was obtained by PHREEQC simulation code (Chapter 4) and from supporting documents for the TSPA-LA. Various data for repository configurations and hydro-geological parameters were referenced from the TSPA-LA report and supporting documents.

The results of the present deterministic performance assessment show the following:

- All of the cases of the groundwater exposure pathway that have been investigated in this study, including the optimistic, nominal and pessimistic cases, have indicated compliance with the regulatory limit for the annual dose to the RMEI, with orders of magnitude margins, despite numerous conservative assumptions. In the nominal case the major contributor to the annual dose is $^{129}$I; other nuclides decay out before they reach the intake point located at 18 km downstream from the repository. Under the pessimistic case the major contributors to the annual dose were $^{99}$Tc, $^{237}$Np, and $^{227}$Ac; high flow conditions in large fractures coupled with high radionuclide solubilities lead to rapid transport of these radionuclides to the observation point.

- With the assumed high durability of graphite, in all of the cases studied, all radionuclides are released congruently with graphite corrosion. This congruency results in nearly linear dependency of the annual dose to RMEI on the graphite lifetime. Congruency also implies that radionuclide concentrations in groundwater are smaller than their solubility limits, resulting in low annual dose to RMEI. This
highlights the possibility and advantage of the use of graphite as a waste matrix for the disposal of HLW, and the need for detailed material scientific studies on the mechanisms of graphite corrosion in repository environments.

- Finally, it must be noted that many of the parameters used are associated with aleatory and epistemic uncertainties. In order to make a more effective assessment of the potential health risk to the public from the disposal of DBSF in the YMR, we must make a probabilistic sampling of the parameter space. Additionally, alternate pathways for exposure must be investigated in order to conclusively determine compliance with regulatory standards. This is the focus of ongoing research.
Chapter 6  Aqueous Transport of an Arbitrary Length Decay Chain through Heterogeneous Geologic Formations

6.1 Introduction

In the previous chapters we have seen the development and implementation of models designed to assess the performance of DBSF in a geological repository. In Chapter 2 we made an initial assessment of the environmental impact of disposing of DBSF in the YMR, with CSNF serving as a basis of comparison using existing models and considering only the TRU content of the DBSF based on two proposed DBHMR fuel cycles. Motivated by the results in Chapter 2 we began to develop the models necessary to make a more complete and rigorous assessment of the performance of DBSF in a geological repository based on a third DBMHR fuel cycle. Chapter 3 saw the development of a detailed source term, including the development of a time dependent failure model for the TRISO particles, and lifetime assessments for both the TRISO particles and the DBSF waste form. Here we saw that the neglecting of the TRISO layers as engineered barriers against the release of radionuclides was well justified given the lifetime of the graphite matrix containing them, given the same geochemical environment. In Chapter 4 we implemented the PHREEQC geochemical simulation package to determine the solubilities of TRU released from DBSF into the near field environment and set recommended maximum and minimum solubility limits for the elements based on that study. This study was necessary because the corrosion product of graphite in an aqueous environment is CO$_2$ which will alter the bicarbonate concentration of the groundwater (solubilities of TRU’s are sensitive to bicarbonate concentrations). The results from Chapter 3 and Chapter 4 were utilized in Chapter 5 to make a performance assessment of DBSF in the YMR. In this study we made use of the existing TTB transport model to assess the dose delivered to the RMEI under various hydrogeologic conditions. An assumption was made that the entire flow path in the saturated zone from the near field interface to the observation point was composed of one rock type with parameters fixed within that transport segment. Using this model we found that DBSF complies with regulatory thresholds for all conditions studied.

While the study above does highlight the applicability of these models across a wide set of parameters and demonstrates its utility in making conservative deterministic bounding analyses, the results also show some of the limitations of the models and call into question a portion of the conservatism. The results clearly show the sensitive dependence of the resultant dose delivered to the RMEI on the hydrogeological conditions which are prevalent. Although in all of the cases the dose to the RMEI was observed to be less than the regulatory threshold, across the conditions which were studied we observed the total peak dose to the RMEI varied by more than ten orders of magnitude. This demonstrates the sensitivity of the system to bulk changes in the hydrogeological parameter. Similarly, although less dramatic, we saw the sensitivity of the system to varying the matrix diffusion coefficient, with the dose varying nearly linearly with changes in the matrix diffusion coefficient over the length of the transport path.

The TSPA-LA recommends utilizing three separate transport regions in the saturated zone to model the flow of radionuclides from the repository to the downstream observation point [10]. The transport path recommended is a path consisting of two
different fractured volcanic sections (5km and 8km in length respectively) follow by a 5km section of alluvium (porous media). However, owing to the limitation of the TTB model, which can accommodate only a single rock type, and because fracture flow is generally considered to be faster than flow through porous media the saturated zone transport path was modeled as a single 18km long fracture. Because of the sensitivity of the system to the hydrogeological parameters it is possible that by neglecting the heterogeneous nature of the transport path that we have not maintained conservatism in assessing the dose to the RMEI. It is in this light that we develop the models for the aqueous transport of radionuclides through heterogeneous geological media.

6.2 Transport of a Single Member Decay Chain through Heterogeneous Geological Media

We begin our study by considering the aqueous transport of a single member decay chain through heterogeneous geological media. This is a reasonable place to begin since many of the main contributors to the dose delivered to the RMEI are either fission products, and members of a single member decay chain, \( ^{99}\text{Tc} \) and \( ^{129}\text{I} \), or (as is the case with \( ^{237}\text{Np} \)) the daughter of relatively short lived parents. For our model of radionuclide transport through heterogeneous geological media we consider the following scenario (Figure 6.1). We consider a single 1-D transport path through an arbitrary number of fractured or porous transport segments. The transport path is assumed to be surrounded by infinite media (porous in the case of a fractured transport segment, and dense in the case of a porous transport segment). In the transport segment we consider sorption with material filling the fracture (or with the porous media in the case of a porous transport segment), and advection along the transport path. Diffusion of the radionuclides into the surrounding host rock in the case of fracture flow is considered, as well as equilibrium sorption between the radionuclides and the host rock. Radioactive decay is also considered. Longitudinal dispersion along the transport path is neglected.

![Figure 6.1 An example of a potential transport path through heterogeneous geological formations. Here three fracture segments join to form the transport path.](image-url)
6.2.1 Theoretical Development

The governing equations for this process may be written as follows:

(for fracture flow) \[ R_p \frac{\partial C_p}{\partial t} + v_p \frac{\partial C_p}{\partial x} + \lambda R_p C_p - \frac{\partial P_p}{\partial w_p} \bigg|_{w_p=0} = 0, \]  

(6.1a)

(for porous flow) \[ R_p \frac{\partial C_p}{\partial t} + v_p \frac{\partial C_p}{\partial x} + \lambda R_p C_p = 0, \]  

(6.1b)

\[ x_0 = 0, \ x_{p-1} \geq x \geq x_p, \ t > 0 \]  

(6.2)

Subject to the boundary conditions:

\[ C_p(x, 0) = 0, \ x_0 = 0, \ x_{p-1} \geq x \geq x_p \]  

(6.3)

\[ P_p(w_p, x, 0) = 0. \ w_p > 0, x_0 = 0, \ x_{p-1} \geq x \geq x_p \]  

(6.4)

\[ \lim_{w \to \infty} \frac{\partial P_p}{\partial w_p} \bigg|_{w_p=w} = 0 \]  

(6.5)

\[ C_1(0, t) = \frac{N_0}{\nu_1 \phi_1 A_1} e^{-\lambda t} \{ h(t) - h(t - T) \} \]  

\[ t > 0, \]  

(6.6)

\[ C_{p-1}(x_{p-1}, t) = C_p(x_{p-1}, t), \ t > 0, \]  

(6.7)
where,
\[ C_p(x,t) = \text{Concentration of the nuclide in the } p\text{th transport segment.} \]
\[ P_p(w_p,x,t) = \text{Concentration of the nuclide in the } p\text{th segment of the host rock.} \]
\[ t = \text{Time after the beginning of the release of nuclides at } t = 0. \]
\[ x = \text{Total distance along the transport pathway.} \]
\[ x_p = \text{Total distance to the exit of the } p\text{th transport segment.} \]
\[ w_p = \text{Distance from the fracture surface into the host rock media in the } p\text{th transport segment.} \]
\[ R_p = \text{Retardation coefficient for material in the } p\text{th transport segment.} \]
\[ \alpha_p = \text{Capacity factor for the } p\text{th segment of host rock.} \]
\[ \lambda = \text{Radioactive decay constant.} \]
\[ v_p = \text{Water velocity in the } p\text{th transport segment.} \]
\[ \phi_p = \text{Porosity of the material in the } p\text{th transport segment.} \]
\[ A_p = \text{The area of the } p\text{th transport segment opening.} \]
\[ b_p = \text{Fracture half-aperture of } p\text{th transport segment.} \]
\[ D_p = \text{Matrix diffusion coefficient for } p\text{th transport segment.} \]
\[ N_0 = \text{Initial mass release rate of the radionuclide at } x = 0, t = 0. \]
\[ h(\cdot) = \text{Heaviside function.} \]
\[ k = \text{Total number of transport segments.} \]

As can be seen by Equation 6.5 we have implemented a band release source term. Given the above governing equations the concentration of the radionuclide in the \( p \)th transport segment may be expressed as (where the details of the solution have been left to Appendix I):

\[ C_p(x,t) = \frac{N_0 \exp(-\lambda t)}{v_p \phi_p A_p} B_p(x,t), \quad t > 0, x_{p-1} \geq x \geq x_p \]  \hspace{1cm} (6.8)

Where,
\[ B_p(x,t) = h \left( t - \left[ \left( \sum_{j=1}^{p-1} R_j L_j \right) + \frac{R_p}{v_p} (x - x_{p-1}) \right] \right) \text{ERFC} \left( \frac{\left( \sum_{j=1}^{p-1} \frac{D_j \alpha_j}{b_j v_j} L_j \right) + \frac{R_p \alpha_p}{b_p v_p} (x - x_{p-1})}{2 \left( t - \left[ \left( \sum_{j=1}^{p-1} R_j L_j \right) + \frac{R_p}{v_p} (x - x_{p-1}) \right] \right)^{\frac{1}{2}}} \right) \]
\[ -h \left( t - \left[ \left( \sum_{j=1}^{p-1} R_j L_j \right) + \frac{R_p}{v_p} (x - x_{p-1}) \right] - T \right) \text{ERFC} \left( \frac{\left( \sum_{j=1}^{p-1} \frac{D_j \alpha_j}{b_j v_j} L_j \right) + \frac{D_p \alpha_p}{b_p v_p} (x - x_{p-1})}{2 \left( t - \left[ \left( \sum_{j=1}^{p-1} R_j L_j \right) + \frac{R_p}{v_p} (x - x_{p-1}) \right] - T \right)^{\frac{1}{2}}} \right) \]  \hspace{1cm} (6.9)

The remaining definitions are:
\[ \text{ERFC}(\cdot) = \text{The complementary error function.} \]
\[ L_p = \text{The length of the } p\text{th transport segment.} \]
\[ T = \text{The leach time of the waste matrix (length of band release).} \]
Note that this solution admits an arbitrary number of interconnecting transport pathways. The pathways may either be fracture flow transport segments, or porous flow transport segments. To utilize the solution above for a transport path that which contains both fracture segments and porous flow segments (a so-called heterogeneous pathway), setting the matrix diffusion coefficient to zero in the porous flow segment(s) yields the appropriate result.

6.2.2 Numerical Illustrations

Given the above analytical solution, we can make an evaluation as to the effects of transport path heterogeneity on the dose delivered to the RMEI in the case of the disposal of DBSF in the YMR. Looking at the results from the previous chapter, we see that the main contributors to the dose in the nominal environmental case were $^{99}$Tc and $^{129}$I. Both of these radionuclides are well suited for this single-member model as they have no precursors. In the pessimistic environmental case, we see that the main contributors to the overall dose received by the RMEI are $^{99}$Tc, $^{227}$Ac, and $^{237}$Np. In our model $^{237}$Np is the fourth member in the following simplified decay chain.

$$
^{245}\text{Cm} \rightarrow ^{241}\text{Pu} \rightarrow ^{241}\text{Am} \rightarrow ^{237}\text{Np}
$$

(6.10)

A review of the inventory of the DBSF shows (see Table 5.2) that $^{245}$Cm and $^{241}$Pu both contribute materials in a much smaller amount than either $^{241}$Am or $^{237}$Np. Further, we see that the half-life of $^{241}$Am (~ 450 years) is substantially less than both the time frame under consideration and the half-life of $^{237}$Np. We, therefore, assume that the entire inventory from the members preceding $^{237}$Np in equation (6.9) is lumped with that of $^{237}$Np at the beginning of the band release. That is, we add to the $^{237}$Np inventory the contribution from $^{245}$Cm, $^{241}$Pu, and $^{241}$Am at the beginning of the band release in the pessimistic environmental case and neglect their contribution after. In the pessimistic environmental case, $^{227}$Ac is also a major contributor in the very long time period ($> 10^5$ years). $^{227}$Ac is the fifth member in simplified decay chain shown below.

$$
^{243}\text{Am} \rightarrow ^{239}\text{Pu} \rightarrow ^{235}\text{U} \rightarrow ^{231}\text{Pa} \rightarrow ^{227}\text{Ac}
$$

(6.11)

Because of the inventory distribution in this instance, and the long lived parents of $^{227}$Ac within this decay chain, $^{227}$Ac is not well suited for use in this model.

6.2.3 Assumptions and Far-field Transport Pathway

Based on the results shown in Chapter 5 we assume that all of the radionuclides are released congruently with the waste and utilize the results obtained by assuming a band release of radionuclides from the graphite waste form. We investigate the dose related to $^{99}$Tc and $^{129}$I in the nominal environmental case, and the dose related to $^{99}$Tc, $^{129}$I, and $^{237}$Np in the pessimistic environmental case. We assume the same package failure time as in Chapter 5, and additionally assume that once radionuclides are released from the waste package they immediately enter the saturated zone in the far-field for transport. Once they have reached the saturated zone, they will be transported down gradient through a network of fractured media and to the alluvium and subsequently to the RMEI, located a total distance of 18 km down gradient from the repository. Transport of radionuclides in the saturated zone occurs, in three regions. In the first two segments
(5km and 8km, respectively) transport occurs via advection in the fractures of fractured volcanic rock. At the 13 km location, the radionuclides enter the alluvial zone, where transport takes place as advection through a porous medium for the next 5km [10].

### 6.2.4 Input Parameters

Table 6.1 and Table 6.2 show the parameters necessary to implement this model.

#### Table 6.1 Inventory, Diffusion Coefficient, Retardation and Capacity Factors.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-Life (years)</th>
<th>Inventory (At 1000yr) (mol)</th>
<th>In the Fracture</th>
<th>In the Fractured Volcanic Rock</th>
<th>In the Alluvium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{237}$Np</td>
<td>2.14E+06</td>
<td>8.96E+00</td>
<td>1.00E+00</td>
<td>4.53E+00</td>
<td>1.58E-03</td>
</tr>
<tr>
<td>$^{99}$Tc</td>
<td>2.13E+05</td>
<td>4.50E+00</td>
<td>1.00E+00</td>
<td>2.00E-01</td>
<td>1.58E-03</td>
</tr>
<tr>
<td>$^{129}$I</td>
<td>1.57E+07</td>
<td>4.08E-02</td>
<td>1.00E+00</td>
<td>2.50E-01</td>
<td>1.58E-03</td>
</tr>
</tbody>
</table>

#### Table 6.2 Assumed Parameters for Use in Transport Calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nominal Case</th>
<th>Pessimistic Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity of the fractured volcanic rock, $\varepsilon_p$</td>
<td>0.2</td>
<td>0.25</td>
</tr>
<tr>
<td>Density of the fractured volcanic rock, $\rho_p$ (kg/m$^3$)</td>
<td>1880</td>
<td>1770</td>
</tr>
<tr>
<td>Water velocity in the fractures, $v$ (m/yr) (first segment/second segment) [41]</td>
<td>0.61/4.12</td>
<td>0.87//7.50</td>
</tr>
<tr>
<td>Fracture hydraulic aperture, $2b$ (m)</td>
<td>1.97E-02</td>
<td>1.45E-01</td>
</tr>
<tr>
<td>Porosity of the alluvium, $\varepsilon_a$ [41]</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>Density of the alluvium, $\rho_a$ (kg/m$^3$) [41]</td>
<td>1910</td>
<td>1754</td>
</tr>
<tr>
<td>Water velocity of the alluvium [41]</td>
<td>14.28</td>
<td>16.75</td>
</tr>
<tr>
<td>Area of alluvial entrance (m$^2$)</td>
<td>0.43</td>
<td>0.43</td>
</tr>
<tr>
<td>Graphite waste-form oxidation rate, $R$ (g/m$^2$/d), (fast oxidation/slow oxidation)</td>
<td>1.28E-05 / 1.70E-08</td>
<td>1.28E-05 / 1.70E-08</td>
</tr>
<tr>
<td>Mass of graphite being degraded (whole element / compact only disposal) (g)</td>
<td>4.93E+06 / 8.77E+00</td>
<td>4.93E+06 / 8.77E+00</td>
</tr>
<tr>
<td>Characteristic Repository Length $L_r$ (m)</td>
<td>20.6</td>
<td>20.6</td>
</tr>
<tr>
<td>Flowing Interval Spacing (m)</td>
<td>19.65</td>
<td>145.08</td>
</tr>
<tr>
<td>Flowing Interval Porosity $\varepsilon_f$</td>
<td>1.00E-03</td>
<td>1.00E-03</td>
</tr>
</tbody>
</table>
6.2.5 Numerical Results

Figure 6.2 shows the results of applying the above model in the nominal environmental case. We see the familiar reduction of annual dose to the RMEI with the extension of the graphite waste matrix lifetime. However, in these cases the reduction is somewhat less than linear. The peak dose from $^{129}$I in the nominal case with the compact only disposal condition and in the fast graphite oxidation regime is less than $10^{-9}$ Sv/yr. In Figure 6.2 we can see that this represents roughly an order of magnitude reduction from the case presented in Chapter 5. In all of the instances studied in the nominal environmental case for flow through the heterogeneous pathway, $^{99}$Tc and $^{237}$Np doses are not observable in the ranges shown here. In Figure 6.3 we observe that transport along the heterogeneous path yields a smaller annual dose to the RMEI. This is likely because of the slow flow region in the first part of the transport pathway and the inclusion of the diffusion barrier in the single region model (TTB).

![Graph showing numerical results]

**Figure 6.2 Total annual dose to the RMEI (entirely from $^{129}$I) in the nominal environmental case from flow along a heterogeneous pathway using the Analytic Solution.**
In Figure 6.4, the results are shown for transport through the heterogeneous (three-region) pathway in the pessimistic environmental case in the compact only disposal condition in the fast graphite oxidation regime (worst case scenario) in comparison with Figure 5.5. The results generated using the analytic solution for the three region model are similar (although reduced in magnitude) to the single region model results generated using TTB. All three radionuclides contribute substantially to the total annual dose to the RMEI. The peak dose is seen to be somewhat less than $10^{-6}$ Sv/yr and is attributable to $^{237}$Np. The later peak associated with $^{227}$Ac, is not observed here because $^{227}$Ac was not modeled.

In Figure 6.5, we see the relation among the disposal conditions and oxidation regimes. Here we observe a nearly linear dependence of the peak dose to matrix lifetime with approximately an order of magnitude reduction in the annual dose to the RMEI with an order magnitude extension in the lifetime of the waste matrix.

In Figure 6.6, a comparison of results from the heterogeneous pathway and the uniform pathway is shown. We see that the peak dose to the RMEI (associate with $^{237}$Np in both cases) is reduced from $2.57 \times 10^{-5}$ Sv/yr in the single region model to $5.46 \times 10^{-7}$ Sv/yr in the three region model. Again, this is likely stemming from the slow flow region in the first segment of the heterogeneous pathway, coupled with relatively retardation of $^{237}$Np with the alluvium. The peaks associated with $^{99}$Tc and $^{129}$I are similarly reduced.
Figure 6.4 Annual dose to the RMEI from $^{237}$Np, $^{129}$I, and $^{99}$Tc in the pessimistic environmental case from flow along a heterogeneous path using Analytic Solution.

Figure 6.5 Effects of the graphite waste lifetime on the annual dose to the RMEI from flow along a heterogeneous path using the Analytic Solution.
6.3 Transport of an Arbitrary Length Decay Chain through Heterogeneous Geological Media (TTBX)

Motivated by the results in the preceding section, we develop a model for the aqueous transport of radionuclides through heterogeneous geologic media for a decay chain of arbitrary length. The admission of an arbitrary length decay chain to the model will allow for the quantification of important decay daughters such as \(^{227}\)Ac, and will allow for a greater amount of flexibility in the range of inventories considered. As this is viewed as an extension of the TTB model, this model is labeled as TTBX (for TTB-extended). Unfortunately, we have not been able to attain an exact solution for the concentration of radionuclides in this case. Instead, we will proceed by presenting the Laplace transformed analytical solution. These results are then inverted numerically \[9\] [45] [46] (see Appendix II).

6.3.1 Theoretical Development

The governing equations for the aqueous transport of an arbitrary length decay chain through heterogeneous geological media are as follows (with \(\lambda_0 = 0\)):

\[
\begin{align*}
R_p \frac{n}{n} \frac{\partial C_p}{\partial t} + v_p \frac{n}{n} \frac{\partial C_p}{\partial x} - \frac{n}{n} \frac{D_p \partial P_p}{b_p \partial w_p} &= \lambda_{n-1} R \frac{n}{n-1} C_p - \lambda_n R_p C_p,
\end{align*}
\]

\[
x_0 = 0, \quad x_{p-1} \geq x \geq x_p, \quad t > 0,
\]

(6.12a)
\[ \frac{\partial P_p}{\partial t} - \frac{D_p}{w_p} \frac{\partial^2 P_p}{\partial w_p^2} = \lambda_{n-1} \alpha_p P_p - \lambda_n \alpha_p P_p \]

subject to the boundary conditions:

\[ C_p(x,0) = 0, \quad x_0 = 0, \quad x_{p-1} \geq x \geq x_p \] (6.14)

\[ P_p(w_p, x, 0) = 0, \quad w_p > 0, x_0 = 0, \quad x_{p-1} \geq x \geq x_p \] (6.15)

\[ P_p(0, x, t) = C_p(x, t), \quad t > 0, \quad x_{p-1} \geq x \geq x_p \] (6.16)

\[ \lim_{w \to \infty} \frac{\partial P_p}{\partial w_p} \bigg|_{w_p = w} = 0 \]

\[ w_p > 0, t > 0, x > 0 \] (6.17)

\[ \frac{C_1(0,t)}{C_p(x_{p-1},t)} = \frac{F_n}{v_1 \phi_1 A_1} \] (6.18)

\[ v_{p-1} \Phi_{p-1} A_p C_{p-1}(x_{p-1}, t) = v_p \Phi_p A_p C_p(x_{p-1}, t) \] (6.19)

where \(C_p\) is the concentration of the \(n\)th member of the decay chain in the \(p\)th transport segment and \(F_n\) is the source term for the \(n\)th radionuclide at the transport pathway genesis. Variables with one subscript are independent of the transport segment number or the position in the decay chain (as in \(\lambda_n\) and \(v_p\), respectively).

The Laplace transformed governing equations are given as:

(for fracture flow)

\[ \frac{R_p}{n} (s + \lambda_n) \tilde{C}_p + v_p \frac{\partial \tilde{C}_p}{\partial x} = \frac{D_p}{\tilde{w}_p} \frac{\partial \tilde{P}_p}{\partial \tilde{w}_p} \bigg|_{\tilde{w}_p = 0} = \lambda_{n-1} \frac{R_p}{n-1} \tilde{C}_p \quad \tilde{C}_p^{\prime} \] (6.20a)
(for porous flow)

\[ R_p \left( s + \lambda_n \right) \bar{C}_p + n \frac{\partial \bar{C}_p}{\partial x} = \lambda_{n-1} R_p \bar{C}_{p-1}, \]

\[ x_0 = 0, \ x_{p-1} \geq x \geq x_p, \quad (6.20b) \]

subject to the boundary conditions:

\[ \bar{P}_p(0, x, s) = \bar{C}_p(x, s), \ x_0 = 0, \ x_{p-1} \geq x \geq x_p, \quad (6.22) \]

\[ \lim_{w \to \infty} \frac{\partial \bar{P}_p}{\partial w_p} \bigg|_{w_p = \infty} = 0, \ w_p > 0, x > 0, \quad (6.23) \]

\[ \bar{C}_1(0, s) = \frac{\bar{F}_n}{v_1 \phi_1 A_1}, \quad (6.24) \]

\[ v_{p-1} \phi_{p-1} A_{p-1} \bar{C}_{p-1}(x_{p-1}, s) = v_p \phi_p A_p \bar{C}_p(x_p, s), \quad (6.25) \]

Here \( \bar{C}_p(x, s) \) is the Laplace-transformed concentration of the \( n \)th nuclide in the \( p \)th transport segment and \( s \) is our Laplace transform variable. The recursive solution for the Laplace-transformed concentration along the transport pathway is given as follows (see Appendix I):

\[ \bar{C}_p = \sum_{m=1}^{n} u_{p} a_{p} \exp\left(-g_p \left( x - x_{p-1} \right)\right), \]

\[ x_{p-1} > x > x_p, \quad (6.26) \]

(see fracture flow)

\[ g_p = \frac{1}{v_p} \left( R_p \left( s + \lambda_n \right) - \frac{D_p \theta_p}{b_p} \right), \quad (6.27a) \]

(for porous flow)

\[ g_p = \frac{1}{v_p} \left( R_p \left( s + \lambda_m \right) \right), \quad (6.27b) \]
\[ \theta_p = \sqrt{\frac{(s + \lambda_m)\alpha_p}{D_p m}} \]  
\hspace{10cm} (6.28)

\[ \bar{P}_p = \sum_{m=1}^{n} Y \frac{\bar{C}_p}{n} \]  
\hspace{10cm} (6.26)

\[ Y_{p mn} = \left( \prod_{k=m}^{n-1} \frac{\alpha_p \lambda_k}{D_p m} \right) \sum_{k=m}^{n} \frac{Y_{p kk}}{\prod_{l=m, l \neq k}^{n} \left( \theta_p - \theta_{p l} \right)} \]  
\hspace{10cm} (for fracture flow)

\[ Y_{p} = \exp(-\theta_p w_p) \]  
\hspace{10cm} (6.29a)

\[ v_p \left( \frac{g_p - g_m}{m} \right) u_p = R_p \lambda_{n-1} u_p \sum_{q=m}^{n-1} B_p u_p \]  
\hspace{10cm} (for porous flow)

\[ u_{nn} = 1 \]  
\hspace{10cm} (6.30)

\[ B_{p qn} = -\frac{D_p}{b_p} \left( \prod_{l=q}^{n-1} \frac{\alpha_p \lambda_l}{D_p m} \right) \sum_{l=q}^{n} \frac{\theta_p}{\prod_{j=q, j \neq l}^{n} \left( \theta_{p j} - \theta_p^2 \right)} \]  
\hspace{10cm} (for fracture flow)

\[ \alpha_p = \sum_{i=1}^{m} \nu_{p im} S_{p i} \]  
\hspace{10cm} (6.32)

\[ \nu_{p im} = -\sum_{j=l}^{m-1} u_{p jm} \nu_{ip} \]  
\hspace{10cm} (6.33a)
\[ v_p = 1 \quad (6.34) \]

\[ S_p = \frac{v_{p-1} \phi_{p-1} A_{p-1}}{v_p \phi_p A_p} \bar{C}_{p-1}(x_{p-1}, s) \quad (6.35) \]

\[ S_1 = \frac{F_i}{v_1 \phi_1 A_1} \quad (6.35) \]

### 6.3.2 Input Parameters

In addition to the information presented in Table 5.4, Table 5.5, Table 5.6, and Table 6.2, Table 6.3 provides the remaining information necessary to quantify the annual dose to the RMEI using the multi-region transport model.

**Table 6.3 Retardation Coefficient for Transport through Alluvial Medium.**

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>In the Alluvium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nominal</td>
</tr>
<tr>
<td>Americium</td>
<td>4.79E+04</td>
</tr>
<tr>
<td>Plutonium</td>
<td>8.71E+02</td>
</tr>
<tr>
<td>Uranium</td>
<td>4.10E+01</td>
</tr>
<tr>
<td>Neptunium</td>
<td>5.63E+01</td>
</tr>
<tr>
<td>Thorium</td>
<td>4.79E+04</td>
</tr>
<tr>
<td>Protactinium</td>
<td>4.79E+04</td>
</tr>
<tr>
<td>Radium</td>
<td>4.79E+03</td>
</tr>
<tr>
<td>Technetium</td>
<td>1.00E+00</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.00E+00</td>
</tr>
<tr>
<td>Strontium</td>
<td>1.83E+03</td>
</tr>
<tr>
<td>Selenium</td>
<td>1.23E+02</td>
</tr>
<tr>
<td>Tin</td>
<td>4.35E+05</td>
</tr>
<tr>
<td>Iodine</td>
<td>1.00E+00</td>
</tr>
<tr>
<td>Cesium</td>
<td>6.34E+03</td>
</tr>
</tbody>
</table>

### 6.3.3 Numerical Results

Figure 6.7 shows the results of radionuclide transport calculations with TTBX in the nominal environmental scenario; fast and slow graphite oxidation is considered along with both compact only and whole element disposal conditions. The results, as expected, closely mirror those found in the previous section using equation (6.9). The peak in this case (Figure 6.7) is observed to be slightly less than that observed in Figure 6.3. This can be attributed to the presence of the diffusion barrier in the case presently studied. We see that the total annual dose to the RMEI is dominated completely by \(^{129}\)I in this time frame.
Not shown is a secondary peak in the period greater than $10^8$ years. This peak occurs just after $10^9$ years and is slightly greater than $10^{10}$ Sv/yr. This peak is not shown because of the extremely long time at which it occurs. We see the comparison across both disposal conditions (whole element and compact only) and both graphite oxidation regimes (fast and slow). Here again we see the familiar dependence of annual dose to the RMEI to the lifetime of the graphite waste form; this dependence is nearly linear (although slightly less). From these figures we can see (as noted in section 6.2.5) that the assumption of fracture flow for the entire 18km pathway from the unsaturated zone interface to the observation point for exposure to the RMEI, was well justified as a conservative assumption. In comparison with Figure 5.6, we can see that overall the use of three regions to model the transport of radionuclides has resulted in about an order of magnitude reduction in the peak annual dose calculated to be received by the RMEI in the nominal environmental case.

Figure 6.7 Annual dose to the RMEI from $^{129}$I in the nominal environmental case from flow along a heterogeneous pathway using the TTBX.

Figure 6.8 shows the results of radionuclide transport through a heterogeneous pathway in the pessimistic environmental case under the compact only disposal condition in the fast graphite oxidation regime (worst case scenario). We see in using the multi-region transport model that the same nuclides that were the main contributors to the overall dose in the single-region transport model (Chapter 5) are also responsible for the majority of annual dose received by the RMEI in this case as well. However, the maximum annual dose received by the RMEI is observed to be more than two orders of
magnitude lower when calculated using TTBX assuming the three transport segments discussed above. This difference can be attributed to the initial slow flow region in the first 5km segment in the multi-region pathway, coupled with relatively strong sorption of two main contributors $^{237}$Np, and $^{235}$U. Although $^{235}$U is not directly seen as a main contributor to the overall dose, its decay daughter $^{227}$Ac (which is in secular equilibrium with $^{235}$U because of the difference in the half-lives) is a main contributor in the longer time periods.

Figure 6.9 shows a comparison of disposal conditions and graphite oxidation regimes in the pessimistic environmental case. Here, we can see the similar dependence of annual dose received by the RMEI on the lifetime of the spent fuel form. The total dose takes on a stepped appearance with three individual plateaus (or peaks). Each of the three successive peaks is attributed to the nuclides $^{99}$Tc, $^{237}$Np, and $^{227}$Ac, respectively. Again, it is clear to see that the assumption of fracture flow for the entire 18km path which was implemented in Chapter 5 was well justified as a conservative simplifying assumption.
6.4 Summary

We have seen in this chapter that the dose to the RMEI is observed to be substantially smaller if we consider transport along a heterogeneous pathway relative to a uniform pathway. This highlights the sensitivity of the system to changes in the hydrogeological parameters associated with radionuclide transport models and the need for models sufficiently generic to accommodate these heterogeneities. With the use of such a model, we have seen that the assumptions made in Chapter 5, particularly the assumption that the radionuclide transport path be along a uniform fracture 18km long, was indeed conservative, because properties of the entire 18-km region were set with the fast-flow region. It appears that doses to the RMEI will be substantially reduced if we consider flow along this heterogeneous pathway.

In our initial numerical illustrations, we only considered a single member decay chain and it is possible that in some cases decay daughters may contribute substantially enough to invalidate the conservatism of the uniform fracture assumption. With this as our motivation we have presented the Laplace transformed analytical solution to the transport of an arbitrary length decay chain through heterogeneous geological media. This solution was numerically inverted to determine the concentration of radionuclides along our heterogeneous transport pathway. The results of this analysis show, much like the results obtained with the analytical solution, that annual dose calculated to be received by the RMEI from the disposal of DBSF in the YMR will be overestimated by
approximately two orders of magnitude in the pessimistic environmental case and by approximately one order of magnitude in the nominal environmental case. These results are important from a performance assessment point of view. Although the DBSF was seen to comply with regulations in all of the cases studied in Chapter 5 using TTB, we were not certain about effects of transport through the heterogeneous pathway. In these cases using our extended model TTBX, we found that transport along a heterogeneous path reduces the overall dose to the RMEI. Additionally, this more detailed analysis maintains significant conservatism while adding fidelity and flexibility to the transport model. The fact that the dose is seen to be substantially lower should serve to build confidence in the performance of the DBSF under the conditions studied for disposal in YMR.
Chapter 7 Conclusions

7.1 Summary of Results and Conclusions

This study represents the first systematic and deterministic evaluation of the performance of DBSF in a geological repository. A study of DBMHR fuel cycles has been made and a comprehensive model for the release and transport of radionuclides from TRISO fuel particles and DBSF in a geological repository environment has been developed. This includes a novel model for the transport of an arbitrary length decay chain through an arbitrary combination of fractured and porous transport segments. The models developed for this study were designed to be generic and will allow for a comparison across a wide range of repository environments. Calculations of the far-field transport of radionuclides released from DBSF have been made in order to evaluate the exposure of the target population and establish compliance of the fuel form with regulatory standards.

Based on the analysis of the DBHMR fuel cycle options, we conclude that the DBMHR fuel cycle is an effective way to extract extra energy from the CSNF while simultaneously reducing the radiotoxicity burden that the subsequent spent fuel will pose. Further, the $^{239}$Pu inventory is substantially reduced, thus illustrating the efficacy of the DBMHR fuel cycle as a means to mitigate the proliferation of weapons grade material.

We have observed that extreme robustness of graphite material has the potential to serve as a highly durable waste matrix for the disposal of HLW. With the assumed high durability of graphite, in all of the cases studied, all radionuclides are released congruently with graphite corrosion. This congruency results in nearly linear dependency of the annual dose to RMEI on the graphite lifetime. Congruency also implies that radionuclide concentrations in groundwater are smaller than their solubility limits, resulting in low annual dose to RMEI. Furthermore, this congruency eliminates the uncertainty associated with the solubilities of the radionuclides (a physical parameter which was demonstrated to have a high degree of uncertainty associated with it). Eliminating this uncertainty greatly enhances and simplifies the performance assessment of DBSF in a geological repository. All of this highlights the possibility and advantage of the use of graphite as a waste matrix for the disposal of HLW.

The existing computer code, TTB, has been utilized to perform a deterministic bounding analysis has to assess the annual dose to the RMEI from the disposal of DBSF in the YMR. An analytical solution for the transport of a single nuclide through an arbitrary combination of fractured and porous transport segments was developed. Based on those results, TTB was extended to also include an arbitrary combination of fractured and porous transport segments, and the computer code TTBX was developed. The results of the present deterministic performance assessment show compliance with the regulatory limit for the annual dose to the RMEI, with orders of magnitude margins, despite numerous conservative assumptions in all of the cases studied. We have seen that the annual dose received by the RMEI from the transport of radionuclides released from the DBSF is observed to be substantially smaller if we consider transport along a heterogeneous pathway. This more detailed analysis maintains significant conservatism while adding fidelity and flexibility to the transport model. The fact that the dose is seen to be substantially lower should serve to build confidence in the performance of the DBSF in the YMR and further highlight the utility of graphite to serve as a waste matrix for the disposal of HLW.
7.2 The Benefits of the DBMHR Fuel Cycle

Throughout this study we have seen the many benefits of utilizing the DBMHR fuel cycle as part of a broader scheme to recycle CSNF. We see a reduction in the radiotoxicity of the DBSF relative to the CSNF. Additionally we see that we can achieve 7.7% additional electricity and a 16.6% reduction in the use of raw fuel materials by recycling CSNF in a once through DBMHR fuel cycle. Beyond the motivation to more efficiently utilize our raw fuel materials there remains a monetary incentive and a more detailed study of the economics of the DBMHR fuel cycle is warranted. Additionally, beyond the scope of this study, DBMHR’s have been proposed, and have shown promise, as a method of reducing stockpiles of Pu from the recycling of CSNF [1] [2] [3]. The high burnup of a DBMHR (up to 60% FIMA) makes DBMHR’s uniquely suited to utilize Pu stockpiles for energy production while simultaneously reducing proliferation risks. Furthermore, it should be mentioned that, given an operational lifetime of thirty years, approximately thirty DBMHR reactors would be needed transmute the 630MT of TRU’s from the recycling of the entire inventory of CSNF which was destined for the YMR.

In the wake of the Fukushima Daiichi nuclear disaster of March 11, 2011, a heightened importance must be placed on reactor safety especially in emergency and disaster situations. DBMHR technology, including the TRISO fuel particles, has so far demonstrated extreme resilience to testing under accident scenarios and appears to be moving towards a reactor which may be passively safe (e.g. a reactor which could utilize convective and radiative cooling in the event of a station blackout and a LOCA accident). The development of passively safe reactors should among the highest priorities of the nuclear reactor community and DBMHR’s appear as an attractive option which should be further developed and explored.

Added to these benefits is the fact that DBSF is composed primarily of graphite which contains the HLW. Graphite as a material is nearly chemically inert [47] as is evidenced by the presence of natural graphite ores in the earth’s crust [48]. This low chemical reactivity with both water and air greatly improves the performance of graphite as a waste form relative to other waste forms currently being considered, such as UO$_2$ or borosilicate glass. Because of its promise as an ultra-durable waste form graphite should be pursued most vigorously as an option for the disposal of HLW in general. The combination of the transmutation of TRU’s into shorter-lived fission products coupled with the extreme lifetime of the graphite waste form is a unique feature of the DBMHR fuel cycle and make this reactor system and fuel cycle highly attractive from a repository standpoint.

7.3 Recommendations for Further Study

The experiments that provided the dissolution rates for graphite that were used in the present study, were not carried out on post-irradiated graphite. In order to provide an accurate estimate of the release rates of radionuclides from DBSF and their subsequent transfer to the biosphere, it is important that experiments be carried out to verify the dissolution rates that have previously been reported, or (if the material properties with respect to leaching behavior are different for post-irradiated graphite) to provide accurate estimates of corrosion behavior. Along with the hydrogeological parameters the lifetime of the graphite waste matrix was seen to have a strong influence on the annual dose received by the RMEI. If systematic studies can demonstrate the robustness of graphite
across a wide range of geochemical environments, especially those which are anticipated to be encountered in geological repositories for HLW, then graphite should be considered as a highly attractive option for the sequestration of radionuclides in a geological repository.

The present study represents a deterministic bounding analysis. The use of the TTBX model has demonstrated the utility in adding fidelity to the present model while maintaining conservatism. A number of areas could be developed to add further fidelity to the model and build confidence in repository performance. A possible area of study is the addition of longitudinal dispersion to the current TTBX model. In any case, it must be noted that many of the parameters used in the transport models are associated with aleatory and epistemic uncertainties. In order to make a more effective assessment of the potential health risk to the public from the disposal of DBSF in the YMR, we must make a probabilistic sampling of the parameter space. Additionally, alternate pathways for exposure must be investigated in order to conclusively determine compliance with regulatory standards.
References


[31] M. Fratoni and E. Greenspan, "Determination of the equilibrium composition of


Appendix I. Verification of Solutions to Heterogeneous Transport Equations

AI.1 Transport of a Single Member Decay Chain through Heterogeneous Geological Media

Following Section 6.3 we have for the Laplace transformed concentration of our nuclide in the pth transport segment:

\[
\tilde{C}_p = S_p \exp(-g_p(x - x_{p-1}))
\]
\[
x_{p-1} > x > x_p
\]

We have dropped the subscripts related to the nuclide number, for convenience and because there is only one member in this decay chain. Recall the following,

(for fracture flow)

\[
g_p = \frac{1}{v_p} \left( R_p (s + \lambda) - \frac{D_p \theta_p}{b_p} \right)
\]

(AI.2a)

(for porous flow)

\[
g_p = \frac{1}{v_p} (R_p (s + \lambda))
\]

(AI.2b)

\[
\theta_p = \sqrt{(s + \lambda)\alpha_p / D_p}
\]

(AI.3)

\[
S_p = \frac{v_{p-1} \phi_{p-1} A_{p-1}}{v_p \phi_p A_p}\tilde{C}_{p-1}(x_{p-1}, s)
\]

(AI.4)

\[
S_1 = \frac{\hat{F}}{v_1 \phi_1 A_1}.
\]

(AI.5)

Beginning with the concentration of the single nuclide in the first fracture, we may write,

\[
\tilde{C}_1(x, s) = \frac{\hat{F}}{v_1 \phi_1 A_1} e^{-g_1 x}
\]

(AI.6)

Rearranging, we have

\[
\tilde{C}_1(x, s) = \frac{\hat{F}}{v_1 \phi_1 A_1} \exp(-Q_1(x) \lambda) \exp(-Q_1(x) s) \exp(-E_1(x) \sqrt{s + \lambda})
\]

(AI.7)
Where
\[ Q_1(x) = \frac{R_1x}{v_1} \quad \text{and} \quad E_1(x) = \frac{\sqrt{D_1\alpha_1}}{b_1v_1}x \]  

(AI.8)

Letting
\[ U = L(u) = \exp(-E_1\sqrt{s} + \lambda) \]  
\[ \hat{f} = L(f) \]  
\[ \Phi(s) = L(u * f) = UF \]  

(AI.9) (AI.10) (AI.11)

Here \( L \) represents the Laplace transform operator, and \( L(u * f) \) is the Laplace transform of the convolution of \( u \) and \( f \). Using these definitions we can rewrite our Laplace transformed concentration as,
\[ \widehat{C}_1 = \frac{\exp(-Q_1\lambda)}{v_1\phi_1A_1} \Phi(s)\exp(-Q_1s) \]  

(AI.12)

Recall that
\[ L^{-1}(\Phi(s)\exp(-Q_1s)) = \Phi(t - Q_1)h(t - Q_1) \]  

(AI.13)

Where
\[ \Phi(t) = L^{-1}(\Phi(s)) \]  

(AI.14)

Using relation (3.472 #5 from [49]) we obtain
\[ u = L^{-1}(U) = \begin{cases} 
\frac{E_1}{2\sqrt{\pi}t^2} \exp \left(-\frac{(E_1/2)^2}{t} - \lambda t \right) & \text{if} \quad E_1 > 0 \\
\delta(t) & \text{if} \quad E_1 = 0
\end{cases} \]  

(AI.15)

Here we note that \( E_1 = 0 \) in the case of flow through a porous transport segment. (AI.15) together with
\[ L^{-1}(UF) = u * f = \int_0^t u(\tau)f(t - \tau)d\tau \]  

(AI.16)

yields for our concentration in the first transport segment,
\[ C_1(x, t) = \frac{N_0\exp(-Q_1\lambda)}{v_1\phi_1A_1} h(t - Q_1) \int_0^{t-Q_1} f(t - Q_1 - \tau)u(\tau)d\tau \]  

(AI.17)
For our source term $f(t)$ we consider a band release solution by the following:

$$\dot{M} = \frac{M_0}{T}$$  \hspace{1cm} (AI.18)

$$f = \dot{M} n(t) \{h(t) - h(t - T)\}$$  \hspace{1cm} (AI.19)

$$= N_o \exp(-\lambda t) \{h(t) - h(t - T)\}$$  \hspace{1cm} (AI.20)

$$n(t) = n_0 \exp(-\lambda t)$$  \hspace{1cm} (AI.21)

$$N_0 = \frac{M_0 n_0}{T}$$  \hspace{1cm} (AI.22)

Where

$M_o$ = initial mass of the waste matrix  
$T$ = total time for matrix to degrade  
$\dot{M}$ = mass release rate of the waste matrix  
n(t) = the fractional amount of nuclide in the waste matrix  
n_o = initial radionuclide inventory  
$N_o$ = initial mass release rate of radionuclide

We can then write our concentration in the 1st transport segment as,

$$C_1(x, t) = \frac{N_0 \exp(-\lambda t)}{v_1 \phi_1 A_1} E_1 I_1$$  \hspace{1cm} (AI.23)

Where

$$I_1 = \frac{1}{2\sqrt{\pi}} \int_0^{t-Q_1} \tau^{-\frac{3}{2}} \exp \left( -\frac{(E_1)^2}{2} \frac{1}{\tau} \right) \{h(t - Q_1 - \tau) - h(t - Q_1 - \tau - T)\} d\tau$$  \hspace{1cm} (AI.24)

We make the following change of variables, and recall the definition of the complimentary error function (EFRC),

$$z = \frac{E_1}{2\sqrt{\tau}} \text{ and } \tau = \left(\frac{E_1}{2}\right)^2 \frac{1}{u^2}$$  \hspace{1cm} (AI.25)
\[ dz = -\frac{E_1}{2\sqrt{\pi}} \]

\[ I_1 = \frac{1}{2\sqrt{\pi}} \int_{E_1}^{\infty} \exp(-z^2) \left\{ h\left(t - Q_1 - \left(\frac{E_1}{2z}\right)^2\right) - h(t - Q_1 - \left(\frac{E_1}{2z}\right)^2 - T) \right\} dz \]

\[ \text{(AI.27)} \]

We may now write the concentration of the radionuclide in the first fracture as,

\[ C_1(x, t) = \frac{N_0 \exp(-\lambda t)}{v_1 \phi_1 A_1} B_1(x, t), \; t > 0, 0 > x \geq x_1 \]

\[ \text{(AI.28)} \]

Where,

\[ B_1(x, t) = h \left(t - \frac{R_1}{v_1} x\right) \text{ERFC} \left(\frac{\sqrt{D_1 \sigma_1}}{b_1 v_1} x\right) - \frac{\sqrt{D_1 \sigma_1}}{b_1 v_1} x \]

\[ \text{(AI.29)} \]

Notice here that the complimentary error functions govern the diffusion of the radionuclide into the host rock in the case of fracture flow. Additionally, we see that the step functions govern the retarded advection of the radionuclide subject to the release conditions from the source. Finally, we notice that if we set the diffusion coefficient to zero that we recover the solution for the concentration of the radionuclide if we consider flow through a porous transport segment.

Continuing, we write the Laplace transformed concentration of our radionuclide in the second transport segment as,

\[ \hat{C}_2 = S_2 \exp(-g_2(x - x_1)) \]

\[ x_1 \geq x \geq x_2 \]

\[ \text{(AI.30)} \]

Where

\[ S_2 = \frac{v_1 \phi_1 A_1}{v_2 \phi_2 A_2} \hat{C}_1(x_1, s) \]

\[ \text{(AI.31)} \]

Substituting appropriately and rearranging, we may write our Laplace transformed concentration as,
\[
\overline{c}_2(x, s) = \frac{\hat{p}}{v_2 \phi_2 A_2} \exp(-Q_2(x)\lambda) \exp(-Q_2(x)s) \exp(-E_2(x)\sqrt{s} + \lambda)
\]

Where

\[
Q_2(x) = \frac{R_1}{v_1} L_1 + \frac{R_2}{v_2} (x - x_1) \quad \text{and} \quad E_2(x) = \frac{\sqrt{D_1 \alpha_1}}{b_1 v_1} L_1 + \frac{\sqrt{D_2 \alpha_2}}{b_2 v_2} (x - x_1)
\]

This is now in the same form as (AI.7) and we can write the concentration of the radionuclide in the second transport segment as,

\[
\overline{c}_2(x, t) = \frac{N_0 \exp(-\lambda t)}{v_2 \phi_2 A_2} B_2(x, t), \quad t > 0, x_1 \leq x \leq x_2
\]

Where,

\[
B_2(x, t) = \left( t - \left[ \frac{R_1}{v_1} L_1 + \frac{R_2}{v_2} (x - x_1) \right] \right) \text{ERFC} \left( \frac{\sqrt{D_1 \alpha_1} L_1 + \sqrt{D_2 \alpha_2} \sqrt{2}(x-x_1)}{2 \left\{ \frac{R_1}{v_1} L_1 + \frac{R_2}{v_2} (x-x_1) \right\} \overline{a}^2} \right)
\]

\[
- \left( t - \left[ \frac{R_1}{v_1} L_1 + \frac{R_2}{v_2} (x - x_1) \right] - T \right) \text{ERFC} \left( \frac{\sqrt{D_1 \alpha_1} L_1 + \sqrt{D_2 \alpha_2} \sqrt{2}(x-x_1)}{2 \left\{ \frac{R_1}{v_1} L_1 + \frac{R_2}{v_2} (x-x_1) \right\} \overline{a}^2} \right)
\]

Here we make similar observations as above. We note the role of the Heaviside functions in representing the retarded advection and the complimentary error functions in representing the matrix diffusion. Additionally, we mention that any combination of fracture or porous transport segments is represented by appropriately setting the matrix diffusion coefficient to zero in the porous transport segment.

Finally, using the same procedure as above we write the solution for the concentration of the radionuclide in the third transport segment as,

\[
\overline{c}_3(x, t) = \frac{N_0 \exp(-\lambda t)}{v_3 \phi_3 A_3} B_3(x, t), \quad t > 0, x_2 \leq x \leq x_3
\]

Where,

\[
B_3(x, t) = \left( t - \left[ \frac{R_1}{v_1} L_1 + \frac{R_2}{v_2} L_2 + \frac{R_3}{v_3} (x - x_2) \right] \right) \text{ERFC} \left( \frac{\sqrt{D_1 \alpha_1} L_1 + \sqrt{D_2 \alpha_2} L_2 + \sqrt{D_3 \alpha_3} \sqrt{2}(x-x_2)}{2 \left\{ \frac{R_1}{v_1} L_1 + \frac{R_2}{v_2} L_2 + \frac{R_3}{v_3} (x-x_2) \right\} \overline{a}^2} \right)
\]

\[
- \left( t - \left[ \frac{R_1}{v_1} L_1 + \frac{R_2}{v_2} L_2 + \frac{R_3}{v_3} (x - x_2) \right] - T \right) \text{ERFC} \left( \frac{\sqrt{D_1 \alpha_1} L_1 + \sqrt{D_2 \alpha_2} L_2 + \sqrt{D_3 \alpha_3} \sqrt{2}(x-x_2)}{2 \left\{ \frac{R_1}{v_1} L_1 + \frac{R_2}{v_2} L_2 + \frac{R_3}{v_3} (x-x_2) \right\} \overline{a}^2} \right)
\]
The pattern is now clearly evident, and we may generalize the solution as was found in Chapter 6 given by equations (6.8) and (6.9).

\[ C_p(x, t) = \frac{N_0 \exp(-\lambda t)}{v_p \Phi_p A_p} B_p(x, t), \quad t > 0, \ x_{p-1} \geq x \geq x_p \]  

(AI.38)

Where,

\[ B_p(x, t) = h \left( t - \left[ \left( \sum_{j=1}^{p-1} \frac{R_j}{v_j} L_j \right) + \frac{R_p}{v_p} (x - x_{p-1}) \right] \right) \text{ERFC} \frac{\left( \sum_{j=1}^{p-1} \frac{D_j}{b_j v_j} \right) + \frac{\sqrt{D_p a_p}}{b_p v_p} (x - x_{p-1})}{2 \left( t - \left[ \left( \sum_{j=1}^{p-1} \frac{R_j}{v_j} L_j \right) + \frac{R_p}{v_p} (x - x_{p-1}) \right] \right)^{1/2}} \]

(AI.39)

Again, we note that any combination of fracture and porous transport segments may be represented using this formulation given the convention that the matrix diffusion coefficient is zero in porous transport segments.

### AI.2 Transport of an Arbitrary Length Decay Chain through Heterogeneous Geological Media

Here we will verify the solution for transport of an arbitrary length decay chain through heterogeneous geological media. The Laplace transformed governing equations are given as,

(fracture flow)

\[ R_p \left( s + \lambda_n \right) \bar{C}_p + v_p \frac{\partial \bar{C}_p}{\partial x} - \frac{D_p \partial \bar{P}_p}{b_p \partial \bar{w}_p} \bigg|_{\bar{w}_p=0} = \lambda_{n-1} R_p \bar{C}_n \]

(AI.40)

(porous flow)

\[ R_p \left( s + \lambda_n \right) \bar{C}_p + v_p \frac{\partial \bar{C}_p}{\partial x} = \lambda_{n-1} R_p \bar{C}_n \]

\[ x_0 = 0, \ x_{p-1} \geq x \geq x_p \]

(AI.41)

\[ \alpha_p \left( s + \lambda_n \right) \bar{P}_p - D_p \frac{\partial^2 \bar{P}_p}{\partial \bar{w}_p^2} = \lambda_{n-1} \alpha_p \bar{P}_n \]

\[ w_p > 0, x_0 = 0, \ x_{p-1} \geq x \geq x_p \]

(AI.42)
Subject to the boundary conditions:

\[
\tilde{P}_p(n, x, s) = \tilde{C}_p(n, x, s), \quad x_0 = 0, \quad x_{p-1} \geq x \geq x_p \quad \text{(AI.43)}
\]

\[
\lim_{w \to 0} \left. \frac{\partial \tilde{P}_p(n, x, s)}{\partial w_p} \right|_{w_p = w} = 0, \quad w_p > 0, x > 0 \quad \text{(AI.44)}
\]

\[
\tilde{C}_1(0, s) = \frac{\tilde{f}_n}{v_1 \phi_1 A_1} \quad \text{(AI.45)}
\]

\[
v_{p-1} \Phi_{p-1} A_{p-1} \tilde{C}_{p-1}(x_{p-1}, s) = v_p \Phi_p A_p \tilde{C}_p(x_p, s) \quad \text{(AI.46)}
\]

The recursive solution for the Laplace transformed concentration along the transport pathway is given as follows,

\[
\tilde{C}_p(n, x, s) = \sum_{m=1}^n u_{mn} \alpha_p \exp \left( -g_p \left( \frac{x - x_{p-1}}{b_p} \right) \right) \quad x_{p-1} > x > x_p \quad \text{(AI.47)}
\]

(for fracture flow)

\[
g_p = \frac{1}{v_p} \left( R_p \left( s + \lambda_m \right) - \frac{D_p \theta_p}{b_p} \right) \quad \text{(AI.48)}
\]

(for porous flow)

\[
g_p = \frac{1}{v_p} \left( R_p \left( s + \lambda_m \right) \right) \quad \text{(AI.49)}
\]

\[
\theta_p = \sqrt{ \frac{(s + \lambda_m) \alpha_p}{D_p m} } \quad \text{(AI.50)}
\]

\[
P_p(n, x, s) = \sum_{m=1}^n Y_p \tilde{C}_p(n, x, s) \quad x_{p-1} > x > x_p \quad \text{(AI.51)}
\]

\[
Y_p = \left( \prod_{k=m}^{n-1} \frac{\alpha_p \lambda_k}{D_p} \right) \sum_{k=m}^n \frac{Y_p}{k_k} \prod_{l=m, l \neq k}^n \left[ \theta_{\frac{L}{k}} - \theta_{\frac{L}{k}} \right] \quad \text{(AI.52)}
\]
\[ Y_p = \exp(-\theta_p w_p) \]  

(for fracture flow)

\[ v_p \left( \frac{g_p - g_m}{n - m} \right) u_p = R_p \lambda_{n-1} u_p + \sum_{q=m}^{n-1} B_{pq} u_p \]  

(for porous flow)

\[ u_p v_p^{(n-m)} = \prod_{k=m}^{n-1} \frac{R_p \lambda_k}{g_p - g_m} \]  

\[ u_{nn} = 1 \]  

\[ B_{pq} = -\frac{D_p}{b_p} \left( \prod_{l=q}^{n-1} \frac{\alpha_p \lambda_l}{D_p} \right) \sum_{l=q}^{n} \frac{\theta_p}{\prod_{j=q,j \neq l}^{n} \left[ \theta_p^2 - \theta_{j,l}^2 \right]} \]  

\[ a_p = \sum_{i=1}^{m} v_p S_p \]  

(for fracture flow)

\[ v_p = -\sum_{j=i}^{m-1} u_p v_p \]  

(for porous flow)

\[ v_p v_p^{(m-i)} = \prod_{k=i}^{m-1} \frac{R_p \lambda_k}{g_p - g_m} \]  

\[ v_p v_p^{(n-m)} = 1 \]  

\[ S_p = \frac{v_{p-1} \phi_{p-1} A_{p-1}}{v_p \phi_p A_p} c_{p-1}(\chi_{p-1}, s) \]  

\[ S_1 = \frac{\tilde{F}_i}{v_1 \phi_1 A_1} \]
Here we make a similar observation as in the previous section. We recover the governing equation and solution for the concentration in a porous transport segment by setting the diffusion coefficient to zero, and using the appropriately derived recursive relations. In this manner any combination of fractured and porous transport segments can be realized. In our discussion we will continue using the equations for transport through fractured transport segments, as they are the more general of the two cases. Beginning with (AI.42) we rewrite the equation as

\[
\frac{\partial^2 \tilde{P}_p}{\partial \theta_p^2} - \frac{\partial^2 \tilde{P}_p}{\partial \theta_p^2} = -\frac{\lambda_{n-1} \alpha_p}{D_p} \tilde{P}_p
\]

(AI.64)

Substituting (AI.51-AI.53) into the left hand side of (AI.64) we obtain

\[
\sum_{m=1}^{n-1} \tilde{C}_m \left( \prod_{k=m}^{n-1} \frac{\alpha_p \lambda_k}{D_p} \right) \sum_{k=m}^{n} \frac{\theta_p^2 - \theta_p^2}{n} Y_p \left( \prod_{l=m, l \neq k}^{n} \left[ \theta_p^2 - \theta_p^2 \right] \right)
\]

\[
= \frac{\alpha_p \lambda_{n-1}}{D_p} \sum_{m=1}^{n-1} \tilde{C}_m \left( \prod_{k=m}^{n-1} \frac{\alpha_p \lambda_k}{D_p} \right) \sum_{k=m}^{n-1} \frac{Y_p}{kk} \left( \prod_{l=m, l \neq k}^{n-1} \left[ \theta_p^2 - \theta_p^2 \right] \right)
\]

\[
= -\frac{\lambda_{n-1} \alpha_p}{D_p} \tilde{P}_p
\]

(AI.65)

We can therefore say that (AI.51) satisfies (AI.42), but the boundary conditions remain to be checked. Continuing, we see that (AI.51) satisfies (AI.44) by inspection, and we are left to check the final boundary condition (AI.43). Using (AI.51-AI.53) we may write

\[
\tilde{P}_p(0, x, s) = \sum_{m=1}^{n-1} \tilde{C}_m \left( \prod_{k=m}^{n-1} \frac{\alpha_p \lambda_k}{D_p} \right) \sum_{k=m}^{n} \frac{1}{\prod_{l=m, l \neq k}^{n} \left[ \theta_p^2 - \theta_p^2 \right]}
\]

(AI.66)

To verify our boundary condition it is sufficient to show,
We continue by showing this inductively. We establish $n=2$ as our base case,

\[
\sum_{k=1}^{2} \frac{1}{\prod_{l=m,l\neq k}^{n} \left[ \frac{\theta_{p}^{2}}{l} - \frac{\theta_{p}^{2}}{k} \right]} = 0
\]

(AI.68)

Assuming our relation holds for arbitrary $n$, we check for $n+1$,

\[
\sum_{m=1}^{n+1} \sum_{k=m}^{n+1} \frac{1}{\prod_{l=m,l\neq k}^{n} \left[ \frac{\theta_{p}^{2}}{l} - \frac{\theta_{p}^{2}}{k} \right]} = \sum_{m=1}^{n+1} \sum_{k=m}^{n+1} \frac{1}{\prod_{l=m,l\neq k}^{n} \left[ \frac{\theta_{p}^{2}}{l} - \frac{\theta_{p}^{2}}{k} \right]} + \left( \frac{1}{\theta_{p}^{2} - \theta_{p}^{2}} \right)_{n+1\rightarrow n} + \left( \frac{1}{\theta_{p}^{2} - \theta_{p}^{2}} \right)_{n\rightarrow n+1} = 0
\]

(AI.69)

We see that (AI.69) is identically zero, therefore by induction, (AI.67) holds, and boundary condition (AI.43) is satisfied. Furthermore, we may conclude that (AI.51) satisfies (AI.42) and its associated boundary conditions.

Continuing, (AI.47) must satisfy the governing equation (AI.40) as well as boundary conditions (AI.45) and (AI.46). Boundary condition (AI.45) is satisfied, by inspection. Rearranging, we may rewrite the left hand side of (AI.40) as,

\[
\frac{R_{p} (s + \lambda_{n})}{n \nu_{p}} \hat{C}_{p} + \frac{\partial \hat{C}_{p}}{\partial x} - \frac{D_{p}}{n \nu_{p}} \frac{\partial \hat{P}_{p}}{\partial w_{p}} \bigg|_{w_{p}=0}
\]

(AI.70)

Substituting (AI.47) and (AI.51) into (AI.70) we obtain

\[
\sum_{m=1}^{n} \left( \frac{R_{p} (s + \lambda_{n})}{n \nu_{p}} - \frac{D_{p}}{b_{p} \nu_{p}} - \frac{g_{m}}{m} \right) u_{p} a_{p} \exp \left( -g_{m} (x - x_{p-1}) \right) - \frac{1}{\nu_{p}} \sum_{m=1}^{n-1} \hat{C}_{p} B_{p}
\]

(AI.71)

Recalling (AI.54) we may rewrite (AI.72) as,
\begin{equation}
\lambda_{n-1} R_p \frac{C_p}{p_n} - W
\end{equation}

Where

\begin{equation}
W = \frac{1}{v_p} \sum_{m=1}^{n-1} \sum_{k=n}^{n-1} B_p u_p a_p \exp \left( -\frac{g_p (x - x_{p-1})}{m} \right)
\end{equation}

\begin{equation}
- \frac{1}{v_p} \sum_{m=1}^{n-1} \sum_{k=1}^{m} B_p u_p a_p \exp \left( -\frac{g_p (x - x_{p-1})}{k} \right)
\end{equation}

Upon inspection we observe that the sums in (AI.74) are identical and \( W = 0 \). Therefore (AI.47) satisfies (AI.40). The remaining boundary condition is (AI.46). We begin with (AI.47) evaluated at \( x_{p-1} \),

\begin{equation}
\overline{C}_p(x_{p-1}, s) = \sum_{m=1}^{n} u_p a_p = a_p + \sum_{m=1}^{n-1} u_p a_p
\end{equation}

Recalling (AI.58) and (AI.59), we may write (AI.75) as,

\begin{equation}
S_p + \sum_{i=1}^{n-1} v_p S_p + \sum_{m=1}^{n-1} \sum_{i=1}^{m} u_p v_p S_p
\end{equation}

Recalling (AI.59), we may write (AI.76) as,

\begin{equation}
S_p + G
\end{equation}

Where

\begin{equation}
G = - \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} u_p v_p S_p + \sum_{m=1}^{n-1} \sum_{i=1}^{m} u_p v_p S_p
\end{equation}

Upon inspection we see that the two sums in (AI.78) are equivalent, and \( G = 0 \). We may then write,

\begin{equation}
\overline{C}_p(x_{p-1}, s) = S_p
\end{equation}

or,

\begin{equation}
\overline{C}_p(x_{p-1}, s) = \frac{v_{p-1}}{v_p} \frac{p_{p-1} A_{p-1}}{p_{p} A_p} \overline{C}_{p-1}(x_{p-1}, s)
\end{equation}
In agreement with boundary condition (AI.46). We have therefore shown that (AI.47) is a valid solution to (AI.40) with its associated boundary conditions. Furthermore, we have shown that the transport of an arbitrary length decay chain through any number and any combination of porous and fractured transport segments may be represented using the above solution.
Appendix II  The Numerical Inversion of the Laplace Transformed Solution to the Radionuclide Transport Equation using Talbot’s Method

AII.1 Talbot’s Method

The following is an overview of some of the important aspects of Talboth’s method for the numerical inversion of Laplace transforms. For a more detailed discussion of the topic the reader is referenced to [46] and [50]. The method of Talbot is based on the inversion of the Laplace transform called variously the Mellin inversion formula, the Fourier-Mellin integral, or the Bromwich integral which is given by,

$$f(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{st} \hat{f}(s) ds$$

where \( c \) is a real number such that \( c > \gamma \) guarantees that all of the singularities lie to the left of the line \( \Re s = c \). The method of Talbot deforms the traditional Bromwich contour and the line \( B: (c-i\infty, c+i\infty) \) is replaced by an equivalent contour \( B' \) which starts and ends in the left half plane with \( \Re s \rightarrow -\infty \) at each end. This replacement is allowed so long as the following two conditions are met:

i) The modified contour \( B' \) must enclose all of the singularities of the Laplace transformed function \( \hat{f}(s) \).

ii) \( |\hat{f}(s)| \rightarrow 0 \) uniformly in \( \Re s \leq \gamma \) as \( |s| \rightarrow \infty \)

Condition (ii) holds for almost any functions we are likely to encounter. Condition (i) may not be met for a given \( \hat{f}(s) \) with a particular modified contour \( B' \). However we may replace \( \hat{f}(s) \) with \( \hat{f}(\lambda s + \sigma) \) for some suitable scaling parameters such that if \( \hat{f}(s) \) has a singularity at \( s_d \) then \( \hat{f}(\lambda s + \sigma) \) has a corresponding singularity at

$$s_d^* = \frac{(s_d - \sigma_d)}{\lambda}$$

and (AII.1) may be rewritten as,

$$f(t) = \frac{\lambda e^{\sigma t}}{2\pi i} \int_{B'} e^{\lambda s t} \hat{f}(\lambda s + \sigma) ds$$

$$t > 0$$

(AII.3)

Talbot suggests a family of a family of mappings (Figure AII.1) given by:

$$B'_\nu; s = s_\nu(\theta) = \alpha + \nu i \theta, \quad -\pi < \theta < \pi$$

(AII.4)
Where

\[ \alpha = \alpha(\theta) = \theta \cot(\theta) \]  

(AII.5)

Note in Figure AII.1 that \( B' \) has \( \nu = 1 \) while \( B'_{\nu} \) has \( \nu > 1 \). Also note the use of the \( \lambda \) and \( \sigma \) scaling parameters to bring the singularity \( s_d \) within \( B'_{\nu} \).

Figure AII.1 The deformed Bromwich contour used by Talbot to invert Laplace transformed functions [50].

Using this parameterization (AII.3) may be approximated using the trapezoidal rule. We may write (AII.3) as \( \hat{f}(t) \), (the approximation to \( f(t) \) as

\[ \hat{f}(t) = \frac{\lambda e^{\sigma t}}{n} \Re \left( \sum_{k=0}^{n-1} a_k e^{ik\psi} \right) \]  

(AII.6)

Where the prime on the summation in (AII.6) indicates the \( k=0 \) term of the summation is multiplied by \( \frac{1}{2} \), and where

\[ a_k = \left[ e^{\alpha \tau} (\nu + i\beta) \hat{f}(\lambda s + \sigma) \right]_{\theta = \theta_k}, \hspace{1cm} \theta_k = \frac{k\pi}{n}, \hspace{1cm} \psi = \tau \nu \pi / n \]  

(AII.7)
The $e^{ik\psi}$ factors in (AII.6) satisfy the same recurrence relation as the Chebyshev polynomials $T_k(\cos \psi)$,

$$e^{i(k+1)\psi} + e^{i(k-1)\psi} = 2\cos \psi \cdot e^{ik\psi}$$  \hspace{1cm} (AII.8)

and (AII.7) can be evaluated by an algorithm,

$$b_n = b_{n+1} = 0$$
$$b_k = a_k + ub_{k+1} - b_{k+2}$$
$$u = 2\cos \psi, k = n - 1, ..., 1$$

We then have

$$\hat{f}(t) = \frac{\lambda e^{\sigma t}}{n} \Re \left[ \frac{1}{2} (a_0 + ub_1) - b_2 + ib_1 \sin \psi \right]$$  \hspace{1cm} (AII.10)

In order to evaluate (AII.10) we need a number of parameters some of which require detailed knowledge about the function being inverted. For instance in order to determine $\sigma$ and $\lambda$ we need to know the location of the singularities of $\hat{f}(s)$, the function being inverted. Talbot suggests a universal strategy for choosing the geometrical parameters, and for the case when the singularities of $\hat{f}(s)$ are all real Talbot suggests using

$$\lambda = \frac{\omega}{t} \quad (\tau = \omega \sim 6)$$
$$\sigma = \sigma_d$$
$$\nu = 1$$

(AII.11)

No rigorous theoretical basis is given for the choice of the parameters; however Talbot notes that “the strategy is based on an intensive study of a large number of experimental results.” In fact, although Talbot’s work was published in 1979, it has been in popular use and the issue of the choice of parameters remains a topic of current research because of the utility of Laplace transforms across a variety of disciplines. Attempts by various authors have been made to automate the process of selecting the geometrical parameters and to improve on Talbot’s choice of parameters have had limited success [51] [52] [53].

**AII.2 Numerical Inversion**

**AII.2.1 Analysis of Laplace Transformed Analytical Solution to the Radionuclide Transport Equation**

In order to implement the numerical inversion outlined above we need to have detailed knowledge about the function(s) to be inverted. In particular we need to know the location of the singularities of $\hat{C}_n$, the Laplace transformed analytical solution to the radionuclide transport equation in order to be certain they lie with the contour on integration. Previous works have implemented Talbot’s method to invert the Laplace...
transformed analytical solution to the radionuclide transport equation for a single region [9] [45]. In particular both of these studies make use of the geometrical parameters assumed above for instances in which the Laplace transformed function to be inverted has only real singularities which do not require shifting to bring them within the contour of integration. In [45] it is mentioned that the numerical accuracy of Talbot’s method for inverting the radionuclide transport equation was verified by comparison with some analytical solutions and benchmark problems. The accuracy of Talbot’s method was also checked for a number of cases for this present study using the analytical solutions to the multi-region case developed in Chapter 6 as well the analytical solution to the two member decay chain case for transport in a single medium [54]. The results generated using Talbot’s method were found to be in good agreement with the results generated using these analytical solutions lending confidence to the choice of geometrical parameters above. Nonetheless, we continue by analyzing the potential singularities of the Laplace transformed analytical solutions to the radionuclide transport equation. Note that although we are using the formulation for transport through a single region, these results will generalize to the multi-region case. Below are the portions of the solution which are most relevant to finding the singularities of the function.

\[
\hat{C}_p = \sum_{m=1}^{n} u_{mn} a_p \exp(-g_p(x - x_{p-1}))
\]  

(AII.12)

\[
v(g_n - g_m)u_{mn} = R_{n-1} \lambda_{n-1} u_{n-1} + \sum_{q=m}^{n-1} B_{qn} u_{mq}
\]  

(AII.13)

\[
B_{qn} = -\frac{D_n}{b} \left( \prod_{l=q}^{n-1} \alpha_l \lambda_l \right) \prod_{l=q}^{n} \frac{\theta_l}{\prod_{j=q, j \neq l}^{n} \left[ \theta_j^2 - \theta_l^2 \right]}
\]  

(AII.14)

\[
g_m = \frac{1}{v} \left( R_m (s + \lambda_m) - \frac{D_m \theta_m}{b} \right)
\]  

(AII.15)

\[
\theta_m = \sqrt{\frac{(s + \lambda_m) \alpha_m}{D_m}}
\]  

(AII.16)

We see from these relations that our function will likely have singularities when

\[
g_n - g_m = 0
\]  

(AII.17)
or
\[ \theta_f^2 - \theta_i^2 = 0 \]  
(AII.18)

From relation (AII.16) we can see that (AII.18) will be satisfied if,
\[
s = \frac{(\alpha_i \lambda_l - \alpha_j \lambda_j)}{\left(\frac{\alpha_i}{D_j} - \frac{\alpha_j}{D_i}\right)}
\]
(AII.19)

This singularity is real and does fall within the contour of integration for the cases considered in this study. However, it should be noted that in the case of a simplified decay chain where one isotope of an element decays to another isotope of the same element we have a singularity (which is removable in the case of a two member decay chain) which resides at either \(+\infty\) or \(-\infty\) depending on which nuclide has the longer half-life. It is unknown whether this singularity is removable for longer decay chains. However numerical result generated with simplified decay chains displaying this feature do not change when the decay chain contains more than two members suggesting that the singularity is removable. However, this remains an area where further research may be fruitful.

Examining (AII.17) we see that singularities in our function could occur when
\[
\left(\frac{R_n(s + \lambda_n)}{v} - \sqrt{\alpha_n D_n(s + \lambda_n)}\right) - \left(\frac{R_m(s + \lambda_m)}{v} - \sqrt{\alpha_m D_m(s + \lambda_m)}\right) = 0
\]
(AII.20)

This is a transcendental equation and it is not immediately clear where this function would be zero, or if \(s\) would be real in these instances (as is required by the assumptions used in implementing the geometrical parameters given by (AII.12)). However, in analogy with the analytical solution and especially referencing equation (AI.7), we might speculate that equation (AII.7) will govern the step function portion and the complimentary error function term in the analytical solution to (AI.40) (assuming the analytical solution has such a form). Given the agreement observed with analytical solutions over a number of cases and the observation of familiar behavior within the numerical results (e.g. secular equilibrium) in the absence of analytical solutions we remain cautiously optimistic that the solution to (AII.20) will yield values for \(s\) which are real valued. From an implementation point of view a roots of (AII.20) could be calculated (if they exist) to ensure they fall within the contour of integration. This also remains an area where further research could be productive. Nevertheless, we conclude based on empirical observations that Talbot’s method remains a powerful tool for the evaluation of the radionuclide transport equation over a wide range of parameter space.