RELEASE OF RADIONUCLIDES TO THE GEOSPHERE FROM A REPOSITORY FOR HIGH LEVEL WASTE—MATHEMATICAL MODEL, RESULTS

R.W. Hartley

February 1985

POLYDYNAMICS Ltd, Zürich
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Le présent rapport a été préparé sur demande de la Cédra. Les opinions et conclusions présentées sont celles des auteurs et ne correspondent pas nécessairement à celles de la Cédra.

This report was prepared as an account of work sponsored by Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.
ACKNOWLEDGEMENT

The work described in this report was carried out at the Swiss Federal Institute for Reactor Research (EIR) in Würenlingen. The author would like to thank Dr. J. Hadermann at the EIR for his guidance and Dr. R.J. Hopkirk at Polydynamics for his support.
A mathematical model is described which enables calculation of the rates of removal of nuclide ions from high level nuclear waste by groundwater flow.

The model, which is incorporated into a computer code, DREG, takes into account release of the nuclides by dissolution from their stabilising matrix, the solubility of each nuclide and where several isotopes of the same element are present, the sharing amongst them of the water's total solution capacity for that element. A running mass balance, which includes the effects of chain-decay is built into the code.

Examples are given of the use of the model in conjunction with a selection of fission products and the four actinide decay chains.
Der vorliegende Bericht beschreibt ein mathematisches Modell, das es ermöglicht, die Freisetzungsrate von Nukliden aus radioaktivem Abfall in einen Grundwasserstrom zu berechnen.

Das Modell, welches in das Computerprogramm DREG eingebaut wurde, berücksichtigt die Herauslösung der Nuklide aus der stabilisierenden Matrix, die Löslichkeit eines jeden Nuklids und, wo mehrere Isotope des gleichen Elements vorhanden sind, den Umstand, dass sich dieselben in das Lösungsvermögen des Wassers für das fragliche Element teilen. Eine fortlaufende Massenbilanz, welche auch die Auswirkungen des radioaktiven Zerfalls in Rechnung zieht, ist in den Code eingebaut.

Der Bericht enthält Beispiele, in denen das Modell auf eine Auswahl von Spaltprodukten und die vier Aktiniden-Zerfallsketten angewendet wurde.
Le présent rapport décrit un modèle mathématique qui permet de calculer les taux de relâchement des nucléides provenant des déchets radioactifs dans un courant d'eau souterrain.

Le modèle, mis en pratique dans le code d'ordinateur DREG, tient compte de la dissolution des nucléides hors de la matrice de stabilisation, de la solubilité de chaque nucléide, et, en présence de plusieurs isotopes d'un même élément du fait que la capacité de solution de l'eau pour cet élément est répartie parmi eux. Un bilan de mass continu, qui considère aussi les effets de désintégration radioactive, est intégré dans le code.

Le rapport contient des exemples, où le modèle est appliqué à une sélection de produits de fission et aux quatre chaînes de désintégration des actinides.
# LIST OF CONTENTS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
</tr>
<tr>
<td>ABSTRACT</td>
</tr>
<tr>
<td>KURZFASSUNG</td>
</tr>
<tr>
<td>RESUME</td>
</tr>
<tr>
<td>LIST OF CONTENTS</td>
</tr>
</tbody>
</table>

1. INTRODUCTION | 1 |
2. METHOD | 2 |
2.1 Matrix Dissolution Model | 2 |
2.2 Intermediate Phase Model | 5 |
2.3 Analytical Solution | 9 |
3. NUMERICAL SOLUTION | 13 |
4. RESULTS | 16 |
5. NOMENCLATURE | 32 |
6. REFERENCES | 33 |

APPENDIX 1: SOLUBILITY LIMIT SHARING AMONG ISOTOPES OF THE SAME ELEMENT | 35 |
A1.1 Discussion of an Alternative Weighting Scheme | 35 |
A1.2 Comparison between Inventory and Production Weighting | 37 |

APPENDIX 2: INTERMEDIATE NUCLIDE SOLIDS PHASE START-UP | 43 |

APPENDIX 3: VERIFICATION TESTS | 45 |
A3.1 Last Nuclide in Chain Non-Decaying | 45 |
A3.2 All Nuclides Non-Decaying | 46 |
A3.3 Effect of Truncation Error Control | 48 |
A3.4 Pure Radioactive Decay, No Water Flow Past Repository | 51 |
A3.5 Pure Matrix Dissolution | 53 |
1. INTRODUCTION

Water, the universal solvent, flowing past the packages containing nuclear waste will eventually penetrate the protective overpacks and start to remove nuclides from the stabilising matrix, e.g. glass, in which they are embedded. Nuclide ions are transported out of the waste by a leaching and solubility-controlled process during the matrix lifetime and thereafter under purely solubility-limited conditions. The contaminated groundwater percolates further through the geological strata before reentering the biosphere.

For a given waste inventory, the rate of removal of nuclides from the repository will be determined by four major factors:

a) Resistance to dissolution of the retaining matrix
b) Nuclide solubilities
c) Transport characteristics in the backfill
d) Water flow past the repository

It is clear that the lower the release rate of nuclides from the repository the lower their rate of reentry into the biosphere and also the greater the amount of decay taking place in the repository. The repository model considered here constitutes a limiting, conservative situation in which no additional protection is given to the waste packages by any form of grouting or backfill in the excavations. Neglecting the presence of the backfill material means further that the decay of nuclides during their diffusive transport out into the groundwater is ignored. This introduces a further important conservatism.

The report is structured so that the second chapter provides an overview of the mathematical model, Chapter 3 contains a description of the numerical solution of the set of equations which the model provides and Chapter 4 contains the results of application of the mathematical model to the safety analysis of a hypothetical high-level waste repository for the NAGRA "Gewähr" project.
2. METHOD

The model represents an extension to a leaching model developed at the EIR Würenlingen [1, 2], employing results of a fundamental review of the processes involved [5]. Allowance has now been made to represent the limited solubility of the nuclides as well as the sharing of solubility amongst the different isotopes of an element.

Thus, during the matrix lifetime the release rate of a nuclide from the inventory is determined by the rate of setting-free from the matrix by dissolution or by the rate of removal by a saturated groundwater flow, whichever is smaller. Following the dissolution of the retaining matrix all remaining elements are removed by the flowing water at their respective solubility limits.

2.1 Matrix Dissolution Model

An essential component of the whole model is the already existing matrix dissolution model, opus cit., which is included without change. Here, the retaining matrix is assumed to dissolve at a rate per unit surface area and time of \( L_0 \). Nuclide specific dissolution rates may be defined \( (L_n) \) similarly for cases of non-congruent leaching, i.e. where the nuclide dissolution rate differs from the glass dissolution rate.

An equivalent geometrical shape may then be chosen freely and its size calculated to provide the ratio of matrix volume/matrix surface area occurring when the containers initially fail (calculations suggest that the shape chosen is of minor importance in the overall safety calculation). For example, the result of using an equivalent cube is numerically identical to that of using an equivalent sphere, even though geometrically a sphere is a more compact body than a cube. The equation for the material removal rate from the waste matrix may be written:

\[
\frac{dV}{dt} = - \frac{L_n A}{\rho},
\]

with initial conditions at time \( t = 0 \): \( V = V_0, A = A_0 \),
where:

- $V$: Matrix volume [m$^3$]
- $t$: Time [years]
- $L_o$: Matrix dissolution rate [kg m$^{-2}$ yr$^{-1}$]
- $\rho$: Matrix density [kg m$^{-3}$]
- $A$: Matrix surface area [m$^2$]

The surface area $A$, being linked to the matrix volume $V$, through the geometry of the shape chosen.

For the special case of a sphere of radius $R$ and a time-independent dissolution rate, substituting for $V = \frac{4}{3} \pi R^3$ and $A = 4 \pi R^2$:

$$\frac{4 \pi R^2 \frac{dR}{dt}}{dt} = -\frac{L_o}{\rho} 4\pi R^2$$

Hence:

$$\frac{dR}{dt} = -\frac{L_o}{\rho}$$

with initial condition at $t = 0$, $R = R_0$ and solution:

$$R = R_0 - \frac{L_0 t}{\rho}$$  \hspace{1cm} (2.2)

whence the matrix life $\tau$ [years] becomes:

$$\tau = \frac{R_0 \rho}{L_0}$$  \hspace{1cm} (2.3)

and substituting for $\tau$ in equations 2.1 and 2.2:

$$R = R_0 \left(1 - \frac{t}{\tau}\right)$$  \hspace{1cm} (2.4)
and

\[
\frac{dV}{dt} = -\frac{4\pi}{\tau} R_0^3 (1 - t/\tau)^2
\]  

(2.5)

Thus, the volume of the matrix is described by a cubic expression in time, i.e.:

\[
v = V_0 (1 - t/\tau)^3
\]  

(2.6)

Now, for N moles of any substance dispersed homogeneously throughout the matrix, the concentration \( C = N/V \) and the corresponding rate at which the substance is leached away or set free, \( \hat{\Phi} \) may be written in general as:

\[
\hat{\Phi} = -C \frac{dV}{dt} = -\frac{N}{V} \frac{dV}{dt}
\]

In particular for a spherical matrix block:

\[
\hat{\Phi} = \frac{3 N L_i}{\rho R_0 (1 - t/\tau)} = \frac{3N}{\tau (1 - t/\tau)} \quad 0 \leq t \leq \tau
\]  

(2.7)

and:

\[
\hat{\Phi} = 0 \quad t > \tau
\]

where \( L_i \), the specific leach rate for nuclide \( i \) is set equal to the matrix dissolution rate \( L_0 \) to represent congruent dissolution.

The mass balance for the dissolution model may now be written down:

\[
\text{Accumulation} = \text{input} + \text{production} - \text{output} - \text{decay}
\]  

(2.8)

\[
\frac{dN}{dt} = 0 + \lambda N^* - \frac{3N}{\tau (1 - t/\tau)} - \lambda N
\]  

(2.9)
where:

\( \lambda \)  
Decay constant for nuclide \([\text{years}^{-1}]\)

\( \lambda^* \)  
Decay constant of parent nuclide \([\text{years}^{-1}]\)

\( N^* \)  
Matrix inventory of precursor nuclide \([\text{moles}]\)

with initial conditions at \( t = 0 \), \( N = N_0 \), \( N^* = N^*_0 \), representing the total initial matrix inventory at canister failure.

This system of ordinary differential equations is valid over the range \( 0 \leq t \leq \tau \) and may be solved by numerical integration.

2.2 Intermediate Phase Model

A second part of the release model represents a quantity \((M)\) of nuclides in an intermediate solid phase. This consists of nuclides set free from the immobilising matrix, but not yet dissolved and carried away by the flowing water because of solubility constraints. In particular, the water flow leaving the repository is assumed to be fully saturated and equilibrated with any elements present in this intermediate phase.

Writing the mass balance for the intermediate solids:

\[
\frac{dM}{dt} = \text{INPUT} + \lambda^* M^* - \text{OUTPUT} - \lambda M
\]  \hspace{1cm} (2.10)\]

where:

\( M^* \)  
Inventory of precursor nuclide in the intermediate solids phase \([\text{moles}]\)

We consider that the intermediate solids phase acts as a temporary store through which nuclides set free by the dissolution model from the matrix, must pass before being transported away by the water. This process is illustrated diagrammatically in Figure 2.1.
Thus, the input term is the rate at which nuclides are set free by the matrix dissolution process:

\[
\text{INPUT} = \dot{F} \quad 0 \leq t \leq \tau \\
\text{INPUT} = 0 \quad t > \tau
\]  

(2.11)

This still leaves the output term, the release rates, \( \dot{R} \) to be described and assembled. These release rates represent the rate at which nuclides are carried away from the repository by the flowing water into the geosphere. At the same time they define a boundary condition for a geosphere transport model [8].

Each nuclide is carried away by the groundwater as fast as it is produced (either directly from the matrix, at rate \( \dot{F} \), or by radioactive decay of a precursor nuclide in the intermediate solids at rate \( \lambda^*M^* \)) up to the limit set by a saturated solution of the element.

\[
\dot{R}_{\text{max}} = \dot{Q} C_{\text{sat}}
\]  

(2.12)

where:

\[
\dot{Q} \quad \text{Water flow rate through repository [l/yr]}
\]

\[
C_{\text{sat}} \quad \text{Molar solubility of element [moles/l]}
\]

Thereafter, excess will not be dissolved, but will accumulate in the intermediate solids phase. Expressing this concept in equation form for an element of which only one isotope is present:

\[
\text{OUTPUT} = \dot{R} = \dot{Q} C_{\text{sat}} \quad \text{for } M > 0 \\
\dot{R} = (\dot{F} + \lambda^*M^*) \leq \dot{Q} C_{\text{sat}} \quad \text{for } M = 0
\]

However, if \( (\dot{F} + \lambda^*M^*) < \dot{Q} C_{\text{sat}} \) and \( M = 0 \), it follows from consideration of the mass balance that \( \frac{dM_{\text{sat}}}{dt} = 0 \) and hence material set free from the matrix is considered to pass straight through the intermediate solids phase without accumulating.
When intermediate solids exist, \( M \neq 0 \), and the mass balance becomes:

\[
\frac{dM}{dt} = \dot{F} + \lambda \cdot M^* - \dot{Q} \cdot C_{\text{sat}} - \lambda M
\]  

(2.14)

with typical initial conditions being:

At \( t = t_s \), \( M = 0 \), \((\dot{F} + \lambda \cdot M^*) = \dot{Q} \cdot C_{\text{sat}} \) and \( \frac{d(\dot{F} + \lambda \cdot M^*)}{dt} > 0 \)

or \( t = 0 \), \( M = 0 \), \((\dot{F} + \lambda \cdot M^*) > \dot{Q} \cdot C_{\text{sat}} \) or \( t = 0 \), \( M = M_0 \)

Here, \( t_s \) is the time when \((\dot{F} + \lambda \cdot M^*)\) equals \( \dot{Q} \cdot C_{\text{sat}} \) and is rising thereafter and \( M_0 \) represents that part of the nuclide inventory (to be subtracted from the waste matrix inventory) which may be present in finely divided form, e.g. powder, sharp edges, flakes and tiny crystals at canister failure.

Where an element is represented in the original waste inventory by more than one of its isotopes, the solution capacity of the water for that element is shared between those isotopes. Two possible methods of sharing based on the law of mass action are discussed in detail in Appendix 1. The approach adopted is "inventory weighting", whereby the solubility limit of the element is shared between the isotopes present according to their relative abundance in the intermediate solids phase:

\[
C(i) = C_{\text{sat}}(K) \frac{M(i)}{ \sum_i M(i) }
\]  

(2.15)

where \( \sum_i \) implies the sum over all isotopes \( i \) of element \( K \). The physical assumption behind this approach is that all isotopes in the intermediate solids phase are equally available for dissolution in the water flow \( \dot{Q} \).

In Chapter 4, the application of the present model to a particular safety analysis is presented. Table 4-2 lists the nuclides considered.
In particular it will be noted that three isotopes of plutonium are treated, $^{239}\text{Pu}$, $^{240}\text{Pu}$ and $^{242}\text{Pu}$. Taking plutonium to illustrate the principle, we have:

$$M(\text{Pu}) = \sum_i M(i) = M(\text{^{239}Pu}) + M(\text{^{240}Pu}) + M(\text{^{242}Pu})$$  \hspace{1cm} (2.16)

The concentration of the isotope $^{239}\text{Pu}$ in solution for example is:

$$C(\text{^{239}Pu}) = C_{\text{sat}(\text{Pu})} \frac{M(\text{^{239}Pu})}{\sum_i M(i)}$$  \hspace{1cm} (2.17)

and its release rate is:

$$R(\text{^{239}Pu}) = Q C(\text{^{239}Pu})$$  \hspace{1cm} (2.18)

A saturated solution of each element leaves the repository as long as that element is present in intermediate solids form. As long as this situation persists, the isotopic composition changes according to the relative amounts of each isotope in the intermediate solids inventory.

The isotopes of an element do not interfere with each others' solubility as long as none of them is present in intermediate solids form and as long as the element's total production rate through all its isotopes is less than the solution capacity of the water.

For the special starting condition when all intermediate solids inventories are zero, yet the total element production rate ($\dot{P}$) exceeds the water carrying capacity, inventory weighting becomes indeterminate at $t = 0$. In this case, application of l'Hôpital's theorem (Appendix 2) and simplification leads to production rate weighting.

Taking plutonium again as an example:
\[ \dot{P}(^{239}\text{Pu}) = \dot{P}(^{239}\text{Pu}) + \lambda(^{243}\text{Am}) M(^{243}\text{Am}) \]
\[ \dot{P}(^{240}\text{Pu}) = \dot{P}(^{240}\text{Pu}) + \lambda(^{244}\text{Pu}) M(^{244}\text{Pu}) \]
\[ \dot{P}(^{242}\text{Pu}) = \dot{P}(^{242}\text{Pu}) + \lambda(^{246}\text{Cm}) M(^{246}\text{Cm}) \]

where short-lived precursors are neglected, and:

\[ \dot{P}_{\text{Pu}} = \sum_{i=1}^{K} \dot{P}(i) \quad \text{(Definition)} \]

we get:

\[ C(^{239}\text{Pu}) = \frac{\dot{R}(^{239}\text{Pu})}{\dot{Q}} = C_{\text{sat}}(\text{Pu}) \frac{\dot{P}(^{239}\text{Pu})}{\sum_{i=1}^{K} \dot{P}(i)} \quad (2.20) \]

The release rates \( \dot{R} \) from the solids model having been defined under all possible conditions the set of ordinary differential equations may be written down and integrated to obtain the release-rates \( \dot{R} \) for each nuclide as a function of time:

\[ \frac{dM}{dt} = \dot{P} + \lambda M^* - \dot{R} - \lambda M \quad (2.21) \]

2.3 Analytical Solutions

Certain simple analytical solutions and properties of the model are worthy of mention as they aid understanding, help to obtain quick estimates, and provide checks on computed results.

a) For a single nuclide with no precursor set free by congruent matrix dissolution \( (L = L_0) \) from a sphere, we have (see equations (2.7) and (2.9)):

\[ \dot{P} = \frac{3N}{t(1 - t/T)} \quad (2.22) \]
\[
\frac{dN}{dt} = -\frac{3N}{\tau(1 - t/\tau)} - \lambda N \quad \text{with } N = N_0 \text{ at } t = 0 \quad (2.23)
\]

Integrating:

\[
N = N_0 e^{-\lambda t(1 - t/\tau)} \quad (2.24)
\]

and substituting for \(N\):

\[
\dot{P} = \frac{3N}{\tau} e^{-\lambda t(1 - t/\tau)} \quad (2.25)
\]

b) For a single nuclide with no precursor and solubility controlled release (\(\dot{P} \geq \dot{Q} C_{\text{sat}} \text{ at } t = 0\)):

\[
\frac{dM}{dt} = \frac{3N_0}{\tau} e^{-\lambda t(1 - t/\tau)} - \dot{Q} C_{\text{sat}} - \lambda M \quad (2.26)
\]

\[
\frac{3N_0}{\tau} \geq \dot{Q} C_{\text{sat}}, \text{ or } M = M_0 \text{ at } t = 0
\]

Integrating:

\[
M = -N_0 e^{-\lambda t(1 - t/\tau)} - \frac{\dot{Q} C_{\text{sat}}}{\lambda} + e^{-\lambda t} \left\{ N_0 + M_0 + \frac{\dot{Q} C_{\text{sat}}}{\lambda} \right\}
\]

for \(0 \leq t \leq \tau\), and

\[
M = -\frac{\dot{Q} C_{\text{sat}}}{\lambda} + e^{-\lambda t} \left\{ N_0 + M_0 + \frac{\dot{Q} C_{\text{sat}}}{\lambda} \right\} \quad \text{for } t > \tau \quad (2.27)
\]
For \( t > \tau \) the solution depends on the total initial inventory \((N_o + M_o)\) and is independent of distribution between \(N_o\) and \(M_o\). At some time greater than \( \tau \) the residual inventory in the intermediate solid phase will be reduced to zero. This and thus also the duration of the release is found by placing \( M \) equal to zero in (4.9):

\[
\begin{align*}
t_{\text{end}} &= \frac{1}{\lambda} \ln \left(1 + \frac{(N_o + M_o) \lambda}{Q \cdot C_{\text{sat}}} \right) \\
& \text{for } t_{\text{end}} \geq \tau
\end{align*}
\]  

(2.28)

and clearly \( R = \frac{Q}{C_{\text{sat}}} \) for \( t < t_{\text{end}} \)  

(2.29)

When the presence of a nuclide spans several half-lives, it should be noted that a doubling of the groundwater flux does not halve the total time-span of the release.

For nuclides with insignificant decay, the equations simplify to the standard solution model:

\[
\begin{align*}
t_{\text{end}} &= \frac{(N_o + M_o)}{Q \cdot C_{\text{sat}}} \\
& \text{for } 0 \leq t \leq \tau
\end{align*}
\]  

(2.30)

Also in this case:

\[
\begin{align*}
M &= -N_o (1 - t/\tau)^3 + (N_o + M_o) - \frac{Q}{C_{\text{sat}}} t \\
& \text{for } 0 \leq t \leq \tau \text{ and:}
\end{align*}
\]

\[
\begin{align*}
M &= N_o + M_o - \frac{Q}{C_{\text{sat}}} t \\
& \text{for } t > \tau
\end{align*}
\]  

(2.31)
1. Groundwater reaches the waste package containing...

2. Dissolution of the matrix leaves...

3. Nuclides dissolve into the groundwater stream which returns to the...

Figure 2.1: Diagram of the nuclide release process from waste form to groundwater
3. NUMERICAL SOLUTION

The mathematical model described in Chapter 2 has been incorporated in a computer program DREG (Direct Radionuclide Escape to the Geosphere) which enables the temporal developments both of the waste inventories, N and M, and of the release rate to the passing groundwater to be calculated.

The integration method used was based on the classic fourth order Runge-Kutta scheme with a one step/two half steps technique providing truncation error control and raising the order of the method to sixth order global.

The integration step-length used is fully variable between wide limits (2 years to 50,000 years).

Besides integrating the nuclide inventories, with two ordinary differential equations for each isotope, one O.D.E. in the matrix dissolution model, and one O.D.E. in the solids model, the release rates for each nuclide were also simply integrated (fourth order method, with no error control, due to the discontinuities or jumps in the release rates) to obtain an accurate count of the amount of each nuclide released into the geosphere.

Special precautions taken include:

a) Negative isotope inventories are set to zero when evaluating the system of O.D.E.'s. This introduces some degree of discontinuity into the higher order differentials near the end of each nuclide inventory in the intermediate solids. However, a gate set 500 years before the end of the intermediate solids inventory removes the isotope from the truncation error control and returns it to the more robust fourth order integration scheme which is then set to obtain an extra data point shortly after each isotope has been removed from the inventory.
b) After the end of the matrix dissolution process, integration of the dissolution model is dropped completely and the rate of input to the intermediate solids phase is set to zero, or algebraically:

\[ F_0, t \geq \tau. \]

c) The terms of the differential equations for the solids are written down in the order:

\[ \frac{dM}{dt} = (F - \dot{R} + \lambda M^*) - \lambda M \]

This is to obtain better numerical resolution when the input, production and output terms are many orders of magnitude larger than the decay component.

d) A noise filter in the model of the intermediate solids was introduced for isotopes being removed as fast as they are formed. Otherwise an error of a single bit in obtaining the zero difference between the input and output terms suffices to cause a small finite inventory to be found at the next function evaluation, which must then be taken as being washed out at the limit of solubility at that instant. This causes a sudden large negative overshoot to appear on the inventory output file, as well as a spurious jump in the release rates.

The noise filter chosen was:

When \( M_i = 0 \) (precondition)

and if \( R_i \times 1.0 \times 10^{-12} \geq \frac{dM_i}{dt} \) set \( \frac{dM_i}{dt} = 0 \)

This has proved useful and compares with the 14-15 significant figures normally used on CDC computers.
e) Output was generated at regular intervals in time, with extra output at particular points of interest, for instance at the end of matrix dissolution and at the time of exhaustion of the intermediate solids phase inventory of each nuclide.

f) Times printed and output by the programme are real times, or the elapsed time after waste manufacture, as distinct from the time, \( t \), used in the model:

\[
\text{real time output} = t_{\text{model}} + t_{\text{canister failure}} \tag{3.1}
\]

A set of five different test calculations has been performed to verify the program function. These tests, which constitute special cases of the general situation, are presented in Appendix 3.
4. RESULTS

Preliminary calculations have been made for six major fission products and the four actinide decay chains, embedded in a glass matrix.

Table 4-1 contains general data, relevant to the vitrified waste and to the overall calculation.

Table 4-2 presents the nuclide specific data for the radioactive nuclides evaluated. Half-life data were taken from [3], and nuclide inventories from [9]. Although estimates of the nuclide inventories vary to some extent, [7], these have little effect on the maximum dose rate calculation, influencing rather the duration of the nuclide release. This is because the majority of release rates are determined by solubility considerations and are hence largely independent of the actual inventory.

Table 4-1: General data for the calculations (see also ref. [11])

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste form glass matrix volume:</td>
<td>150 l/waste package</td>
</tr>
<tr>
<td>Density ($\rho$):</td>
<td>2'700 kg m$^{-3}$</td>
</tr>
<tr>
<td>Shape: equivalent spheres with radius</td>
<td></td>
</tr>
<tr>
<td>Geometry factor for spheres:</td>
<td>3</td>
</tr>
<tr>
<td>Matrix dissolution rate ($L_o$):</td>
<td>$\begin{cases} 1 \times 10^{-7} \text{ gram cm}^{-2} \text{ day}^{-1} \ \equiv (4 \times 10^{-4} \text{ kg m}^{-2} \text{ yr}^{-1}) \end{cases}$</td>
</tr>
<tr>
<td>Matrix lifetime ($\tau$).</td>
<td>155236.1 years</td>
</tr>
<tr>
<td>Time span of calculation:</td>
<td>$10^8$ years</td>
</tr>
<tr>
<td>Number of waste packages:</td>
<td>5895</td>
</tr>
<tr>
<td>Water flow past repository ($Q$):</td>
<td>$4.2 \text{ m}^3 \text{ yr}^{-1}$</td>
</tr>
</tbody>
</table>
Table 4-2: Nuclide data used in the calculations. The inventory is defined at the time of waste package failure (1'000 years) [7, 9]. The solubilities for the actinides are from ref. [10], those of the other elements are estimates (see also ref. [11]).

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half-Life [years]</th>
<th>Inventory [moles per package]</th>
<th>Solubility (realistic) [moles/l]</th>
<th>Solubility (conservative) [moles/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{245}$Cm</td>
<td>8'500.0</td>
<td>3.454 E-3</td>
<td>5.0 E-5</td>
<td>1.0 E-4</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>432.2</td>
<td>0.2707</td>
<td>5.0 E-5</td>
<td>1.0 E-4</td>
</tr>
<tr>
<td>$^{237}$Np</td>
<td>2.140 E+6</td>
<td>3.583</td>
<td>2.0 E-9</td>
<td>1.0 E-8</td>
</tr>
<tr>
<td>$^{233}$U</td>
<td>1.592 E+5</td>
<td>1.027 E-3</td>
<td>2.5 E-9</td>
<td>2.5 E-7</td>
</tr>
<tr>
<td>$^{229}$Th</td>
<td>7'340.0</td>
<td>2.060 E-6</td>
<td>1.6 E-8</td>
<td>1.6 E-6</td>
</tr>
<tr>
<td>$^{246}$Cm</td>
<td>4'730.0</td>
<td>3.437 E-4</td>
<td>5.0 E-5</td>
<td>1.0 E-4</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>3.763 E+5</td>
<td>0.02250</td>
<td>1.0 E-7</td>
<td>1.0 E-6</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>4.468 E+9</td>
<td>7.957</td>
<td>2.5 E-9</td>
<td>2.5 E-7</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>2.450 E+5</td>
<td>0.01246</td>
<td>2.5 E-9</td>
<td>2.5 E-7</td>
</tr>
<tr>
<td>$^{230}$Th</td>
<td>7.538 E+4</td>
<td>4.905 E-5</td>
<td>1.6 E-8</td>
<td>1.6 E-6</td>
</tr>
<tr>
<td>$^{226}$Ra</td>
<td>1'600.0</td>
<td>2.428 E-7</td>
<td>1.0 E-4</td>
<td>1.0 E-3</td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td>7'380.0</td>
<td>0.3530</td>
<td>5.0 E-5</td>
<td>1.0 E-4</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>2.412 E+4</td>
<td>0.3080</td>
<td>1.0 E-7</td>
<td>1.0 E-6</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>7.038 E+8</td>
<td>0.1430</td>
<td>2.5 E-9</td>
<td>2.5 E-7</td>
</tr>
<tr>
<td>$^{231}$Pa</td>
<td>3.276 E+4</td>
<td>1.900 E-6</td>
<td>1.6 E-8</td>
<td>1.6 E-6</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>6'537.0</td>
<td>0.1930</td>
<td>1.0 E-7</td>
<td>1.0 E-6</td>
</tr>
<tr>
<td>$^{236}$U</td>
<td>2.342 E+7</td>
<td>0.08140</td>
<td>2.5 E-9</td>
<td>2.5 E-7</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>1.405 E+10</td>
<td>5.270 E-6</td>
<td>1.6 E-8</td>
<td>1.6 E-6</td>
</tr>
<tr>
<td>$^{99}$Tc</td>
<td>2.130 E+5</td>
<td>10.45</td>
<td>1.0 E-6</td>
<td>5.0 E-5</td>
</tr>
<tr>
<td>$^{59}$Ni</td>
<td>7.500 E+4</td>
<td>0.01080</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>$^{79}$Se</td>
<td>6.500 E+4</td>
<td>0.09832</td>
<td>1.3 E-8</td>
<td>1.3 E-6</td>
</tr>
<tr>
<td>$^{107}$Pd</td>
<td>6.500 E+6</td>
<td>2.597</td>
<td>1.0 E-8</td>
<td>1.0 E-6</td>
</tr>
<tr>
<td>$^{126}$Sn</td>
<td>1.000 E+5</td>
<td>0.3470</td>
<td>8.0 E-9</td>
<td>8.0 E-7</td>
</tr>
<tr>
<td>$^{135}$Cs</td>
<td>2.300 E+6</td>
<td>3.186</td>
<td>high</td>
<td>high</td>
</tr>
</tbody>
</table>

Solubilities labelled "high" are unspecified because they do not influence model results.
Typical release rates for the four actinide chains and certain other nuclides are plotted in Figures 4.1 to 4.10. These correspond to the numerical data tabulated in Tables 4-1 and 4-2. The information is plotted on log-log scales because of the large range covered by the data.

Figures 4.1 to 4.4 illustrate the release rates for the four actinide decay chains from the time of overpack failure (1'000 years) up to a time of $10^8$ years. These are calculations made with realistic solubilities, the lower of the values in Table 4-2.

Figure 4.5 shows the release rate for six important fission products, again with realistic solubilities.

Figures 4.6 to 4.10 depict the same nuclide release rates, this time using conservative solubility limits in the calculation. The conservative solubilities are up to a factor 100 times larger than the realistic solubilities.

Nuclides whose release rates are controlled by the waste form matrix dissolution, e.g. $^{245}$Cm, $^{243}$Am and $^{59}$Ni, display a typical "waterfall" shape on the log-log plots, with $^{241}$Am displaying the characteristic double arc as it decays rapidly ($t_{1/2} = 430$ years) to attain dynamic equilibrium with its precursor, $^{245}$Cm, after about 7'000 years.

The release rates of the matrix-controlled nuclides are usually highest at canister failure because by chance these nuclides either have no direct precursor, (e.g. fission products, such as $^{135}$Cs or chain headers, such as $^{245}$Cm) or decay faster than their precursor, e.g. $^{241}$Am.

Notable exceptions to this rule of thumb would be the thorium, radium or protactinium release rates, which rise initially because these nuclides, occurring near the bottom of the decay chain and being largely absent from freshly prepared waste, are generated internally at ever increasing rates for many years.
However, after the complete dissolution of the matrix (about 150'000 years) the release rates of all these highly soluble nuclides drop to the rates at which they are produced from their respective parent nuclides in the intermediate solids phase.

The majority of nuclides exhibit solubility-limited release. An element which is present as only a single isotope, e.g. $^{237}\text{Np}$, $^{99}\text{Tc}$, $^{79}\text{Se}$ displays a rectangular "top hat" release rate pattern. The release rate is constant at the level determined by a saturated solution for as long as some inventory still remains. Thereafter it drops suddenly to the instantaneous rate of production by decay of the parent nuclide, if there is one in the remaining inventory.

For some elements, e.g. uranium and plutonium, the solubility is shared between the isotopes present in the intermediate solids inventory. This causes a reduction in the amount of each isotope released below the level expected if that isotope alone were present and results in a linking across the decay chains in the intermediate solids. The effect of this solubility linkage is to tend to produce long, slow waves in the release rates, due to the chain production and decay rate constants varying from isotope to isotope, although as the water is still saturated with regard to the element overall, these waves are out of phase with each other. When one release rate climbs another one falls away. It may be observed from the figures that the release rate for the longest-lived isotope of a solubility-controlled element, for instance $^{242}\text{Pu}$ or $^{232}\text{Th}$, always rises towards the end of the inventory.

In Figure 4.1, the release rate curve for the $^{229}\text{Th}$ isotope displays three anomalies. The two sudden changes of slope at about 6000 years and 16.5 million years occur at the beginning and end respectively of the thorium element inventory in the intermediate solids phase. Between these times the solubility limit constraint is exactly met, whilst outside these times each of the three thorium isotopes is removed at its production rate.

The intermediate minimum occurring around 8 million years may be explained partly by the changeover in the effective precursors of the
thorium and partly by the inertia of the system caused by the inventory weighting acting in conjunction with an essentially non-decaying nuclide \((232\text{ Th})\).

At a time of 1.3 million years the \(233\text{ U}\) has attained dynamic equilibrium with its precursor \(237\text{ Np}\). Later, at about 2 million years the \(234\text{ U}\) has also attained dynamic equilibrium with its parent nuclide \(238\text{ U}\). This may be seen in Figure 4.2 where the release rates for the \(234\text{ U}\) and \(238\text{ U}\) isotopes are in the same ratio as their half-lives \((1 : 1.8 \times 10^4)\) from 2 million years onwards. Hence, by this time two of the half-lives governing the thorium production have completely changed, as shown in Table 4-3.

Table 4-3: Effective precursors of thorium isotopes

<table>
<thead>
<tr>
<th>Nuclide (half-life) [years]</th>
<th>Effective precursor (half-life) [years]</th>
<th>long term</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>short term</td>
<td></td>
</tr>
<tr>
<td>(229\text{ Th}) ((7.3 \times 10^3))</td>
<td>(233\text{ U}) ((1.6 \times 10^5))</td>
<td>(237\text{ Np}) ((2.1 \times 10^6))</td>
</tr>
<tr>
<td>(230\text{ Th}) ((7.5 \times 10^4))</td>
<td>(234\text{ U}) ((2.5 \times 10^5))</td>
<td>(238\text{ U}) ((4.5 \times 10^9))</td>
</tr>
<tr>
<td>(232\text{ Th}) ((1.4 \times 10^{10}))</td>
<td>(236\text{ U}) ((2.4 \times 10^7))</td>
<td>(236\text{ U}) ((2.4 \times 10^7))</td>
</tr>
</tbody>
</table>

However, the release rates cannot adapt to the new situation immediately, because the \(232\text{ Th}\) present, acting via the inventory weighting of the solubilities provides a massive system inertia. The 48 moles present at a time of 2 million years, with a production rate of \(4.4 \times 10^{-5}\) moles/year and a possible removal rate of \(6.7 \times 10^{-5}\) moles/year are sufficient to delay response by at least a further 2 million years.

The smooth curves displayed by \(226\text{ Ra}\) and \(231\text{ Pu}\) in all plots and by the three thorium isotopes in the plots with conservative solubility limits are typical for nuclides carried away by the water as fast as they are set free or produced. The solubility limit is never reached so that:

\[
M = 0, \quad \frac{dM}{dt} = 0 \quad \text{for all } t
\]  

(4.1)
and \( R = \dot{Y} + \lambda M \) for all \( t \) \hspace{1cm} (4.2)

The release rate for the \(^{226}\text{Ra}\) drops smoothly away to zero as the inventory of the precursor \(^{230}\text{Th}\) is used up. However, the release rate for \(^{230}\text{Th}\) displays hardly any change at this point due to its own precursor \(^{234}\text{U}\) still being present, i.e.:

\[ A(^{230}\text{Th}) = \lambda M (^{234}\text{U}) \] \hspace{1cm} (4.3)
FIGURE 4.1: RELEASE FROM THE WASTE TO THE GEOSPHERE: CURIUM-245 DECAY CHAIN
REALISTIC SOLUBILITY LIMITS
FIGURE 4.2: RELEASE FROM THE WASTE TO THE GEOSPHERE: CURIUM-246 DECAY CHAIN
REALISTIC SOLUBILITY LIMITS
FIGURE 4.3: RELEASE FROM THE WASTE TO THE GEOSPHERE: CURIUM-247 DECAY CHAIN REALISTIC SOLUBILITY LIMITS
FIGURE 4.4: RELEASE FROM THE WASTE TO THE GEOSPHERE: CURIUM-248 DECAY CHAIN
REALISTIC SOLUBILITY LIMITS
FIGURE 4.5: RELEASE FROM THE WASTE TO THE GEOSPHERE: FISSION AND ACTIVATION PRODUCTS
REALISTIC SOLUBILITY LIMITS
FIGURE 4.6:

RELEASE FROM THE WASTE TO THE GEOSPHERE: CURIUM-245 DECAY CHAIN
CONSERVATIVE SOLUBILITY LIMITS
FIGURE 4.7: RELEASE FROM THE WASTE TO THE GEOSPHERE: CURIUM-246 DECAY CHAIN CONSERVATIVE SOLUBILITY LIMITS
FIGURE 4.8: RELEASE FROM THE WASTE TO THE GEOSPHERE: CURIUM-247 DECAY CHAIN CONSERVATIVE SOLUBILITY LIMITS
FIGURE 4.9: RELEASE FROM THE WASTE TO THE GEOSPHERE: CURIUM-248 DECAY CHAIN CONSERVATIVE SOLUBILITY LIMITS
FIGURE 4.10: Release from the waste to the geosphere: Fission and activation products conservative solubility limits
5. NOMENCLATURE

A Matrix surface area \([\text{m}^2]\)

C, \(C_{\text{sat}}\) Molar concentration in solution or saturated solution [moles/litre]

\(\dot{R}\) Rate of setting free from matrix [moles/year]

L\(_o\), \(L_1\) Dissolution rate of matrix or nuclide i respectively [kg m\(^{-2}\) yr\(^{-1}\)]

M Inventory of intermediate solids phase [moles]

N Inventory of waste form matrix [moles]

\(\dot{P}\) Production rate [moles/year]

\(\dot{Q}\) Water flow rate past repository [litres/year]

R Hydraulic radius for waste matrix blocks [m]

\(R\) Release rate from repository [moles/year]

\(t\) Time [years]

V Volume of matrix [m\(^3\)]

\(\rho\) Matrix density [kg m\(^{-3}\)]

\(\tau\) Matrix life [years]

\(\lambda\) Decay constant [years\(^{-1}\)]

Superscript

* Refers to the parent nuclide, where relevant
6. REFERENCES


A1.1 A Discussion of An Alternative Weighting Scheme

The principle of inventory weighting of the solubility is derived as an interpretation of the law of mass action which states that: "the driving force of a chemical reaction is proportional to the active masses of the reactants".

However, a chemical reaction is not necessarily involved in the process of solution of a solid and furthermore the active masses are largely unknown too.

It is to be noted that in the model the assumption has been made that the solids are homogeneous in composition throughout or that all molecules in the intermediate solids phase are equally available for solution.

Also assumed in the model is that the active mass of a nuclide equals its total mass. This makes no allowance for the possibility that freshly liberated nuclides are likely to be in a more finely divided form (larger surface area/mole) than those which have been in the solid form for long times and have had time to clump together in crystal formations or become covered by later solid growths.

A further interpretation of the law of mass action could thus be that of production rate weighting. This would be expressed for an isotope i, which is one of several of the element K, in the form:
where:

\[ \dot{P}(i) = \dot{P}(i) + \lambda * M^* \]  

as distinct from the inventory weighting which, expressed similarly, would be written:

\[ C(i) = \frac{M(i)}{K} \sum_{i} M(i) C_{sat}(K) = \frac{M(i)}{M(K)} C_{sat}(K) \]  

Now in Appendix 2 it will be shown that these two methods are also related via l'Hôpital's theorem.

Furthermore any linear combination of these weighting methods is also possible, e.g.:

\[ C(i) = \left[ \theta \frac{\dot{P}(i)}{K} + (1 - \theta) \frac{M(i)}{M(K)} \right] C_{sat}(K) \]  

where:

\( \theta \) is the combination factor.

The following section contains a detailed comparison of the results obtained by applying the two different weighting principles to the same data.
A1.2 A Comparison between Inventory and Production Weighting

In the previous section, the broad principles of inventory weighting and production weighting of shared solubility, have been derived from the law of mass action. In this section the effects of adopting one weighting system or the other will be examined in more detail. The "realistic" element solubilities from Table 4-2 are used to produce sets of results for each weighting system, which are compared in Tables A1-1 and A1-2 at the end of this Appendix.

Clearly, for those elements which are released slowly enough (e.g. Cm, Am), the release rate is determined by the dissolution rates of the isotopes with no necessity for sharing the solubility limit. These remain unaffected by the model chosen.

Similarly, single nuclides of an element, e.g. $^{237}$Np and $^{99}$Tc, have identical release patterns in both models, being always at the solubility limit, because no other isotope competes for the solubility of that element.

The nuclides $^{231}$Pa and $^{226}$Ra are carried away by the water as fast as they are produced, so that beyond the matrix leaching time their release rates are directly proportional to the amount of precursors $^{236}$U and $^{230}$Th respectively, which are present. In these cases only very minor changes in the amounts released and in the patterns of release occur, although this is not necessarily the case.

One aspect of the production weighting model not explicitly mentioned in the introduction in section A1.1, is for the special case, when the production rate of the element is insufficient to raise the groundwater flux to the solubility limit, but at the same time an inventory of intermediate solids phase of the element exists. This implies that the production of the element is nearing its end. Clearly, the element is still being removed overall at the solubility limit, even though its total production rate is too low to achieve saturation.
In this situation, the model assumes that each isotope is removed at its production rate, while the remaining available solution capacity is distributed according to the principle of inventory weighting.

For the situation when:

\[ \sum_{i} \dot{P}(i) < \dot{Q} C_{sat}(K) \quad \text{and} \quad M(K) > 0 \]

the release rate of isotope \( i \) is:

\[ R(i) = \dot{P}(i) + \left( \dot{Q} C_{sat} - \sum_{i}^{K} \dot{P}(i) \right) \frac{M(i)}{\sum_{i}^{K} M(i)} \]  

(A1.5)

It is this feature, which allows for a smooth transition between the models and their results, for example the \(^{239}\text{Pu}, \(^{240}\text{Pu} \text{ and } ^{242}\text{Pu} \) release rates are almost identical for both models. This is because during the process of waste form matrix dissolution, their precursors \(^{246}\text{Cm} \text{ and } ^{243}\text{Am} \) have identical histories.

The rate of production by dissolution from the waste form at any time is directly proportional to the instantaneous matrix inventory. Thus, for those nuclides whose only source of production is dissolution as distinct from decay of the precursor in the intermediate solids phase, production weighting is exactly equivalent to inventory weighting. With no solids inventory available, it is shown in Appendix 2 that both models may be arranged into identical forms via l'Hôpital's theorem.

The above reasoning accounts for the initial release rates at waste package failure being identical in both models (see Table A1-1). It also accounts for great similarities between release rates of, for example, the plutonium isotopes for the first 100'000 years produced by the two weighting schemes.
Beyond the matrix lifetime, none of the plutonium isotopes has any precursor available, so both the production weighting and inventory weighting models make the same prediction. Hence the great similarity between all of the plutonium release rates resulting from both calculations.

The nuclides affected by the two different models belong to the elements uranium and thorium. Here, quite large differences in the total released in $10^8$ years (up to factor $10^000$ for $^{234}\text{U}$) can be observed. Nuclides which are high in the decay chain (e.g. $^{235}\text{U}$, $^{236}\text{U}$ and $^{238}\text{U}$) tend to be inhibited relative to the daughter nuclides, such as $^{233}\text{U}$ which is produced from $^{237}\text{Np}$, and $^{234}\text{U}$ which is produced from $^{238}\text{U}$.

Comparing the predicted release rates at $10^5$ years (during the glass matrix lifetime) (Table A1-2), it is apparent that the majority of the release rates vary by less than $\pm 10\%$, although the production weighting model does predict an increase by a factor 5 in the $^{233}\text{U}$ and by factor 1.5 in the $^{235}\text{U}$ release-rate and a complete redistribution in the release rates for the thorium isotopes. $^{229}\text{Th}$ increases with use of the production weighting by 45%, $^{230}\text{Th}$ decreases by factor 4 and $^{232}\text{Th}$ by factor 4.5, whereas the $^{226}\text{Ra}$ and $^{231}\text{Pa}$ release rates scarcely change (less than 10%).

Fission products are not shown because none of those treated has to compete for solubility with other isotopes of the same element.

At a time of 1 million years, beyond the glass matrix life, differences are more pronounced. (See Table A1-2). The $^{233}\text{U}$ release rate increases by factor 40 from $2.52 \times 10^{-7}$ with inventory weighting to $1.05 \times 10^{-5}$ moles/year with production weighting. $^{238}\text{U}$ is now completely absent, as it is no longer being formed at the repository. The $^{234}\text{U}$ release rate increases by factor 11 from $1.32 \times 10^{-9}$ moles/year to $1.44 \times 10^{-8}$ moles/year. $^{235}\text{U}$ and $^{236}\text{U}$ are also absent from the solution (but not the solids) in the production weighted model, their release being inhibited by the freshly produced $^{233}\text{U}$ from $^{237}\text{Np}$ and $^{234}\text{U}$ from $^{238}\text{U}$. 
The effects of production weighting on the release rates of the thorium isotopes are as follows: $^{229}$Th release increases by 50% as at $10^5$ years, with $^{230}$Th cut back by factor 8 from 1.72 E-6 moles/year to 2.26 E-7 moles/year. $^{232}$Th release is reduced by factor 40, with $^{226}$Ra and $^{231}$Pa scarcely affected (+10%).

Comparing the peak release rates predicted by the different models, the differences are much less pronounced: $^{233}$U release is increased by factor 40, $^{234}$U raised by factor 45, $^{235}$U by factor 16, $^{236}$U unchanged to within 10%, and $^{238}$U staying the same.

Considering the peak release rates of the thorium isotopes: $^{229}$Th release is increased by 45%, $^{230}$Th is unchanged, and $^{232}$Th up by 40%, in the production weighted model.

The peak release rates for the remainder of the nuclides being the same in both models.
Table A1-1: Nuclide release data for inventory and production weighted models (using realistic solubility limits).

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Initial Release Rate [moles/year] at 1000 yrs</th>
<th>Peak Release Rate [moles/year]</th>
<th>Total Release [moles] up to 10^8 yrs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IW ≡ PW</td>
<td>IW</td>
<td>PW</td>
</tr>
<tr>
<td>245Cm</td>
<td>3.94 E-4</td>
<td>3.94 E-4</td>
<td>3.94 E-4</td>
</tr>
<tr>
<td>241Am</td>
<td>3.09 E-2</td>
<td>3.09 E-2</td>
<td>3.09 E-2</td>
</tr>
<tr>
<td>237Np</td>
<td>8.40 E-6</td>
<td>8.40 E-6</td>
<td>8.40 E-6</td>
</tr>
<tr>
<td>233U</td>
<td>1.32 E-9</td>
<td>2.66 E-7</td>
<td>1.05 E-5</td>
</tr>
<tr>
<td>229Th</td>
<td>2.35 E-7</td>
<td>4.74 E-5</td>
<td>6.65 E-5</td>
</tr>
<tr>
<td>246Cm</td>
<td>3.92 E-5</td>
<td>3.92 E-5</td>
<td>3.92 E-5</td>
</tr>
<tr>
<td>242Pu</td>
<td>1.81 E-5</td>
<td>4.20 E-4</td>
<td>4.20 E-4</td>
</tr>
<tr>
<td>238U</td>
<td>1.02 E-5</td>
<td>1.02 E-5</td>
<td>1.02 E-5</td>
</tr>
<tr>
<td>234U</td>
<td>1.60 E-8</td>
<td>1.60 E-8</td>
<td>7.27 E-6</td>
</tr>
<tr>
<td>230Th</td>
<td>5.59 E-6</td>
<td>3.95 E-5</td>
<td>3.93 E-5</td>
</tr>
<tr>
<td>226Ra</td>
<td>2.77 E-8</td>
<td>1.11 E-4</td>
<td>1.21 E-4</td>
</tr>
<tr>
<td>243Am</td>
<td>4.03 E-2</td>
<td>4.03 E-2</td>
<td>4.03 E-2</td>
</tr>
<tr>
<td>239Pu</td>
<td>2.48 E-4</td>
<td>3.76 E-4</td>
<td>3.85 E-4</td>
</tr>
<tr>
<td>235U</td>
<td>1.84 E-7</td>
<td>8.57 E-7</td>
<td>1.57 E-6</td>
</tr>
<tr>
<td>231Pa</td>
<td>2.17 E-7</td>
<td>4.27 E-6</td>
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</tr>
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<td>240Pu</td>
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<td>1.55 E-4</td>
<td>1.55 E-4</td>
</tr>
<tr>
<td>236U</td>
<td>1.05 E-7</td>
<td>3.24 E-7</td>
<td>3.65 E-7</td>
</tr>
<tr>
<td>232Th</td>
<td>6.01 E-7</td>
<td>5.05 E-5</td>
<td>6.72 E-5</td>
</tr>
<tr>
<td>99Tc</td>
<td>4.20 E-3</td>
<td>4.20 E-3</td>
<td>4.20 E-3</td>
</tr>
</tbody>
</table>

IW = Inventory weighting
PW = Production weighting
Table A1-2: Nuclide release data for inventory and production weighted models, release rates 100'000 and 1'000'000 years after waste preparation.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Release Rate [moles/year] at 10^5 years</th>
<th>Release Rate [moles/year] at 10^6 years</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IW</td>
<td>PW</td>
</tr>
<tr>
<td>245 Cm</td>
<td>1.61 E-8</td>
<td>1.61 E-8</td>
</tr>
<tr>
<td>241 Am</td>
<td>8.63 E-10</td>
<td>8.63 E-10</td>
</tr>
<tr>
<td>237 Np</td>
<td>8.40 E-6</td>
<td>8.40 E-6</td>
</tr>
<tr>
<td>233 U</td>
<td>1.16 E-7</td>
<td>5.83 E-7</td>
</tr>
<tr>
<td>246 Cm</td>
<td>2.58 E-12</td>
<td>2.58 E-12</td>
</tr>
<tr>
<td>242 Pu</td>
<td>1.36 E-4</td>
<td>1.21 E-4</td>
</tr>
<tr>
<td>238 U</td>
<td>9.25 E-6</td>
<td>8.40 E-6</td>
</tr>
<tr>
<td>234 U</td>
<td>1.11 E-8</td>
<td>1.06 E-8</td>
</tr>
<tr>
<td>230 Th</td>
<td>1.80 E-5</td>
<td>4.46 E-6</td>
</tr>
<tr>
<td>226 Ra</td>
<td>9.02 E-5</td>
<td>9.68 E-5</td>
</tr>
<tr>
<td>243 Am</td>
<td>4.84 E-7</td>
<td>4.84 E-7</td>
</tr>
<tr>
<td>239 Pu</td>
<td>2.85 E-4</td>
<td>3.00 E-4</td>
</tr>
<tr>
<td>235 U</td>
<td>8.06 E-7</td>
<td>1.23 E-6</td>
</tr>
<tr>
<td>231 Pa</td>
<td>4.23 E-6</td>
<td>4.23 E-6</td>
</tr>
<tr>
<td>240 Pu</td>
<td>3.79 E-8</td>
<td>3.37 E-8</td>
</tr>
<tr>
<td>236 U</td>
<td>3.18 E-7</td>
<td>2.89 E-7</td>
</tr>
<tr>
<td>232 Th</td>
<td>6.77 E-6</td>
<td>1.40 E-6</td>
</tr>
<tr>
<td>99 Tc</td>
<td>4.20 E-3</td>
<td>4.20 E-3</td>
</tr>
</tbody>
</table>

IW = Inventory weighting  
PW = Production weighting
APPENDIX 2

INTERMEDIATE NUCLIDE SOLIDS PHASE START-UP

Application of l'Hôpital's theorem to the principle of inventory weighing to determine the release rates.

For one isotope i of an element K the release rate calculated from inventory weighting would be:

\[
\dot{R}(i) = \dot{Q} C_{\text{sat}}(K) \frac{M(i)}{\sum_{i} M(i)}
\]  

(A2.1)

Initially no solids may exist, in which case:

\[
M(i) = \sum_{i} M = 0
\]

yet the total production rate:

\[
\sum_{i} \dot{P}(i)
\]

exceeds the carrying capacity of the water:

\[
\sum_{i} \dot{P}(i) > \dot{Q} C_{\text{sat}}(K)
\]

The release rate calculated by inventory weighting is indeterminate.

However, applications of l'Hôpital's rule, in equation form:
\[ \lim_{x \to a} \frac{f_1(x)}{f_2(x)} = \frac{f_1'(a)}{f_2'(a)} \quad \text{when} \quad \frac{f_1(x)}{f_2(x)} = 0 \quad \text{or} \quad \infty \quad \text{at} \quad x = a, \]

leads to a solution, e.g.:

\[ \frac{K}{\sum_i M(i)} \frac{d}{dt} \sum_i M(i) = \sum_i \dot{P}(i) - \dot{Q} C_{\text{sat}}(K) \quad \text{(A2.2)} \]

It should be noted that when \( M = 0 \), there is no decay term to be considered. Also now for each isotope in particular:

\[ \frac{d}{dt} M(i) = \dot{P}(i) - \dot{R}(i) \quad \text{(A2.3)} \]

Applying l'Hôpital's rule to (A1.1), we obtain:

\[ \dot{R}(i) = \dot{Q} C_{\text{sat}}(K) \frac{d M(i)/dt}{\sum_i M(i)/dt} \quad \text{(A2.4)} \]

Now, substituting from (A1.2) and (A1.4) into (A1.3) and rearranging:

\[ \frac{d}{dt} M(i) = \dot{P}(i) - \dot{R}(i) = \dot{P}(i) - \dot{Q} C_{\text{sat}}(K) \frac{\sum_i P(i)}{K} \quad \text{(A2.5)} \]

whence:

\[ \dot{R}(i) = \dot{Q} C_{\text{sat}}(K) \frac{\sum_i \dot{P}(i)}{K} \quad \text{(A2.6)} \]

This corresponds to production rate weighting of the available solubility.
A.3.1 Last Nuclide in Chain Non-Decaying

By raising the half-life of the last nuclide in the chain to a very large value (1.0 E+30 years) then the molal balance for the chain may be written:

\[
\text{chain} \sum_i \text{inventories} + \sum_i \int_{t_{\text{start}}}^{t_{\text{end}}} \dot{R} \, dt
\]

This sum must be a constant independent of time.

At one million years discrepancies in the seventh significant figure can be seen in the \(^{247}\text{Cm}\) chain in Table A3-1, below:

Table A3-1: Overall mass balances of the actinide decay chains

<table>
<thead>
<tr>
<th>Chain</th>
<th>Time [years]</th>
<th>1000.0 [moles overall]</th>
<th>1.019117912 E+06 [moles overall]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{245}\text{Cm})</td>
<td>2.2743989 E+4</td>
<td>2.2743989 E+4</td>
<td></td>
</tr>
<tr>
<td>(^{246}\text{Cm})</td>
<td>4.7114921 E+4</td>
<td>4.7114922 E+4</td>
<td></td>
</tr>
<tr>
<td>(^{247}\text{Cm})</td>
<td>4.7395912 E+3</td>
<td>4.7395921 E+3</td>
<td></td>
</tr>
<tr>
<td>(^{248}\text{Cm})</td>
<td>1.6176191 E+3</td>
<td>1.6176191 E+3</td>
<td></td>
</tr>
</tbody>
</table>

It will be seen that the first figure, in which a difference occurs between the two columns is underlined in each case. The same procedure is employed in all subsequent tables in this Appendix.
A3.2 All Nuclides Non-Decaying

This test allows individual mass balances to be examined. A further check is possible since the release-rates for solubility sharing nuclides must be constant and time-independent. A first order Euler integration would give exact results for the solubility-limited nuclides, although the dissolution rate-controlled isotopes require a high order integration method. To the five significant figures printed on the computer output, there are no noticeable discrepancies, either in the inventories or in the release-rates.

From the mass balance (Table A3-2) at one million years we see that agreement is exact to at least eight significant figures for the nuclides with solubility-controlled release, whilst the remainder having dissolution rate-controlled release, i.e. the nine nuclides $^{245}$Cm, $^{246}$Cm, $^{241}$Am, $^{243}$Am, $^{229}$Th, $^{230}$Th, $^{232}$Th, $^{226}$Ra and $^{231}$Pa, all show the same discrepancy of $-0.000741\%$ in the mass balance, less being released than was originally present. Although this is thus not a conservative error, its magnitude is small enough to be neglected.
Table A3-2: Mass balances - all nuclides assumed stable

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Moles remaining A</th>
<th>Moles released B</th>
<th>Total moles (A + B)</th>
<th>Total moles at overpack failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>245_{Cm}</td>
<td>0</td>
<td>20.361179</td>
<td>20.361179</td>
<td>20.361330</td>
</tr>
<tr>
<td>241_{Am}</td>
<td>0</td>
<td>1595.76467</td>
<td>1595.7647</td>
<td>1595.7765</td>
</tr>
<tr>
<td>237_{Np}</td>
<td>21078.8625</td>
<td>42.9225486</td>
<td>21121.785</td>
<td>21121.785</td>
</tr>
<tr>
<td>233_{U}</td>
<td>5.91968646</td>
<td>0.134478539</td>
<td>6.0541650</td>
<td>6.0541650</td>
</tr>
<tr>
<td>229_{Th}</td>
<td>0</td>
<td>0.0121436100</td>
<td>0.012143610</td>
<td>0.012143700</td>
</tr>
<tr>
<td>246_{Cm}</td>
<td>0</td>
<td>2.02609648</td>
<td>2.0260965</td>
<td>2.0261115</td>
</tr>
<tr>
<td>242_{Pu}</td>
<td>-3.882 E-08</td>
<td>132.637500</td>
<td>132.63750</td>
<td>132.63750</td>
</tr>
<tr>
<td>238_{U}</td>
<td>45864.6009</td>
<td>1041.91406</td>
<td>46906.515</td>
<td>46906.515</td>
</tr>
<tr>
<td>234_{U}</td>
<td>71.8201493</td>
<td>1.63155073</td>
<td>73.451700</td>
<td>73.451700</td>
</tr>
<tr>
<td>230_{Th}</td>
<td>0</td>
<td>0.289147607</td>
<td>0.28914761</td>
<td>0.28914975</td>
</tr>
<tr>
<td>226_{Ra}</td>
<td>0</td>
<td>0.00143129539</td>
<td>0.0014312954</td>
<td>0.0014313060</td>
</tr>
<tr>
<td>243_{Am}</td>
<td>0</td>
<td>2080.91958</td>
<td>2080.9196</td>
<td>2080.9250</td>
</tr>
<tr>
<td>239_{Pu}</td>
<td>-5.314 E-07</td>
<td>1815.66000</td>
<td>1815.6600</td>
<td>1815.6600</td>
</tr>
<tr>
<td>235_{U}</td>
<td>824.260140</td>
<td>18.7248599</td>
<td>842.98500</td>
<td>842.98500</td>
</tr>
<tr>
<td>231_{Pa}</td>
<td>0</td>
<td>0.011200417</td>
<td>0.011200417</td>
<td>0.011200500</td>
</tr>
<tr>
<td>240_{Pu}</td>
<td>-3.330 E-07</td>
<td>1137.73500</td>
<td>1137.7350</td>
<td>1137.7350</td>
</tr>
<tr>
<td>236_{U}</td>
<td>469.194234</td>
<td>10.6587664</td>
<td>479.85300</td>
<td>479.85300</td>
</tr>
<tr>
<td>232_{Th}</td>
<td>0</td>
<td>0.0310664197</td>
<td>0.03106642</td>
<td>0.031066650</td>
</tr>
<tr>
<td>99_{Tc}</td>
<td>-5.115 E-05</td>
<td>61602.7501</td>
<td>61602.750</td>
<td>61602.750</td>
</tr>
</tbody>
</table>
A3.3 Effect of Truncation Error Control

Safety calculations are made routinely with a truncation error of $1.0 \times 10^{-07}$ and a maximum step size.

Repeat test calculations using truncation errors of $1.0 \times 10^{-06}$ and $1.0 \times 10^{-08}$ to a time of one million years show agreement to eight significant figures in the inventory levels (calculated with a 6th order integration and error control) with an error of one part per hundred thousand in the total moles released, a quantity calculated without error control and with 4th order integration. (See Table A3-3).

Conservative solubilities (see Chapter 4, Table 4-2) were used and the time of one million years chosen as being sufficiently large to allow any build-up of errors to be noticed and also as being beyond the matrix life span.

Thus, errors due to the integration of the differential equations may be neglected in comparison with other sources of error.
Table A3-3: Comparison Table - Effect of Truncation Error

Time = 1.019117912 E+06 years

<table>
<thead>
<tr>
<th>Truncation Error</th>
<th>1.0 E-06 Coarse</th>
<th>1.0 E-07 Normal</th>
<th>1.0 E-08 Fine</th>
</tr>
</thead>
<tbody>
<tr>
<td>245 Cm INV REL</td>
<td>4.12319932 E+00</td>
<td>4.12320418 E+00</td>
<td>4.12320558 E+00</td>
</tr>
<tr>
<td>241 Am INV REL</td>
<td>1.92826024 E+01</td>
<td>1.92829692 E+01</td>
<td>1.92830814 E+01</td>
</tr>
<tr>
<td>237 Np INV REL</td>
<td>1.62976176 E+04</td>
<td>1.62976176 E+04</td>
<td>1.62976176 E+04</td>
</tr>
<tr>
<td>233 U INV REL</td>
<td>2.30487891 E+01</td>
<td>2.30487891 E+01</td>
<td>2.30487891 E+01</td>
</tr>
<tr>
<td>229 Th INV REL</td>
<td>5.04794323 E+03</td>
<td>5.04794323 E+03</td>
<td>5.04784323 E+03</td>
</tr>
<tr>
<td>246 Cm INV REL</td>
<td>2.44734956 E-01</td>
<td>2.44735800 E-01</td>
<td>2.44736049 E-01</td>
</tr>
<tr>
<td>242 Pu INV REL</td>
<td>-9.81206122 E-04</td>
<td>-1.02558931 E-03</td>
<td>-9.93453156 E-04</td>
</tr>
<tr>
<td>238 U INV REL</td>
<td>1.13556471 E+02</td>
<td>1.13556457 E+02</td>
<td>1.13556412 E+02</td>
</tr>
<tr>
<td>234 U INV REL</td>
<td>9.37564811 E+02</td>
<td>9.37564811 E+02</td>
<td>9.37564811 E+02</td>
</tr>
<tr>
<td>230 Th INV REL</td>
<td>6.41910770 E+00</td>
<td>6.41910770 E+00</td>
<td>6.41910770 E+00</td>
</tr>
<tr>
<td>226 Ra INV REL</td>
<td>5.19430987 E-01</td>
<td>5.19430987 E-01</td>
<td>5.19430987 E-01</td>
</tr>
</tbody>
</table>

INV = Total inventory M at time specified [moles]
REL = Total amount released at time specified [moles]
Table A3-3: (continued)

Time = 1.019117912 E+06 years

<table>
<thead>
<tr>
<th>Truncation</th>
<th>1.0 E-06</th>
<th>1.0 E-07</th>
<th>1.0 E-08</th>
</tr>
</thead>
<tbody>
<tr>
<td>Error</td>
<td>Coarse</td>
<td>Normal</td>
<td>Fine</td>
</tr>
<tr>
<td>243 Am INV</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>REL</td>
<td>3.73465578 E+02</td>
<td>3.73466161 E+02</td>
<td>3.73466329 E+02</td>
</tr>
<tr>
<td>239 Pu INV</td>
<td>-1.10761345 E-03</td>
<td>-1.15840914 E-03</td>
<td>-1.12183595 E-03</td>
</tr>
<tr>
<td>REL</td>
<td>4.20206041 E+02</td>
<td>4.20206191 E+02</td>
<td>4.20206168 E+02</td>
</tr>
<tr>
<td>235 U INV</td>
<td>3.86544982 E+03</td>
<td>3.86544980 E+03</td>
<td>3.86544981 E+03</td>
</tr>
<tr>
<td>REL</td>
<td>7.66370685 E+01</td>
<td>7.66370684 E+01</td>
<td>7.66370685 E+01</td>
</tr>
<tr>
<td>231 Pa INV</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>REL</td>
<td>3.78974075 E+00</td>
<td>3.78974075 E+00</td>
<td>3.78974075 E+00</td>
</tr>
<tr>
<td>240 Pu INV</td>
<td>-9.80417801 E-09</td>
<td>-1.04670269 E-08</td>
<td>-9.98539006 E-09</td>
</tr>
<tr>
<td>REL</td>
<td>1.82645587 E+01</td>
<td>1.82645316 E+01</td>
<td>1.82645237 E+01</td>
</tr>
<tr>
<td>236 U INV</td>
<td>1.52136119 E+03</td>
<td>1.52136119 E+03</td>
<td>1.52136119 E+03</td>
</tr>
<tr>
<td>REL</td>
<td>3.12537081 E+01</td>
<td>3.12537083 E+01</td>
<td>3.12537084 E+01</td>
</tr>
<tr>
<td>232 Th INV</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>REL</td>
<td>4.67396488 E+00</td>
<td>4.67396490 E+01</td>
<td>4.67396491 E+01</td>
</tr>
<tr>
<td>99 Tc INV</td>
<td>-4.18569523 E-05</td>
<td>-4.18569523 E-05</td>
<td>-4.18569523 E-05</td>
</tr>
<tr>
<td>REL</td>
<td>4.32486257 E+04</td>
<td>4.32486257 E+04</td>
<td>4.32486257 E+04</td>
</tr>
</tbody>
</table>

INV Inventory [moles] 6th order method with error control
REL Amount released [moles] 4th order method, no error control
A3.4 Pure Radioactive Decay, No Water Flow Past Repository

For the case of zero water flow past the repository or totally insoluble nuclides, the equations simplify to those of pure radioactive chain decay: the Bateman equations, with a known analytic solution, [6].

Numerical results were compared with the analytical solutions at a time of 300'000 years. Agreement was to about eleven significant figures compared with the starting inventory as shown in Table A3-4.

The analytic solutions were calculated using programme BATEM, [4].
Table A3-4: Radioactive Chain Decay (Bateman)

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Initial inventory [1000 years]</th>
<th>Inventory at 302441.8021 years Numerical</th>
<th>Analytic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{245}$Cm</td>
<td>20.36133</td>
<td>4.2968865 E-10</td>
<td>4.2969096 E-10</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>1595.7765</td>
<td>2.3018844 E-11</td>
<td>2.3018968 E-11</td>
</tr>
<tr>
<td>$^{237}$Np</td>
<td>21121.785</td>
<td>20623.164</td>
<td>20623.164</td>
</tr>
<tr>
<td>$^{233}$U</td>
<td>6.054165</td>
<td>1167.1452</td>
<td>1167.1452</td>
</tr>
<tr>
<td>$^{229}$Th</td>
<td>0.0121437</td>
<td>52.982090</td>
<td>52.982090</td>
</tr>
<tr>
<td>$^{246}$Cm</td>
<td>2.0261115</td>
<td>1.3255487 E-19</td>
<td>1.3246209 E-19</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>132.6375</td>
<td>77.301514</td>
<td>77.301514</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>46906.515</td>
<td>46961.682</td>
<td>46961.682</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>73.4517</td>
<td>32.782528</td>
<td>32.782528</td>
</tr>
<tr>
<td>$^{230}$Th</td>
<td>0.28914975</td>
<td>12.215217</td>
<td>12.215217</td>
</tr>
<tr>
<td>$^{226}$Ra</td>
<td>0.001431306</td>
<td>0.26022944</td>
<td>0.26022944</td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td>2080.935</td>
<td>1.0530528 E-9</td>
<td>1.0530664 E-9</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>1815.66</td>
<td>0.83244808</td>
<td>0.83244809</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>842.985</td>
<td>4737.4960</td>
<td>4737.4960</td>
</tr>
<tr>
<td>$^{231}$Pa</td>
<td>0.0112005</td>
<td>0.21927774</td>
<td>0.21927774</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>1137.735</td>
<td>1.4947941 E-11</td>
<td>1.4948351 E-11</td>
</tr>
<tr>
<td>$^{236}$U</td>
<td>479.853</td>
<td>1603.5356</td>
<td>1603.5356</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>0.03106665</td>
<td>14.083397</td>
<td>14.083397</td>
</tr>
<tr>
<td>$^{99}$Tc</td>
<td>61602.75</td>
<td>23098.114</td>
<td>23098.114</td>
</tr>
</tbody>
</table>
A3.5 Pure Matrix Dissolution

For a very large water flow rate or very high nuclide solubilities, all the nuclides will be removed in solution by the flowing water as fast as the retaining glass matrix is removed. In this case the process simplifies to dissolution alone, with no intermediate solid phase being formed.

For congruent dissolution from a sphere, (Chapter 2), the ordinary differential equations may be integrated analytically, and the analytical solution compared with that obtained by numerical integration.

Analytic Solution for First and Second Nuclides in a Chain, Dissolution Only

For the dissolution model, under the conditions described above, we may write the rate of setting free of any nuclide as:

\[ \dot{\nu} = \frac{3N}{\tau(1 - t/\tau)} \]  \hspace{1cm} (A3.1)

The O.D.E. for the first nuclide in the chain may be written:

\[ \frac{dN^*}{dt} = -\lambda N^* - \frac{3N^*}{\tau(1 - t/\tau)} \]  \hspace{1cm} (A3.2)

(A linear differential equation)

with initial condition \( t = 0, N^* = N^*_0 \) and solution:

\[ N^*_t = N^*_0 e^{-\lambda t}(1 - t/\tau)^3 \]  \hspace{1cm} (A3.3)

The O.D.E. for the 2nd nuclide in the chain becomes:

\[ \frac{dN}{dt} = -\lambda N + \lambda N^* - \frac{3N}{\tau(1 - t/\tau)} \]  \hspace{1cm} (A3.4)
(again a linear equation)

With the initial condition \( t = 0, N = N_0, N^* = N^*_0 \) this may be integrated to give:

\[
N_t = (1 - t/\tau)^3 e^{-\lambda t} \left\{ N_0 + \frac{\lambda^* N^*_0}{(\lambda - \lambda^*)} [e^{(\lambda - \lambda^*) t} - 1] \right\}
\]  

(A3.5)

Equations A3.3 and A3.5 describe the nuclide inventory as a function of time for the first and second nuclides of a decay chain respectively.

The values predicted by these analytical equations are compared with the numerical solutions at a time of 100894.3521 years in the following table:

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Runge-Kutta (EPS = 1.0 E-7)</th>
<th>Analytic</th>
</tr>
</thead>
<tbody>
<tr>
<td>245\text{Cm}</td>
<td>2.6742282 E-4</td>
<td>2.6742338 E-4</td>
</tr>
<tr>
<td>241\text{Am}</td>
<td>1.4326104 E-5</td>
<td>1.4326134 E-5</td>
</tr>
<tr>
<td>246\text{Cm}</td>
<td>4.0297942 E-8</td>
<td>4.0299307 E-8</td>
</tr>
<tr>
<td>242\text{Pu}</td>
<td>5.0769355 E+0</td>
<td>5.0769355 E+0</td>
</tr>
<tr>
<td>243\text{Am}</td>
<td>7.9387109 E-3</td>
<td>7.9387423 E-3</td>
</tr>
<tr>
<td>239\text{Pu}</td>
<td>1.2346725 E+1</td>
<td>1.2346726 E+1</td>
</tr>
<tr>
<td>240\text{Pu}</td>
<td>1.2943947 E-3</td>
<td>1.2944037 E-3</td>
</tr>
<tr>
<td>236\text{U}</td>
<td>7.3087406 E+1</td>
<td>7.3087406 E+1</td>
</tr>
<tr>
<td>99\text{Tc}</td>
<td>2.0165167 E+3</td>
<td>2.0165167 E+3</td>
</tr>
</tbody>
</table>

Examination of Table A3-5 reveals a maximum error of \( \pm 1 \) digit in the fifth significant figure after 100'000 years, or about 10 significant figures when compared with the initial inventory.