REVERSE ENGINEERING OF GETTER

A FISSION PRODUCT RELEASE CODE FOR PBMR

J B Keshaw BSc (Hons), MSc

Dissertation submitted in partial fulfilment of the requirements for the degree of Master of Science in Nuclear Engineering at the Potchefstroom Campus of the North-West University

Supervisor: Hanno van der Merwe

November 2007

ABSTRACT

Fission product release from spherical fuel spheres under different irradiation and heat-up conditions is one of the key criteria used in High Temperature Reactor (HTR) design. Accurate analyses of fuel performance and fission product behaviour is therefore essential in justifying the safe behaviour of the Pebble Bed Modular Reactor (PBMR). GETTER proved to be a very versatile tool for evaluating fission product transport problems; ranging from heating experiments (up to 1 800°C) to full core analyses under operating and accident conditions.

GETTER includes subroutines, which calculate the burnup and power history of a fuel sphere in the core, and the temperature distribution in the sphere based on given neutron cross-sections and gas temperatures. These values are then used to determine fission product inventories in the fuel materials. Transport through the coating layers of TRISO-particles, graphitic matrix material, and into the coolant gas are based on Ficks' laws of diffusion and evaporative mass transfer.

A description is given of the physical laws and correlations used by GETTER to simulate fission product, activation product, or heavy metal migration in spherical HTR fuel elements. Reverse engineering of GETTER was carried out to obtain the mathematical derivations from these laws to the equations that were implementated in the source code of GETTER. In addition, some important anomalies regarding the derivations and implementation in the code are presented in this document; together with suggested resolution mechanisms in certain cases. The flow of theory implementation in the code is also discussed briefly.

Declaration

I, the undersigned, hereby declare that the work contained in this project is my own original work.

Jeetesh Bhana Keshaw

Date: 22 November 2007

Centurion

Preface

The outcome and results of the reverse engineering presented in this work was done as part of the PBMR company effort at verifying the software used for fission product transport. Much of this work is repeated, partially in a conference proceeding [1], or in greater detail in official PBMR documentation [2], [3], [4].

Due to several reasons, one being an underestimation of the magnitude of this exercise from the planning stages, it has taken about two years to complete the work, double the estimated time required. As a result, time spent on this work exceeds the requirements for a mini-dissertation, and the volume of work presented here is only a fraction (~25%) of the total documentation of the reverse engineering effort. However, it is hoped that the information reported in this document be self-consistent and sufficient to understand the theory employed by GETTER.

One of the key outcomes of this work was the realisation that a large amount of effort would be required to fully verify the legacy code GETTER. It may be more efficient to develop a new code, based on the same theory principles (and perhaps newer ones), but coded in a modern, modular way. This will allow verification of individual modules on a test bases, in line with future software verification procedures in development at PBMR.

Acknowledgments

Mr Hanno van der Merwe, under whom this work was done, for his patience and assistance.

Pebble Bed Modular Reactor (Pty) Ltd, for the use of their facilities and sponsorship for the MSc. degree.

CONTENTS

FIGURES

TABLES

ABBREVIATIONS

This list contains the abbreviations used in this document.

Abbreviation or Acronym	Definition
BISO	Binary Coated Particle (fuel particle with two coatings of PyC)
FIMA	Fissions per Initial Metal Atom
HTI	High-temperature Isotropic
HTR	High-temperature Reactor
KTA	Kerntechnischer Ausschuss (German Nuclear Safety Standards Commission)
PBMR	Pebble Bed Modular Reactor
PyC	Pyrolytic Carbon
Re	Reynolds number
SiC	Silicon Carbide
TRISO	Triple Coated Isotropic Particle

DEFINITIONS

Word or phrase	Definition
Heavy Metal	A metal of relatively high mass number, in this case greater than 230 atomic mass units per nuclide. e.g. U-233, U-235, Pu-239.
Legacy Code	Computer codes developed decades ago, in the old computer languages, and still in use today.
Reverse Engineering of Software	The process using a software programme's source code to trace back its origins to fundamental physical theories, models and correlations.

1. INTRODUCTION

1.1 BACKGROUND

Graphite fuel with embedded TRISO particles have been used successfully in high temperature reactors for the past four decades [7]. This fuel arrangement has demonstrated good fission product retention capability during normal modes of operation and accident conditions for burnups of up to 12% FIMA [7].

However, not all manufactured fuel is of the same quality and variations in operating conditions of a nuclear power plant cannot easily be taken into account without justifiable calculations. In the event of fuel being subjected to extreme conditions (beyond fuel design intent), increased fission product release rates could present a radiological hazard for plant personnel during operation and maintenance of the plant. This is more important for direct cycle high temperature reactors, such as the PBMR [8] , because excess metallic fission product would plate out on primary system components, making maintenance difficult, and in some cases impossible.

For metallic fission product release calculations, PBMR uses a German legacy programme called GETTER [9], which was acquired from Westinghouse Reaktor GmbH in 2001. It was originally developed and used by the German utility consortium HRB (Hochtemperatur Reaktorbau) during the German HTR programme.

FRESCO II [10] is another fission product release programme developed at Forschungszentrum Jülich, Germany during the German HTR programme. It would later be used towards the validation of GETTER.

GETTER calculates metallic fission product release from a single spherical fuel sphere. This sphere may be exposed to a variety of conditions, simulating many possible scenarios such as normal operation cores, accident condition cores, irradiation tests, and post irradiation heat-up tests. For the first two conditions, two methods could be used to calculate the total core release, namely

- a single “typical” sphere release is calculated and scaled to represent all the pebbles in the core,
- many random sphere releases are calculated (each being a single GETTER run), averaged, and scaled to represent all the pebbles in the core.

Irradiation and post irradiation test simulations are done by using a single sphere calculation with conditions defined by the test.

Being a legacy programme, GETTER had not been well documented and hence it was necessary to reverse engineer its Fortran 77 source code in order to understand its theoretical base and algorithms. The base and algorithms are summarized in this work, together with details about current validation status, and future plans for validation and model improvement.

1.2 PURPOSE

Metallic fission product release from Pebble Bed Modular Reactor (PBMR) fuel presents a safety hazard and operational problem. When radioactive metallic fission products (e.g. ^{137}Cs, ^{90}Sr, ^{110m}Ag) are released from spherical fuel elements into the helium coolant gas, they can contaminate major components of the primary system; such as the turbine and recuperator. Build-up of radioactive contaminants increase the radioactivity of these primary components such that they may eventually become very difficult or impossible to maintain without violating radiation safety limits imposed on plant personnel. Another safety aspect is that of an accident which exposes the primary system to the environment. In this case, metallic fission products could contaminate the plant building, installation site and even the surrounding "green" areas.

In the light of these safety and operational issues, it is important that the PBMR company is able to quantitatively estimate the contribution that metallic fission product release has on the radiological safety of the plant. If these estimations predict unsafe radiological scenarios, then further planning and construction of the plant would be a very risky project for all stakeholders. Estimations on the radiological impact of the PBMR are an integral part of the PBMR safety justification to the National Nuclear Regulator (NNR), the authority that issues licenses to construct and operate the plant. In addition, if they predict sufficiently low radiation release under all conditions of operation and design based accidents, then the risk for stakeholders would be reduced.

It is important for all stakeholders (NNR, PBMR, and ESKOM) that the techniques used at obtaining these estimations are justified as scientifically acceptable. At the PBMR, calculations are used to estimate fission product release. For this technique, the NNR describes the requirements in a Requirements Document [11], which basically outlines the extent of verification and validation necessary for all safety calculations. In brief, the process of verification [11] includes demonstrating the

- scientific applicability of all physical models and correlations used in the calculation,
- correct mathematical treatment and implementation of physical models and correlations in the calculation,
- clearly defined origin of each data item within the plant documentation,
- claim to conservatism of calculations which are described as pessimistic,
- overall modeling uncertainty due to neglect or simplification of phenomena.

The process of validation on the other hand involves showing that the calculation (or parts of it) yields similar results to that of benchmark physical experiments or validated calculations. For the case of metallic fission product release calculations, there is no known source of benchmark calculations, however, there exists some past experiments [7], and future planned experiments that could be used towards validation.

Most of the theoretical knowledge and understanding of fission product release mechanisms from spherical High Temperature Reactor (HTR) fuel was acquired during the German HTR research programme in the 70s and 80s. However, most of it was trade secret and hence was not documented openly or published in international journals. Also most experts in the field have since retired or embarked on research in other fields. It is therefore not easy to acquire detailed information on fission product release models, making it difficult to develop new calculation techniques.

Fortunately, PBMR obtained GETTER, a legacy Fortran 77 programme, which can calculate metallic fission product release from the reactor core. It does this by calculating the release from a single "typical" fuel sphere, and scales the result in order to estimate the total core release. The GETTER model employs equations and correlations from various disciplines of science and engineering; such as thermal hydraulics, nuclear physics, and mass transfer. This software was purchased together with its programme description manual [9] from Westinghouse (Germany) during 2001. Unfortunately, the accompanying documentation is not up to the standard required for verification [11], and hence a project was established to verify and validate the software.

This project is part of the verification and validation effort, more specifically the verification aspect of it. As the software has already been developed, the verification will take place by extracting and justifying all correlations and physical model solutions used in the Fortran 77 code. This is contrary to the usual way of software development (provides a typical flow for calculation software design), and hence it can be referred to as the **reverse engineering** of the software.

Obtaining all physical models and correlations from the software would also serve as a baseline for development of later calculation models. For example, later models could incorporate other mechanisms of fission product transport not covered in the current software.

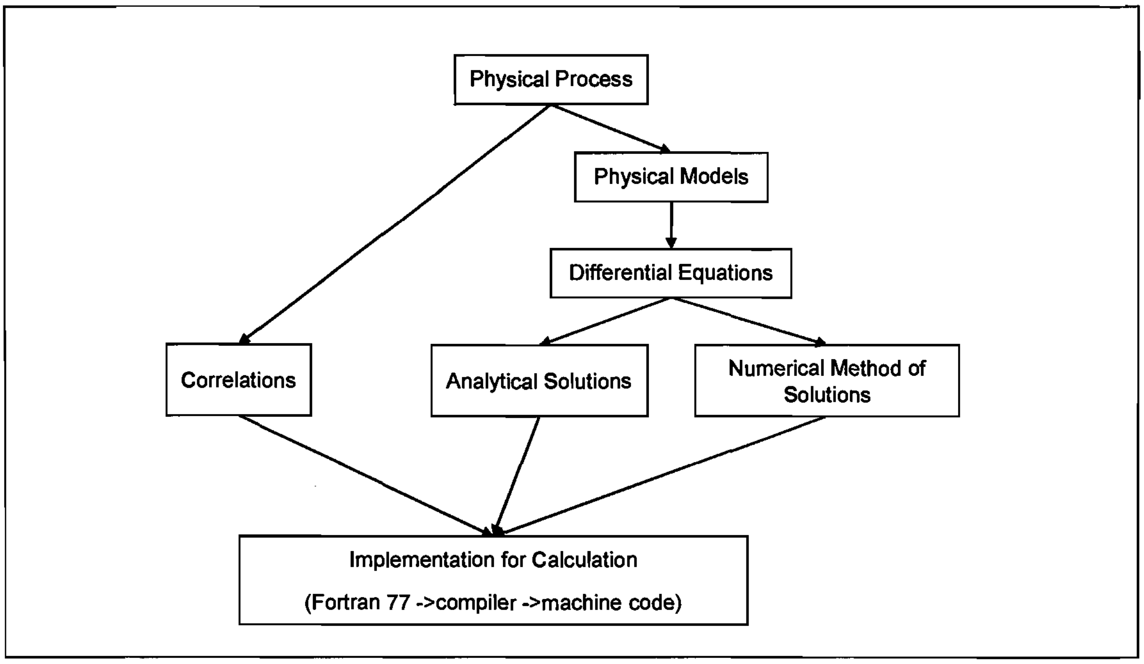


Figure 1: Diagrammatic representation of the level of abstraction to be used for reverse engineering of GETTER.

In summary, reverse engineering of GETTER will serve three key purposes, namely, it will

- form part of the verification effort to meet NNR requirements,
- aid in identifying bugs and anomalies in the code,
- provide the baseline for development of improved metallic fission product release models to be implemented at a later stage of the PBMR project.

The purpose of this work is to present a detailed description of the theory employed by the software programme GETTER in order to calculate material release from a spherical high temperature reactor (HTR) fuel element. The physical laws and/or correlations used by GETTER are discussed, together with details regarding their mathematical treatment and derivation for implementation in the code.

Being a legacy software product, it was necessary to reverse engineer GETTER's Fortran 77 source code in order to obtain this information. Anomalies encountered in this process are also discussed.

1.3 SCOPE

The scope of this document is to

a. Describe the physical models and correlations employed by GETTER,
b. Demonstrate the mathematical treatment of these for implementation in the code,
c. Discuss anomalies and topics requiring further investigation.

2. MODELLING POSSIBILITIES

GETTER is able to calculate the material release from spherical HTR fuel elements exposed to a variety of environments. It needs to be flexible with regard to the

1. materials transported,
2. spherical fuel element types, and
3. environmental conditions to which the element is exposed to.

Examples of a few possibilities for each of these three options are given in Table 1.

Table 1: Some options for GETTER calculation of material release from an HTR fuel Element

Material types	Spherical Fuel Element types	Environment types
• Fission products (^{131}I, ^{90}Sr, etc.) • Activation products (^{110m}Ag, ^{134}Cs) • Heavy metals (^{235}U, ^{238}U, ^{241}Pu, etc.) • Noble metals (^{109}Ag) • Any isotope of long half life (>5 days), with known diffusion parameters in fuel materials	• BISO particle based fuel • TRISO particle based fuel • Advanced particle fuel designs • A3-3 graphite matrix fuel • A3-27 graphite matrix fuel • Any spherical fuel element type whose material properties are known	• PBMR core • Past German reactor Core • Fuel test rig in a research reactor core • Pre-irradiation heat-up furnace • Post-irradiation heat-up furnace • Storage tanks • Final disposal sites • Any environment whose conditions are known

As can be seen from Table 1, many different material release calculations can be done using GETTER. However, for the current scope of analyses at PBMR, only a few of these are required in the near future, all of which are based on TRISO fuel, namely

a. Fission or activation product release (^{110m}Ag, ^{90}Sr, ^{131}I, ^{137}Cs, ^{134}Cs, ^{111}Ag, ^{136}Cs, ^{134}Cs) from fuel consisting of an A3-3 graphite matrix, and exposed to conditions of the PBMR core.

b. Fission product release (^{110m}Ag, ^{90}Sr, ^{137}Cs, ^{134}Cs) from fuel consisting of an A3-3 or A3-27 graphite matrix, and exposed to conditions of a fuel test rig in a research reactor core and/or post-irradiation heat-up furnace.

c. Fission product release (^{110m}Ag, ^{90}Sr, ^{131}I, ^{137}Cs) from fuel consisting of an A3-3 or A3-27 graphite matrix, and exposed to conditions of past German reactor cores and/or post-irradiation heat-up furnaces.

d. Noble metal release (^{109}Ag) from fuel consisting of an A3-3 graphite matrix, and exposed to conditions a pre-irradiation heat-up furnace.

Further details of these calculations and applications of GETTER are beyond the scope of this work and are described elsewhere [12], [13].

3. MODELLING DESCRIPTION

The main process of material transport through the spherical fuel element, used in GETTER, is diffusion, but several other processes such as fission product recoil are also present. A discussion is presented of all the physical models used by GETTER, these include those obtained from physical laws and correlations.

3.1 PHYSICAL PROCESS

Several physical processes are simulated by GETTER. These are outlined below, and detailed derivations from these are made in section 3.2.

3.1.1 Fission, Decay and Transmutation

The decay and transmutation chains (for nuclear reactor fuel) are well known [5], and summarized diagrammatically in Figure 2. Calculation of the fuel sphere's heavy metal inventory is most efficiently done by using transmutation and decay chains of the nuclides that contribute to fission product and power production; namely the fissile nuclides ^{233}U, ^{235}U, ^{239}U, ^{239}Pu, and ^{241}Pu. Simplifying the chain by removing the irrelevant nuclei and eliminating relatively short-lived isotopes yields the modified chains illustrated in Figure 3.

This simplification needs to be validated correctly, as there exists some problems, for example, it ignores the large absorption cross section ^{233}Th, at about 1000barns, which can reduce the yield of ^{233}Pa and hence ^{233}U. This effect needs to be assessed, and is recorded as an **anomaly** that needs resolution.

The time dependence of each nuclide in the chain can be determined from Bateman equations [14] of the form,

$$\frac{dN_i}{dt} = \phi y_{i,i-1}\sigma_{c,i-1}N_{i-1} + \lambda_p v_{i,p} N_p - \lambda_i N_i - \phi\sigma_{f,i}N_i - \phi\sigma_{c,i}N_i \qquad (3.1)$$

where

N_i = number of nuclei i (atoms),

ϕ = neutron flux (neutrons.cm^{-2}.s^{-1}),

$y_{i,i-1}$ = yield of nuclide i from neutron capture by nuclide $i-1$ (number of nuclei i per capture by nuclide $i-1$),

$\sigma_{c,i-1}$ = capture cross-section of nuclide $i-1$ (cm^2),

N_{i-1} = number of nuclei $i-1$ (atoms),

λ_p = decay constant of nuclide p (s^{-1}),

$v_{i,p}$ = yield of nuclide i from decay of nuclide p (number of nuclei i per decay of nuclide p),

N_p = number of nuclei p (atoms),

λ_i = decay constant of nuclide i (s^{-1}),

$\sigma_{f,i}$ = fission cross-section of nuclide i (cm^2), and

$\sigma_{c,i}$ = capture cross-section of nuclide i (cm^2).

It was necessary to use non standard characters for yield, namely $y_{i,i-1}$ and $v_{i,p}$, due to requirements of other characters in later sections.

Together these make up a set of coupled differential equations, the analytical solution of which is used to calculate the following parameters at the end of each time interval:

- N_i for the heavy metals, i.e. heavy metal inventory of the fuel sphere,
- B_i'' - the number of fissions from fissile nuclide i per initial metal atom,
- B_T'' - the FIMA (Fissions per Initial Metal Atom), from $B_T'' = \sum_i B_i''$ (3.2)

Details of these solutions are given in section 3.2.1.

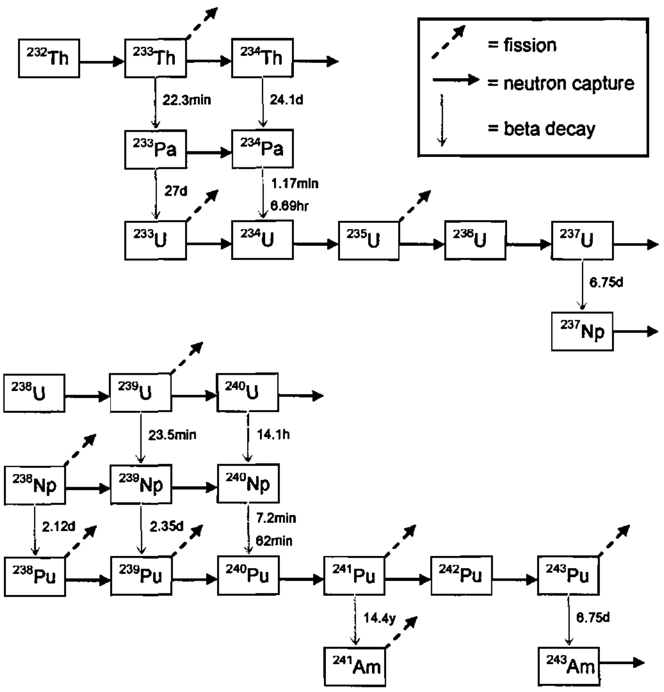


Figure 2: Detailed nuclide decay and transmutation chains for heavy metal nuclear reactor fuel. Adapted from Stacey [5]

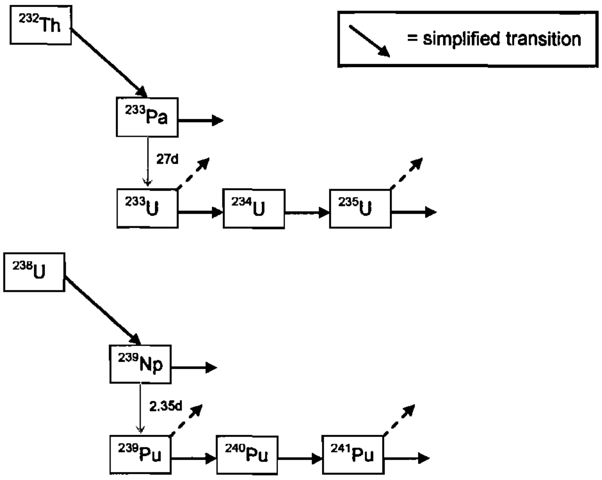


Figure 3: Simplified nuclide decay and transmutation chains for heavy metal nuclear reactor fuel. Adapted from Stacey [5]

3.1.2 Power and Fission Product Production

The average power $\dot{Q}_{av}$ of the sphere during the time interval is calculated by the relation

$$\dot{Q}_{av} = \frac{B_T^u \cdot N_{HM}^0 \cdot E_f}{\tau}, \tag{3.3}$$

where

N_{HM}^0 = initial number of heavy metal atoms (atoms),

$\dot{Q}_{av}$ = average power produced in sphere over time interval (W),

E_f = average energy per fission (J/fission), and

τ = length of time interval (s).

Direct (Y_{FD}) and cumulative (Y_{FC}) yield fractions of the fission product are weighted according to the yield from the fissile nuclides

$$Y_{FD} = \frac{\sum_i \gamma_i B_i^u}{B_T^u}, \tag{3.4}$$

$$Y_{FC} = \frac{\sum_i \Gamma_i B_i^u}{B_T^u}, \tag{3.5}$$

where

γ_i = direct fission yield of fission product from fissile nuclide i,

Γ_i = cumulative fission yield of fission product from fissile nuclide i.

Hence the corresponding average fission product production rates, over the time interval, are

$$W_{p,D} = \frac{B_T^u \cdot N_{HM}^0 \cdot Y_{FD}}{\tau}, \tag{3.6}$$

$$W_{p,C} = \frac{B_T^u \cdot N_{HM}^0 \cdot Y_{FC}}{\tau}, \tag{3.7}$$

for direct and cumulative yield respectively. These rates are proportioned to calculate the production rate from the fuel kernels and/or contamination (see section 3.2.5).

The time dependence of fission product content is taken into account using analytical solutions of equations of the form given by equation (3.1), where the production rate is given by equations (3.6) and (3.7).

3.1.3 Fission Product Recoil

Recoil of fission product adds to the fission product source rate in

- the coating layers of the the TRISO particle, and
- the fuel zone matrix material.

The origin of this recoil is from the UO_2 kernels, and uranium contamination of the coating layers of the coated particle. Recoil also reduces the fission product source rate in the regions they originate from.

Assuming a simplified geometric model of the recoil, where recoil is assumed to be isotropic in all directions, the recoil release rate from a sphere of radius r_a is given by [10]

$$W_{R,n} = w_{p,n} \cdot \pi \cdot \left(\ell_n \cdot r_a^2 - \frac{\ell_n^3}{12} \right), \tag{3.8}$$

where

$w_{p,n}$ = rate density of fission product production from fissions in material n (atoms.cm^{-3}.s^{-1}), and

ℓ_n = recoil range of fission product in material n (cm).

Proof of this equation is the subject of section 3.2.6.

3.1.4 Gas Precursor Contribution

It is assumed that the only significant contribution of the fission product transport via its gas precursor is that originating from the uranium contamination of the fuel sphere matrix material. This assumption remains valid as long as the gas precursor release rate from the coated particles is much lower than the precursor decay rate, which in most cases it is.

Gas precursor diffusion may be described by the diffusion equation

$$\frac{\partial c_g}{\partial t} = \nabla \bullet \left(D_{g,n} \nabla c_g \right) + w_{s,g} - \lambda_g c_g, \tag{3.9}$$

where

c_g $= c_g(r,t)$ = concentration of gas precursor (atoms.cm^{-3}),

$D_{g,n}$ = $D_{g,n}(T)$ diffusion coefficient of gas precursor in material n at temperature T (cm^2.s^{-1}),

λ_g = decay constant of gas precursor (s^{-1}), and

$w_{s,g}$ = source rate density of gas precursor (atoms.cm^{-3}.s^{-1}).

Assuming release from a uniform sphere of radius a, and making the conservative assumption of a steady-state concentration, an analytical solution to equation (3.9) was derived [15] and is given as

$$R_B = \frac{3D_{g,n}}{\lambda_g \cdot a}\left(\sqrt{\frac{\lambda_g}{D_{g,n}}}\coth\left(\sqrt{\frac{\lambda_g}{D_{g,n}}}a\right)-\frac{1}{a}\right), \tag{3.10}$$

where

R_B = release rate to birth rate ratio of gas precursor at steady state.

By assuming spherical grains, or equivalent spheres, this relation is applied to diffusive release of the gas precursor from graphite grains into the pores of the fuel sphere. Diffusive release from the pores to the outside of the fuel sphere is calculated using the same formulation.

An analytical solution [15] to the gas precursor diffusion equation (3.9) for steady state conditions also yields the radial dependence of the concentration of the gas precursor

$$c_g^s(r)=\frac{w_{s,g}}{\lambda_g}\left(1-\frac{a\sinh\left(\sqrt{\frac{\lambda_g}{D_{g,n}}}r\right)}{r\sinh\left(\sqrt{\frac{\lambda_g}{D_{g,n}}}a\right)}\right), \tag{3.11}$$

which can be used directly to calculate the spatial dependence of the fission product production rate in the graphite matrix pores (i.e. fission product production from decay of gas precursors).

3.1.5 Heat Transport

The rate of diffusion of diffusant (fission product, activation product or heavy metal) is highly temperature dependent [7], and hence the temperature distribution in the fuel sphere needs to be calculated in order to model the diffusion process correctly.

It can be reasonably assumed that convection is the predominant heat transfer mechanism from the fuel, and so the temperature of the surface (T_s) is calculated from the surrounding gas temperature (T_g) and average sphere power production $(\dot{Q}_{av})$ using Newton's law of cooling [16], [17],

$$\dot{Q}_{av} = A_s \cdot \alpha \cdot (T_s - T_g), \tag{3.12}$$

where A_s is the surface area of the sphere and the convection heat transfer coefficient (α) is given by [16], [17],

$$\alpha = \frac{Nu \cdot k_c}{d}, \tag{3.13}$$

where k_c is the thermal conductivity of the coolant, and d the diameter of the pebble.

For the case of fluid flow in a bed of spheres, a correlation for the Nusselt number (Nu) has been obtained during the German HTR programme [16]. This is given by

$$Nu = 1.27\frac{Pr^{1/3}}{\varepsilon^{1.18}}Re^{0.36} + 0.033\frac{Pr^{1/2}}{\varepsilon^{1.07}}Re^{0.86}, \tag{3.14}$$

where

ε = porosity of bed,

Re = Reynolds number of coolant flow, and

Pr = Prandtl number of coolant.

To obtain the temperature distribution in the fuel-free zone of the sphere, use is made of the analytical solution of the heat diffusion equation [17]

$$\nabla \bullet (k_m \nabla T) + \dot{q} = \rho C_{p,m}\frac{\partial T}{\partial t}, \tag{3.15}$$

where

k_m = $k_m(F,T)$ thermal conductivity of matrix material (W.m.K^{-1}),

T = $T(r,t)$ is temperature of matrix material at radial position r and at time t,

$C_{p,m}$ = specific heat of matrix material (J.kg^{-1}.K^{-1}),

$\dot{q}$ = $\dot{q}(r)$ power density in matrix material of fuel as a function of radial position (W.m^{-3}),

ρ = density of matrix material (kg.m^{-3}), and

F = fast neutron fluence (neutrons.cm^{-2}).

This is solved for the steady state case, with no power generation in the fuel free zone, and with boundary conditions such that

- the surface temperature is determined by equation (3.12) , and
- the rate of heat flowing through the outer surface is equal to the power of the sphere - $\dot{Q}_{av}$.

For the temperature distribution in the fuel zone, use is made of the analytical solution (see section 3.2.8 for the derivation of the solution) of the steady state heat diffusion equation (3.15) with the given average power density $(\bar{\dot{q}}_{fz})$ in the fuel zone volume (V_{fz})

$$\bar{\dot{q}}_{fz} = \frac{\dot{Q}_{av}}{V_{fz}} \tag{3.16}$$

and boundary conditions such that

- the temperature at the interface between the fuel and fuel free zone is as determined above, and
- the rate of heat flowing through the fuel zone surface is equal to the power of the sphere.

The thermal conductivity (k_m) of the fuel sphere graphite is dependent on the fast neutron dose and temperature. It is calculated from interpolations of experimental data, for example that of Kania and Nickel [6], as described in section 3.3.1.

3.1.6 Diffusion Coefficients

Once the temperature profile in the fuel sphere has been determined, the diffusion coefficients $D_n(T)$ for the diffusant in the different fuel sphere structural materials can be determined using the Arrhenius relation, namely

$$D_n(T) = D_n^0 e^{\frac{-E_n}{\underline{R}_g T}}, \tag{3.17}$$

where

D_n^0 = frequency factor or diffusion constant (cm^2.s^{-1}) in material n,

E_n = activation energy for diffusion (cal.mol^{-1}) in material n, and

$\underline{R}_g$ = 1.98721(cal.mol^{-1}.K^{-1}) = universal gas constant.

Diffusion coefficients of a gas precursor in the graphite grains are determined by using the Arrhenius relation (3.17). However, in the fuel sphere pores a combination of binary gas diffusion and Knudsen diffusion is used. The equation for the binary diffusion coefficient (gas in He coolant) is given by Chapman-Enskog kinetic theory [18]

$$D_{g,b}(p,T_g) = 0.0018583 \cdot \sqrt{\frac{1}{M_{He}} + \frac{1}{M_g}} \frac{T_{He}^{\frac{3}{2}}}{p_g \cdot \sigma_b \cdot \Omega_b}, \tag{3.18}$$

where

M_{He} = molecular weight of Helium (g.mol^{-1}),

M_g = molecular weight of gas diffusant (g.mol^{-1}),

p_g = pressure of coolant (atm),

σ_b = collision diameter of binary mixture (Å),

Ω_b = collision integral for diffusion, and

T_{He} = He gas temperature (K).

For the Knudsen diffusion through the graphite matrix pores, the diffusion coefficient is given by [19]

$$D_{g,p}(T) = K_s \cdot \bar{v}, \tag{3.19}$$

where

K_s = Knudsen constant for gas diffusant in matrix pores (cm), and

$$\bar{v} = \bar{v}(T) = \left(\frac{8\underline{R}_g T}{\pi M_g} \right)^{1/2} \tag{3.20}$$

is the mean speed of gas diffusant atoms at temperature T (cm.s^{-1}).

The diffusion coefficient for the gas diffusant in the pores of the graphite matrix $(D_{g,m})$ is obtained by combining these two diffusion coefficients using the Bosanquet relationship [20]

$$\frac{1}{D_{g,m}} = \frac{1}{D_{g,p}} + \frac{1}{K_t \cdot D_{g,b}} \tag{3.21}$$

where K_t is an empirically determined constant for the matrix material and takes into account the porosity/tortuosity factor of the matrix pores.

3.1.7 Surface Sorption and Mass Transfer

Graphite has the ability to adsorb some metallic atoms at its surface, and hence at the surface of a fuel sphere, the release rate of diffusant is governed by a combination of phenomena such as surface sorption and convective mass transfer [10].

It is assumed that the diffusant forms a very thin gaseous boundary layer at the surface of the fuel sphere, and the convective mass transfer of diffusant to the coolant is based on the difference between the boundary layer (c_{bl}) and coolant concentration (c_∞), namely

$$J_s = -D_m \left(\nabla c|_s \right) = \beta \cdot \left(c_{bl} - c_\infty \right), \tag{3.22}$$

where

J_s = flux of material transfer at the surface

$\nabla c|_s$ = concentration gradient of diffusant at the fuel sphere surface, and

β = the mass transfer coefficient,

which is calculated from analogous correlations [18] used for heat transfer (equations (3.12)-(3.14)), by substitution of Nu and Pr with the Sherwood (Sh) and Schmidt (Sc) numbers respectively, so

$$\beta = \frac{Sh \cdot D_{g,b}}{d}, \text{ and} \tag{3.23}$$

$$Sh = 1.27 \frac{Sc^{1/3}}{\varepsilon^{1.18}} Re^{0.36} + 0.033 \frac{Sc^{1/2}}{\varepsilon^{1.07}} Re^{0.86}. \tag{3.24}$$

For low diffusant boundary layer pressures and high temperatures, the concentration in the boundary layer is related to the partial pressure (p_{bl}) by the ideal gas relation

$$c_{bl} = \frac{p_{bl}}{\underline{R}_a T_s} N_A, \tag{3.25}$$

where

N_A = 6.022×10^{23} (mol^{-1}) = Avogadro's number, and

$\underline{R}_a$ = 82.057 (cm^3.atm.mol^{-1}.K^{-1}) = gas constant.

The partial pressure in the boundary layer is determined from the Henry or Freundlich Isotherms [7], which give the relationship between partial pressure and matrix surface concentration.

3.1.8 Time Dependent Concentration

The space and time dependence of the diffusant concentration (c_n) is found by the use of the diffusion equation

$$\frac{\partial c_n}{\partial t} = \nabla \bullet (D_n \nabla c_n) + w_{s,n} - \lambda c_n , \qquad (3.26)$$

where

$w_{s,n}$ = source rate density of diffusant in material n (atoms.cm^{-3}.s^{-1}), and

λ = decay constant of diffusant (s^{-1}).

Solution of this is obtained by an implicit numerical method, which uses discretizations in both time and space. It also takes into account spatial (temperature and material) dependence of the diffusion coefficient, as well as appropriate boundary conditions across material interfaces.

3.1.9 Diffusion in Coated Particles

Numerical solution of the diffusion equation for the coated particle is carried out by taking into account UO_2 kernel and four layers (buffer, pyrocarbon, SiC, pyrocarbon), and the temperature of the matrix region in which the coated particle lies.

The non-diffusion source of fission product for each layer is calculated from various creation and loss mechanisms outlined in Table 2.

Table 2: Non-diffusion fission product sources taken into account for the coated particle.

Layer	Creation	Loss
UO_2 kernel	Production from fission of heavy metal content.	Recoil fraction out to buffer layer.
Buffer and InnerPyC	Recoil fraction from UO_2 kernel. GETTER considers Buffer and InnerPyC as a single layer with PyC properties. Production from fission in contamination.	Not taken into account.
SiC	Recoil fraction from Inner PyC layer.	None.
Outer PyC	Production from fission of heavy metal contamination of the outer PyC layer.	Recoil fraction out to the fuel sphere graphite matrix.

3.1.10 Diffusion in Naked Kernels

Coated particles that are defective (having damaged SiC layers) are conservatively assumed to have no SiC or PyC layers and hence their UO_2 kernels are considered "exposed" to the graphite matrix of the fuel sphere. The fraction of these naked kernels in the fuel sphere is fixed over a time interval. Calculation of the failure rate of coated particles is done external to GETTER and is based on fuel temperature and burnup.

Diffusion of diffusant out of these kernels is treated in almost the same way as that of coated particles, with the major difference being that no buffer, PyC, or SiC layers are used.

3.1.11 Diffusion in Fuel Sphere Graphite

Just as in the case of the coated particle and naked kernel, the numerical method solution of the diffusion equation is applied to calculate the diffusion of diffusant through the fuel sphere. However, the source term in this case consists of many contributions:

- Diffusive release from coated particles and/or recoil fractions (fission product) from coated particles' outer pyrocarbon contamination fissions.
- Diffusive release from naked kernels and/or recoil fractions (fission product) from the kernel fissions.
- Decay of the gas precursors in the pores of the graphite matrix.
- Fission in heavy metal contamination of the graphite matrix.
- Failure of coated particles with diffusant stored in its coating layers.

3.1.12 Activation Product

In the case of activation product calculations (e.g. ^{110m}Ag from fission product ^{109}Ag), GETTER calculates and stores the time and spatial dependence of the fission product concentration over all time intervals. Thereafter it uses this to calculate the source terms (activation of fission product) and hence the transport of activation product through coated particles, naked kernels and the fuel sphere. It is important to note that in the GETTER model, activation product source terms do not include recoil or gas precursor source terms, contrary to the case of fission product source terms.

3.2 DERIVATION OF EQUATIONS

3.2.1 Fission, Decay and Transmutation

3.2.1.1 Heavy metal inventory

The individual nuclide Bateman equations, derived from the general equation (3.1) for the nuclides in the chain presented by Figure 3, are presented below. These equations form two sets of coupled differential equations; the first five belonging to the Thorium chain, and the remainder to the Uranium chain.

In order to simplify the notation, use is made of the two-digit code [21] for nuclides. The nuclide is identified by two digits made up from the last digit from the atomic number and mass number of the isotope. For reference purposes, those used are listed in Table 3. The non standard characters $v_{i,p}$ and $y_{i,i-1}$ are described in section 3.1.1.

$$\frac{dN_{02}}{dt} = -\phi\sigma_{c,02}N_{02} \tag{3.27}$$

$$\frac{dN_{13}}{dt} = y_{13,02}\phi\sigma_{c,02}N_{02} - \lambda_{13}N_{13} - \phi\sigma_{c,13}N_{13} \tag{3.28}$$

$$\frac{dN_{23}}{dt} = v_{23,13}\lambda_{13}N_{13} - \phi\sigma_{f,23}N_{23} - \phi\sigma_{c,23}N_{23} \tag{3.29}$$

$$\frac{dN_{24}}{dt} = y_{24,23}\phi\sigma_{c,23}N_{23} - \phi\sigma_{c,24}N_{24} \tag{3.30}$$

$$\frac{dN_{25}}{dt} = y_{25,24}\phi\sigma_{c,24}N_{24} - \phi\sigma_{c,25}N_{25} - \phi\sigma_{f,25}N_{25} \tag{3.31}$$

$$\frac{dN_{28}}{dt} = -\phi\sigma_{c,28}N_{28} \tag{3.32}$$

$$\frac{dN_{39}}{dt} = y_{39,28}\phi\sigma_{c,28}N_{28} - \phi\sigma_{c,39}N_{39} - \lambda_{39}N_{39} \tag{3.33}$$

$$\frac{dN_{49}}{dt} = v_{49,39}\lambda_{39}N_{39} - \phi\sigma_{f,49}N_{49} - \phi\sigma_{c,49}N_{49} \tag{3.34}$$

$$\frac{dN_{40}}{dt} = y_{40,49}\phi\sigma_{c,49}N_{49} - \phi\sigma_{c,40}N_{40} \tag{3.35}$$

$$\frac{dN_{41}}{dt} = y_{41,40}\phi\sigma_{c,40}N_{40} - \phi\sigma_{f,41}N_{41} - \phi\sigma_{c,41}N_{41} \tag{3.36}$$

Table 3: Reference for nuclide index notation

Index	Nuclide	Index	Nuclide
02	$^{232}_{90}\mathrm{Th}$	28	$^{238}_{92}\mathrm{U}$
13	$^{233}_{91}\mathrm{Pa}$	39	$^{239}_{93}\mathrm{Np}$
23	$^{233}_{92}\mathrm{U}$	49	$^{239}_{94}\mathrm{Pu}$
24	$^{234}_{92}\mathrm{U}$	40	$^{240}_{94}\mathrm{Pu}$
25	$^{235}_{92}\mathrm{U}$	41	$^{241}_{94}\mathrm{Pu}$

Analytical solution of a set of coupled differential equations is obtained by solving each equation in sequence. Starting by rearranging equation (3.27), the first equation of the Thorium series,

$$\frac{dN_{02}}{N_{02}} = -\phi\sigma_{c,02}dt, \tag{3.37}$$

and integrating both sides from $t = 0$ to $t = t$

$$\int_{N_{02}(0)}^{N_{02}(t)} \frac{dN_{02}}{N_{02}} = -\phi\sigma_{c,02}\int_0^t dt \tag{3.38}$$

$$\ln\left(\frac{N_{02}(t)}{N_{02}(0)}\right) = -\phi\sigma_{c,02}t \tag{3.39}$$

which can be simplified to yield the time dependence of ^{232}Th inventory,

$$N_{02}(t)=N_{02}(0)e^{-\phi\sigma_{c,02}t}. \tag{3.40}$$

Substituting this solution (3.40) into the next Bateman equation (3.28) in the set gives

$$\frac{dN_{13}}{dt}=y_{13,02}\phi\sigma_{c,02}N_{02}(0)e^{-\phi\sigma_{c,02}t}-\lambda_{13}N_{13}-\phi\sigma_{c,13}N_{13} \tag{3.41}$$

and rearranging this by taking all the N_{13} terms to the LHS yields

$$\frac{dN_{13}}{dt}+\left(\lambda_{13}+\phi\sigma_{c,13}\right)N_{13}=y_{13,02}\phi\sigma_{c,02}N_{02}(0)e^{-\phi\sigma_{c,02}t} \tag{3.42}$$

which can be solved by multiplying out both sides by an integrating factor [22],[23] $e^{(\lambda_{13}+\phi\sigma_{c,13})}$

$$e^{(\lambda_{13}+\phi\sigma_{c,13})t}\frac{dN_{13}}{dt}+e^{(\lambda_{13}+\phi\sigma_{c,13})t}\left(\lambda_{13}+\phi\sigma_{c,13}\right)N_{13}=y_{13,02}\phi\sigma_{c,02}N_{02}(0)e^{(\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02})t} \tag{3.43}$$

and noting that the left hand side can be expressed as a single differential

$$\frac{d\left(N_{13}e^{(\lambda_{13}+\phi\sigma_{c,13})t}\right)}{dt}=y_{13,02}\phi\sigma_{c,02}N_{02}(0)e^{(\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02})t} \tag{3.44}$$

followed by rearranging

$$d\left(N_{13}e^{(\lambda_{13}+\phi\sigma_{c,13})t}\right)=y_{13,02}\phi\sigma_{c,02}N_{02}(0)e^{(\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02})t}dt \tag{3.45}$$

and integrating from $t=0$ to $t=t$

$$\int_{t=0}^{t=t}d\left(N_{13}e^{(\lambda_{13}+\phi\sigma_{c,13})t}\right)=y_{13,02}\phi\sigma_{c,02}N_{02}(0)\int_{0}^{t}e^{(\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02})t}dt \tag{3.46}$$

$$N_{13}(t)e^{(\lambda_{13}+\phi\sigma_{c,13})t}-N_{13}(0)=\frac{y_{13,02}\phi\sigma_{c,02}N_{02}(0)}{\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02}}\left(e^{(\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02})t}-1\right) \tag{3.47}$$

$$N_{13}(t)e^{(\lambda_{13}+\phi\sigma_{c,13})t}-N_{13}(0)=\frac{y_{13,02}\phi\sigma_{c,02}N_{02}(0)}{\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02}}\left(e^{(\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02})t}-1\right). \tag{3.48}$$

Rearranging to obtain an explicit equation for the time dependent concentration of $^{233}_{91}$Pa

$$N_{13}(t)=N_{13}(0)e^{-(\lambda_{13}+\phi\sigma_{c,13})t}+\frac{y_{13,02}\phi\sigma_{c,02}N_{02}(0)}{\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02}}\left(e^{-\phi\sigma_{c,02}t}-e^{-(\lambda_{13}+\phi\sigma_{c,13})t}\right) \tag{3.49}$$

and gathering like exponentials yields

$$N_{13}(t)=\frac{y_{13,02}\phi\sigma_{c,02}N_{02}(0)}{\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02}}e^{-\phi\sigma_{c,02}t}+\left(N_{13}(0)-\frac{y_{13,02}\phi\sigma_{c,02}N_{02}(0)}{\lambda_{13}+\phi\sigma_{c,13}-\phi\sigma_{c,02}}\right)e^{-(\lambda_{13}+\phi\sigma_{c,13})t} \tag{3.50}$$

Dividing through the numerators and denominators of the fractional expressions by the flux ϕ

$$N_{13}(t)=\frac{y_{13,02}\sigma_{c,02}N_{02}(0)}{\lambda_{13}/\phi+\sigma_{c,13}-\sigma_{c,02}}e^{-\phi\sigma_{c,02}t}+\left(N_{13}(0)-\frac{y_{13,02}\sigma_{c,02}N_{02}(0)}{\lambda_{13}/\phi+\sigma_{c,13}-\sigma_{c,02}}\right)e^{-(\lambda_{13}+\phi\sigma_{c,13})t}, \tag{3.51}$$

and simplifying by making substitutions for the coefficients of the exponentials, yields the time dependent ^{233}Pa inventory solution

$$N_{13}(t)=A_{13}e^{-\phi\sigma_{c,02}t}+B_{13}e^{-(\lambda_{13}+\phi\sigma_{c,13})t}. \tag{3.52}$$

By substituting this solution into equation (3.29)

$$\frac{dN_{23}}{dt}=\nu_{23,13}\lambda_{13}\left(A_{13}e^{-\phi\sigma_{c,02}t}+B_{13}e^{-(\lambda_{13}+\phi\sigma_{c,13})t}\right)-\phi\sigma_{f,23}N_{23}-\phi\sigma_{c,23}N_{23} \tag{3.53}$$

and carrying out steps similar to that from (3.41) to (3.51), where full details are available in [2], the solution for the inventory of ^{233}U can be given by

$$N_{23}(t)=\left(N_{23}(0)-\frac{\nu_{23,13}(\lambda_{13}/\phi)A_{13}}{\sigma_{f,23}+\sigma_{c,23}-\sigma_{c,02}}-\frac{\nu_{23,13}(\lambda_{13}/\phi)B_{13}}{\sigma_{f,23}+\sigma_{c,23}-(\lambda_{13}/\phi)-\sigma_{c,13}}\right)e^{-(\phi\sigma_{f,23}+\phi\sigma_{c,23})t}+ \\ \frac{\nu_{23,13}\lambda_{13}B_{13}}{\sigma_{f,23}+\sigma_{c,23}-(\lambda_{13}/\phi)-\sigma_{c,13}}e^{-(\lambda_{13}+\phi\sigma_{c,13})t}+\frac{\nu_{23,13}(\lambda_{13}/\phi)A_{13}}{\sigma_{f,23}+\sigma_{c,23}-\sigma_{c,02}}e^{-\phi\sigma_{c,02}t}, \tag{3.54}$$

and where simplification by renaming exponential coefficients results in

$$N_{23}(t)=A_{23}e^{-(\phi\sigma_{f,23}+\phi\sigma_{c,23})t}+B_{23}e^{-(\lambda_{13}+\phi\sigma_{c,13})t}+C_{23}e^{-\phi\sigma_{c,02}t}. \tag{3.55}$$

Once again substituting this into (3.30) and solving as done above yields the ^{234}U inventory

$$N_{24}(t)=\left(N_{24}(0)-\frac{y_{24,23}\sigma_{c,23}A_{23}}{\sigma_{c,24}-(\sigma_{f,23}+\sigma_{c,23})}-\frac{y_{24,23}\sigma_{c,23}B_{23}}{\sigma_{c,24}-\lambda_{13}/\phi-\sigma_{c,13}}-\frac{y_{24,23}\sigma_{c,23}C_{23}}{\sigma_{c,24}-\sigma_{c,02}}\right)e^{-\phi\sigma_{c,24}t}+ \\ \frac{y_{24,23}\sigma_{c,23}A_{23}}{\sigma_{c,24}-(\sigma_{f,23}+\sigma_{c,23})}e^{-(\phi\sigma_{f,23}+\phi\sigma_{c,23})t}+\frac{y_{24,23}\sigma_{c,23}B_{23}}{\sigma_{c,24}-\lambda_{13}/\phi-\sigma_{c,13}}e^{-(\lambda_{13}+\phi\sigma_{c,13})t}+\frac{y_{24,23}\sigma_{c,23}C_{23}}{\sigma_{c,24}-\sigma_{c,02}}e^{-\phi\sigma_{c,02}t} \tag{3.56}$$

and renaming exponential coefficients yields

$$N_{24}(t)=A_{24}e^{-\phi\sigma_{c,24}t}+B_{24}e^{-(\phi\sigma_{f,23}+\phi\sigma_{c,23})t}+C_{24}e^{-(\lambda_{13}+\phi\sigma_{c,13})t}+D_{24}e^{-\phi\sigma_{c,02}t} \tag{3.57}$$

Substituting this into (3.31) and once again solving as done above yields the ^{235}U inventory

$$N_{25}(t)=e^{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})t}\left(\begin{array}{l}N_{25}(0)-\frac{y_{25,24}\sigma_{c,24}A_{24}}{\sigma_{c,25}+\sigma_{f,25}-\sigma_{c,24}}-\frac{y_{25,24}\sigma_{c,24}B_{24}}{\sigma_{c,25}+\sigma_{f,25}-(\sigma_{f,23}+\sigma_{c,23})}- \\ \frac{y_{25,24}\sigma_{c,24}C_{24}}{\sigma_{c,25}+\sigma_{f,25}-(\lambda_{13}/\phi+\sigma_{c,13})}-\frac{y_{25,24}\sigma_{c,24}D_{24}}{\sigma_{c,25}+\sigma_{f,25}-\sigma_{c,02}}\end{array}\right)+ \\ \frac{y_{25,24}\sigma_{c,24}A_{24}e^{-\phi\sigma_{c,24}t}}{\sigma_{c,25}+\sigma_{f,25}-\sigma_{c,24}}+\frac{y_{25,24}\sigma_{c,24}B_{24}e^{-(\phi\sigma_{f,23}+\phi\sigma_{c,23})t}}{\sigma_{c,25}+\sigma_{f,25}-(\sigma_{f,23}+\sigma_{c,23})}+ \\ \frac{y_{25,24}\sigma_{c,24}C_{24}e^{-(\lambda_{13}+\phi\sigma_{c,13})t}}{\sigma_{c,25}+\sigma_{f,25}-(\lambda_{13}/\phi+\sigma_{c,13})}+\frac{y_{25,24}\sigma_{c,24}D_{24}e^{-\phi\sigma_{c,02}t}}{\sigma_{c,25}+\sigma_{f,25}-\sigma_{c,02}} \tag{3.58}$$

and renaming exponential coefficients gives

$$N_{25}(t)=A_{25}e^{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})t}+B_{25}e^{-\phi\sigma_{c,24}t}+C_{25}e^{-(\phi\sigma_{f,23}+\phi\sigma_{c,23})t}+D_{25}e^{-(\lambda_{13}+\phi\sigma_{c,13})t}+E_{25}e^{-\phi\sigma_{c,02}t} \tag{3.59}$$

Similarly for the Uranium 238 series, starting with ^{238}U starting with equation (3.32)

$$N_{28}(t)=N_{28}(0)e^{-\phi\sigma_{c,28}t}. \tag{3.60}$$

and substituting this into equation (3.33) in order to solve for the Neptunium 239 inventory

$$N_{39}(t)=\left(N_{39}(0)-\frac{y_{39,28}\sigma_{c,28}N_{28}(0)}{\sigma_{c,39}+\lambda_{39}/\phi-\sigma_{c,28}}\right)e^{-(\phi\sigma_{c,39}+\lambda_{39})t}+\frac{y_{39,28}\sigma_{c,28}N_{28}(0)}{\sigma_{c,39}+\lambda_{39}/\phi-\sigma_{c,28}}e^{-\phi\sigma_{c,28}t}, \tag{3.61}$$

followed by simplification of the exponential coefficients to yield

$$N_{39}(t)=A_{39}e^{-(\phi\sigma_{c,39}+\lambda_{39})t}+B_{39}e^{-\phi\sigma_{c,28}t}. \tag{3.62}$$

Substituting this into equation (3.34) and solving for the ^{239}Pu inventory

$$N_{49}(t)=\left(N_{49}(0)-\frac{v_{49,39}(\lambda_{39}/\phi)A_{39}}{\sigma_{f,49}+\sigma_{c,49}-\sigma_{c,39}-\lambda_{39}}-\frac{v_{49,39}(\lambda_{39}/\phi)B_{39}}{\sigma_{f,49}+\sigma_{c,49}-\sigma_{c,28}}\right)e^{-(\phi\sigma_{f,49}+\phi\sigma_{c,49})t}+\frac{v_{49,39}(\lambda_{39}/\phi)A_{39}e^{-(\phi\sigma_{c,39}+\lambda_{39})t}}{\sigma_{f,49}+\sigma_{c,49}-\sigma_{c,39}-\lambda_{39}/\phi}+\frac{v_{49,39}(\lambda_{39}/\phi)B_{39}e^{-\phi\sigma_{c,28}t}}{\sigma_{f,49}+\sigma_{c,49}-\sigma_{c,28}} \tag{3.63}$$

and renaming exponential coefficients yields

$$N_{49}(t)=A_{49}e^{-(\phi\sigma_{f,49}+\phi\sigma_{c,49})t}+B_{49}e^{-(\phi\sigma_{c,39}+\lambda_{39})t}+C_{49}e^{-\phi\sigma_{c,28}t} \tag{3.64}$$

Substituting this solution into equation (3.35) and solving for the ^{240}Pu inventory (as done similarly above, and described in full detail in [2])

$$N_{40}(t)=\left(N_{40}(0)-\left(\frac{A_{49}y_{40,49}\sigma_{c,49}}{\sigma_{c,40}-\sigma_{f,49}-\sigma_{c,49}}+\frac{y_{40,49}\phi\sigma_{c,49}B_{49}}{\phi\sigma_{c,40}-\phi\sigma_{c,39}-\lambda_{39}}+\frac{y_{40,49}\sigma_{c,49}C_{49}}{\sigma_{c,40}-\sigma_{c,28}}\right)\right)e^{-\phi\sigma_{c,40}t}+\frac{y_{40,49}\sigma_{c,49}A_{49}e^{-(\phi\sigma_{f,49}+\phi\sigma_{c,49})t}}{\sigma_{c,40}-\sigma_{f,49}-\sigma_{c,49}}+\frac{y_{40,49}\phi\sigma_{c,49}B_{49}e^{-(\phi\sigma_{c,39}+\lambda_{39})t}}{\phi\sigma_{c,40}-\phi\sigma_{c,39}-\lambda_{39}}+\frac{y_{40,49}\sigma_{c,49}C_{49}e^{-\phi\sigma_{c,28}t}}{\sigma_{c,40}-\sigma_{c,28}}, \tag{3.65}$$

and renaming exponentials to simplify the expression finally yields the solution

$$N_{40}(t)=A_{40}e^{-\phi\sigma_{c,40}t}+B_{40}e^{-(\phi\sigma_{f,49}+\phi\sigma_{c,49})t}+C_{40}e^{-(\phi\sigma_{c,39}+\lambda_{39})t}+D_{40}e^{-\phi\sigma_{c,28}t} \tag{3.66}$$

Similarly by substituting this solution into equation (3.36) and solving for the ^{241}Pu inventory

$$N_{41}(t)=\left(\begin{array}{l}N_{41}(0)-\dfrac{y_{41,40}\sigma_{c,40}A_{40}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{c,40}}-\dfrac{y_{41,40}\sigma_{c,40}B_{40}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{f,49}-\sigma_{c,49}}-\\ \dfrac{y_{41,40}\sigma_{c,40}C_{40}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{c,39}-\lambda_{39}}-\dfrac{y_{41,40}\sigma_{c,40}D_{40}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{c,28}}\end{array}\right)e^{-(\phi\sigma_{f,41}+\phi\sigma_{c,41})t}+\frac{y_{41,40}\sigma_{c,40}A_{40}e^{-\phi\sigma_{c,40}t}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{c,40}}+\frac{y_{41,40}\sigma_{c,40}B_{40}e^{-(\phi\sigma_{f,49}+\phi\sigma_{c,49})t}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{f,49}-\sigma_{c,49}}+\frac{y_{41,40}\sigma_{c,40}C_{40}e^{-(\phi\sigma_{c,39}+\lambda_{39})t}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{c,39}-\lambda_{39}/\phi}+\frac{y_{41,40}\sigma_{c,40}D_{40}e^{-\phi\sigma_{c,28}t}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{c,28}} \tag{3.67}$$

and simplifying exponential coefficients to give the solution

$$N_{41}(t)=A_{41}e^{-(\phi\sigma_{f,41}+\phi\sigma_{c,41})t}+B_{41}e^{-\phi\sigma_{c,40}t}+C_{41}e^{-(\phi\sigma_{f,49}+\phi\sigma_{c,49})t}+D_{41}e^{-(\phi\sigma_{c,39}+\lambda_{39})t}+E_{41}e^{-\phi\sigma_{c,28}t} \tag{3.68}$$

3.2.1.2 Heavy metal inventory – number fractions and simplifications

Re-expressing the major inventory equations derived in section 3.2.1.1 in terms of number fractions of the total heavy metal inventory present in the system originally is a simple matter of dividing the equations by the total number of heavy metal atoms originally in the system, N_{HM}^0. Consider first the case of $^{232}_{90}$Th inventory, given by equation (3.40), when divided by N_{HM}^0 yields the number fraction of $^{232}_{90}$Th in the system at the end of the timestep of length t

$$\cancel{N}_{02}(t)=\frac{N_{02}(t)}{N_{HM}^0}=\frac{N_{02}(0)}{N_{HM}^0}e^{-\phi\sigma_{c,02}t}. \tag{3.69}$$

Letting the time independent coefficient of the exponential be renamed as

$$\mathcal{N}_{02}(0) = \frac{N_{02}(0)}{N_{HM}^{0}}, \tag{3.70}$$

and the exponential be renamed as

$$e_{02} = e^{-\phi\sigma_{c,02}t} \tag{3.71}$$

gives the equation for number fraction of ${}^{232}_{90}\text{Th}$ at the end of the timestep as

$$\mathcal{N}_{02}(t) = \mathcal{N}_{02}(0)e_{02}\,. \tag{3.72}$$

Next consider the case of ${}^{233}_{91}\text{Pa}$ inventory, given by equation (3.54), when divided by N_{HM}^{0} yields the number fraction of ${}^{233}_{91}\text{Pa}$ in the system at the end of the timestep of length t

$$\begin{aligned}\mathcal{N}_{13}(t) = \frac{N_{13}(t)}{N_{HM}^{0}} = {} & \frac{y_{13,02}\sigma_{c,02}}{\lambda_{13}/\phi + \sigma_{c,13} - \sigma_{c,02}}\frac{N_{02}(0)}{N_{HM}^{0}}e^{-\phi\sigma_{c,02}t} + \\ & \left(\frac{N_{13}(0)}{N_{HM}^{0}} - \frac{y_{13,02}\sigma_{c,02}}{\lambda_{13}/\phi + \sigma_{c,13} - \sigma_{c,02}}\frac{N_{02}(0)}{N_{HM}^{0}}\right)e^{-(\lambda_{13}+\phi\sigma_{c,13})t}\end{aligned} \tag{3.73}$$

Substituting (3.70) and (3.71) into this, letting

$$\mathcal{N}_{13}(0) = \frac{N_{13}(0)}{N_{HM}^{0}}, \tag{3.74}$$

and the exponential

$$e_{13} = e^{-(\lambda_{13}+\phi\sigma_{c,13})t} \tag{3.75}$$

yields the number fraction of ${}^{233}_{91}\text{Pa}$ as

$$\mathcal{N}_{13}(t) = \frac{\mathcal{N}_{02}(0)y_{13,02}\sigma_{c,02}}{\lambda_{13}/\phi + \sigma_{c,13} - \sigma_{c,02}}e_{02} + \left(\mathcal{N}_{13}(0) - \frac{\mathcal{N}_{02}(0)y_{13,02}\sigma_{c,02}}{\lambda_{13}/\phi + \sigma_{c,13} - \sigma_{c,02}}\right)e_{13} \tag{3.76}$$

where the exponential coefficients can be renamed to $A_{13,1}$ and $A_{13,2}$, so finally

$$\mathcal{N}_{13}(t) = A_{13,1}e_{02} + A_{13,2}e_{13}\,. \tag{3.77}$$

Similar simplifications can be made for all the other isotopes, yielding the results shown in Table 4, Table 5 and Table 6 below.

Table 4: Inventory equations in terms of number fractions of isotopes

Isotope	Equation
$^{232}_{90}\mathrm{Th}$	$\mathcal{N}_{02}(t)=\mathcal{N}_{02}(0)e_{02}$
$^{233}_{91}\mathrm{Pa}$	$\mathcal{N}_{13}(t)=\mathcal{A}_{13,1}e_{02}+\mathcal{A}_{13,2}e_{13}$
$^{233}_{92}\mathrm{U}$	$\mathcal{N}_{23}(t)=\mathcal{A}_{23,3}e_{23}+\mathcal{A}_{23,2}e_{13}+\mathcal{A}_{23,1}e_{02}$
$^{234}_{92}\mathrm{U}$	$\mathcal{N}_{24}(t)=\mathcal{A}_{24,4}e_{24}+\mathcal{A}_{24,3}e_{23}+\mathcal{A}_{24,2}e_{13}+\mathcal{A}_{24,1}e_{02}$
$^{235}_{92}\mathrm{U}$	$\mathcal{N}_{25}(t)=\mathcal{A}_{25,5}e_{25}+\mathcal{A}_{25,4}e_{24}+\mathcal{A}_{25,3}e_{23}+\mathcal{A}_{25,2}e_{13}+\mathcal{A}_{25,1}e_{02}$
$^{238}_{92}\mathrm{U}$	$\mathcal{N}_{28}(t)=\mathcal{N}_{28}(0)e_{28}$
$^{239}_{93}\mathrm{Np}$	$\mathcal{N}_{39}(t)=\mathcal{A}_{39,2}e_{39}+\mathcal{A}_{39,1}e_{28}$
$^{239}_{94}\mathrm{Pu}$	$\mathcal{N}_{49}(t)=\mathcal{A}_{49,3}e_{49}+\mathcal{A}_{49,2}e_{39}+\mathcal{A}_{49,1}e_{28}$
$^{240}_{94}\mathrm{Pu}$	$\mathcal{N}_{40}(t)=\mathcal{A}_{40,4}e_{40}+\mathcal{A}_{40,3}e_{49}+\mathcal{A}_{40,2}e_{39}+\mathcal{A}_{40,1}e_{28}$
$^{241}_{94}\mathrm{Pu}$	$\mathcal{N}_{41}(t)=\mathcal{A}_{41,5}e_{41}+\mathcal{A}_{41,4}e_{40}+\mathcal{A}_{41,3}e_{49}+\mathcal{A}_{41,2}e_{39}+\mathcal{A}_{41,1}e_{28}$

Table 5: Expansions of exponential factors for number fraction inventory equations

Short form	Expanded form
e_{02}	$e^{-\phi\sigma_{c,02}t}$
e_{13}	$e^{-(\lambda_{13}+\phi\sigma_{c,13})t}$
e_{23}	$e^{-(\phi\sigma_{f,23}+\phi\sigma_{c,23})t}$
e_{24}	$e^{-\phi\sigma_{c,24}t}$
e_{25}	$e^{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})t}$
e_{28}	$e^{-\phi\sigma_{c,28}t}$
e_{39}	$e^{-(\phi\sigma_{c,39}+\lambda_{39})t}$
e_{49}	$e^{-(\phi\sigma_{f,49}+\phi\sigma_{c,49})t}$
e_{40}	$e^{-\phi\sigma_{c,40}t}$
e_{41}	$e^{-(\phi\sigma_{f,41}+\phi\sigma_{c,41})t}$

Table 6: Expansions of exponential coefficients for number fraction inventory equations

Short form	Alternate form	Expanded form
$\mathcal{A}_{13,1}$	A_{13}/N^0_{HM}	$\dfrac{\mathcal{N}_{02}(0)y_{13,02}\sigma_{c,02}}{\lambda_{13}/\phi+\sigma_{c,13}-\sigma_{c,02}}$
$\mathcal{A}_{13,2}$	B_{13}/N^0_{HM}	$\mathcal{N}_{13}(0)-\mathcal{A}_{13,1}$
$\mathcal{A}_{23,1}$	C_{23}/N^0_{HM}	$\dfrac{\nu_{23,13}(\lambda_{13}/\phi)\mathcal{A}_{13,1}}{\sigma_{f,23}+\sigma_{c,23}-\sigma_{c,02}}$
$\mathcal{A}_{23,2}$	B_{23}/N^0_{HM}	$\dfrac{\nu_{23,13}\lambda_{13}\mathcal{A}_{13,2}}{\sigma_{f,23}+\sigma_{c,23}-(\lambda_{13}/\phi)-\sigma_{c,13}}$

Short form	Alternate form	Expanded form
$A_{23,3}$	A_{23}/N_{HM}^{0}	$\mathcal{N}_{23}(0)-A_{23,1}-A_{23,2}$
$A_{24,1}$	D_{24}/N_{HM}^{0}	$\dfrac{y_{24,23}\sigma_{c,23}A_{23,3}}{\sigma_{c,24}-\sigma_{c,02}}$
$A_{24,2}$	C_{24}/N_{HM}^{0}	$\dfrac{y_{24,23}\sigma_{c,23}A_{23,2}}{\sigma_{c,24}-\lambda_{13}/\phi-\sigma_{c,13}}$
$A_{24,3}$	B_{24}/N_{HM}^{0}	$\dfrac{y_{24,23}\sigma_{c,23}A_{23,1}}{\sigma_{c,24}-\left(\sigma_{f,23}+\sigma_{c,23}\right)}$
$A_{24,4}$	A_{24}/N_{HM}^{0}	$\mathcal{N}_{24}(0)-A_{24,3}-A_{24,2}-A_{24,1}$
$A_{25,1}$	E_{25}/N_{HM}^{0}	$\dfrac{y_{25,24}\sigma_{c,24}A_{24,4}}{\sigma_{c,25}+\sigma_{f,25}-\sigma_{c,02}}$
$A_{25,2}$	D_{25}/N_{HM}^{0}	$\dfrac{y_{25,24}\sigma_{c,24}A_{24,3}}{\sigma_{c,25}+\sigma_{f,25}-\left(\lambda_{13}/\phi+\sigma_{c,13}\right)}$
$A_{25,3}$	C_{25}/N_{HM}^{0}	$\dfrac{y_{25,24}\sigma_{c,24}A_{24,2}}{\sigma_{c,25}+\sigma_{f,25}-\left(\sigma_{f,23}+\sigma_{c,23}\right)}$
$A_{25,4}$	B_{25}/N_{HM}^{0}	$\dfrac{y_{25,24}\sigma_{c,24}A_{24,1}}{\sigma_{c,25}+\sigma_{f,25}-\sigma_{c,24}}$
$A_{25,5}$	A_{25}/N_{HM}^{0}	$\mathcal{N}_{25}(0)-A_{25,4}-A_{25,3}-A_{25,2}-A_{25,1}$
$A_{39,1}$	B_{39}/N_{HM}^{0}	$\dfrac{y_{39,28}\sigma_{c,28}\mathcal{N}_{28}(0)}{\sigma_{c,39}+\lambda_{39}/\phi-\sigma_{c,28}}$
$A_{39,2}$	A_{39}/N_{HM}^{0}	$\mathcal{N}_{39}(0)-A_{39,1}$
$A_{49,1}$	C_{49}/N_{HM}^{0}	$\dfrac{v_{49,39}\left(\lambda_{39}/\phi\right)A_{39,2}}{\sigma_{f,49}+\sigma_{c,49}-\sigma_{c,28}}$
$A_{49,2}$	B_{49}/N_{HM}^{0}	$\dfrac{v_{49,39}\left(\lambda_{39}/\phi\right)A_{39,1}}{\sigma_{f,49}+\sigma_{c,49}-\sigma_{c,39}-\lambda_{39}/\phi}$
$A_{49,3}$	A_{49}/N_{HM}^{0}	$\mathcal{N}_{49}(0)-A_{49,2}-A_{49,1}$
$A_{40,1}$	D_{40}/N_{HM}^{0}	$\dfrac{y_{40,49}\sigma_{c,49}A_{49,3}}{\sigma_{c,40}-\sigma_{c,28}}$
$A_{40,2}$	C_{40}/N_{HM}^{0}	$\dfrac{y_{40,49}\phi\sigma_{c,49}A_{49,2}}{\phi\sigma_{c,40}-\phi\sigma_{c,39}-\lambda_{39}}$
$A_{40,3}$	B_{40}/N_{HM}^{0}	$\dfrac{y_{40,49}\sigma_{c,49}A_{49,1}}{\sigma_{c,40}-\sigma_{f,49}-\sigma_{c,49}}$
$A_{40,4}$	A_{40}/N_{HM}^{0}	$\mathcal{N}_{40}(0)-A_{40,3}-A_{40,2}-A_{40,1}$
$A_{41,1}$	E_{41}/N_{HM}^{0}	$\dfrac{y_{41,40}\sigma_{c,40}A_{40,4}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{c,28}}$

Short form	Alternate form	Expanded form
$A_{41,2}$	D_{41}/N_{HM}^0	$\frac{y_{41,40}\sigma_{c,40}A_{40,3}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{c,39}-\lambda_{39}/\phi}$
$A_{41,3}$	C_{41}/N_{HM}^0	$\frac{y_{41,40}\sigma_{c,40}A_{40,2}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{f,49}-\sigma_{c,49}}$
$A_{41,4}$	B_{41}/N_{HM}^0	$\frac{y_{41,40}\sigma_{c,40}A_{40,1}}{\sigma_{f,41}+\sigma_{c,41}-\sigma_{c,40}}$
$A_{41,5}$	A_{41}/N_{HM}^0	$\cancel{N}_{41}(0)-A_{41,4}-A_{41,3}-A_{41,2}-A_{41,1}$

3.2.1.3 Burnup fractions of fissile isotopes

Calculation of the fission rate of each fissile isotope (^{233}U, ^{235}U, ^{239}Pu, and ^{241}Pu) is important, as they each have different fission yields of fission product. The number of fissions that each of these isotopes have per timestep can be expressed as the ratio of the amount of isotope fissioned to the total initial heavy metal inventory.

For ^{233}U, this can be expressed as

$$B_{23}^u(t)=\frac{\int_0^t \phi\sigma_{f,23}N_{23}(t)dt}{N_{HM}^0}, \tag{3.78}$$

where the numerator gives the total number of ^{233}U fissions over the timestep (using $t=0$ and $t=t$ as the beginning and end respectively). Substitution of (3.55) into this equation yields

$$B_{23}^u(t)=\frac{1}{N_{HM}^0}\int_0^t \phi\sigma_{f,23}\left(A_{23}e^{-(\phi\sigma_{f,23}+\phi\sigma_{c,23})t}+B_{23}e^{-(\lambda_{13}+\phi\sigma_{c,13})t}+C_{23}e^{-\phi\sigma_{c,02}t}\right)dt \tag{3.79}$$

and also using the assumption of constant flux over a timestep, and the coefficients of the exponentials are time independent, yields

$$B_{23}^u(t)=\frac{\phi\sigma_{f,23}}{N_{HM}^0}\left(\frac{A_{23}\left(1-e^{-(\phi\sigma_{f,23}+\phi\sigma_{c,23})t}\right)}{\phi\sigma_{f,23}+\phi\sigma_{c,23}}+\frac{B_{23}\left(1-e^{-(\lambda_{13}+\phi\sigma_{c,13})t}\right)}{\lambda_{13}+\phi\sigma_{c,13}}+\frac{C_{23}\left(1-e^{-\phi\sigma_{c,02}t}\right)}{\phi\sigma_{c,02}}\right) \tag{3.80}$$

which can also be written as (using short forms from Table 5 and Table 6)

$$B_{23}^u(t)=\sigma_{f,23}\left(\frac{A_{23,3}(1-e_{23})}{\sigma_{f,23}+\sigma_{c,23}}+\frac{A_{23,2}(1-e_{13})}{\lambda_{13}/\phi+\sigma_{c,13}}+\frac{A_{23,1}(1-e_{02})}{\sigma_{c,02}}\right). \tag{3.81}$$

Similarly for ^{235}U ,

$$B_{25}^u(t)=\frac{\int_0^t \phi\sigma_{f,25}N_{25}(t)dt}{N_{HM}^0}. \tag{3.82}$$

Substituting (3.59) into this and integrating yields

$$B_{25}^{u}(t)=\frac{\phi\sigma_{f,25}}{N_{HM}^{0}}\left(\begin{array}{l}\dfrac{A_{25}\left(1-e^{-\left(\phi\sigma_{c,25}+\phi\sigma_{f,25}\right)t}\right)}{\phi\sigma_{c,25}+\phi\sigma_{f,25}}+\dfrac{B_{25}\left(1-e^{-\phi\sigma_{c,24}t}\right)}{\phi\sigma_{c,24}}+\dfrac{C_{25}\left(1-e^{-\left(\phi\sigma_{f,23}+\phi\sigma_{c,23}\right)t}\right)}{\phi\sigma_{f,23}+\phi\sigma_{c,23}}\\+\dfrac{D_{25}\left(1-e^{-\left(\lambda_{13}+\phi\sigma_{c,13}\right)t}\right)}{\lambda_{13}+\phi\sigma_{c,13}}+\dfrac{E_{25}\left(1-e^{-\phi\sigma_{c,02}t}\right)}{\phi\sigma_{c,02}}\end{array}\right). \tag{3.83}$$

which can also be written as (using short forms from Table 5 and Table 6)

$$B_{25}^{u}(t)=\sigma_{f,25}\left(\frac{A_{25,5}\left(1-e_{25}\right)}{\sigma_{c,25}+\sigma_{f,25}}+\frac{A_{25,4}\left(1-e_{24}\right)}{\sigma_{c,24}}+\frac{A_{25,3}\left(1-e_{23}\right)}{\sigma_{f,23}+\sigma_{c,23}}+\frac{A_{25,2}\left(1-e_{13}\right)}{\lambda_{13}/\phi+\sigma_{c,13}}+\frac{A_{25,1}\left(1-e_{02}\right)}{\sigma_{c,02}}\right) \tag{3.84}$$

For ^{239}Pu

$$B_{49}^{u}(t)=\frac{\int_{0}^{t}\phi\sigma_{f,49}N_{49}(t)dt}{N_{HM}^{0}}, \tag{3.85}$$

where substituting (3.64) into this and integrating yields

$$B_{49}^{u}(t)=\frac{\phi\sigma_{f,49}}{N_{HM}^{0}}\left(\frac{A_{49}\left(1-e^{-\left(\phi\sigma_{f,49}+\phi\sigma_{c,49}\right)t}\right)}{\phi\sigma_{f,49}+\phi\sigma_{c,49}}+\frac{B_{49}\left(1-e^{-\left(\phi\sigma_{c,39}+\lambda_{39}\right)t}\right)}{\phi\sigma_{c,39}+\lambda_{39}}+\frac{C_{49}e^{-\phi\sigma_{c,28}t}}{\phi\sigma_{c,28}}\right), \tag{3.86}$$

which can also be written as (using short forms from Table 5 and Table 6)

$$B_{49}^{u}(t)=\sigma_{f,49}\left(\frac{A_{49,3}\left(1-e_{49}\right)}{\sigma_{f,49}+\sigma_{c,49}}+\frac{A_{49,2}\left(1-e_{39}\right)}{\sigma_{c,39}+\lambda_{39}/\phi}+\frac{A_{49,1}e_{28}}{\sigma_{c,28}}\right). \tag{3.87}$$

For ^{241}Pu

$$B_{41}^{u}(t)=\frac{\int_{0}^{t}\phi\sigma_{f,41}N_{41}(t)dt}{N_{HM}^{0}}, \tag{3.88}$$

where substitution of (3.68) and integration yields

$$B_{41}^{u}(t)=\frac{\phi\sigma_{f,41}}{N_{HM}^{0}}\left(\begin{array}{l}\dfrac{A_{41}\left(1-e^{-\left(\phi\sigma_{f,41}+\phi\sigma_{c,41}\right)t}\right)}{\phi\sigma_{f,41}+\phi\sigma_{c,41}}+\dfrac{B_{41}\left(1-e^{-\phi\sigma_{c,40}t}\right)}{\phi\sigma_{c,40}}+\dfrac{C_{41}\left(1-e^{-\left(\phi\sigma_{f,49}+\phi\sigma_{c,49}\right)t}\right)}{\phi\sigma_{f,49}+\phi\sigma_{c,49}}\\+\dfrac{D_{41}\left(1-e^{-\left(\phi\sigma_{c,39}+\lambda_{39}\right)t}\right)}{\phi\sigma_{c,39}+\lambda_{39}}+\dfrac{E_{41}\left(1-e^{-\phi\sigma_{c,28}t}\right)}{\phi\sigma_{c,28}}\end{array}\right), \tag{3.89}$$

which can also be written as (using short forms from Table 5 and Table 6)

$$B_{41}^{u}(t)=\sigma_{f,41}\left(\frac{A_{41,5}\left(1-e_{41}\right)}{\sigma_{f,41}+\sigma_{c,41}}+\frac{A_{41,4}\left(1-e_{40}\right)}{\sigma_{c,40}}+\frac{A_{41,3}\left(1-e_{49}\right)}{\sigma_{f,49}+\sigma_{c,49}}+\frac{A_{41,2}\left(1-e_{39}\right)}{\sigma_{c,39}+\lambda_{39}/\phi}+\frac{A_{41,1}\left(1-e_{28}\right)}{\sigma_{c,28}}\right). \tag{3.90}$$

The fraction of fissions per initial metal atom (FIMA) over the timestep can then given by summing the burnup fractions of each of the fissile isotopes according to equation (3.2),

$$B_{T}^{u}=B_{23}^{u}+B_{25}^{u}+B_{49}^{u}+B_{41}^{u} \tag{3.91}$$

and the FIMA from plutonium fissions is determined by the sum of plutonium fission fractions only, namely

$$B_{Pu}^{u} = B_{49}^{u} + B_{41}^{u} \tag{3.92}$$

3.2.2 Power and Fission Product Production

The average power generated in the fuel sphere is calculated using equation (3.3), and the power generated from plutonium fissions ($\dot{Q}_{avP}$) during the time interval is given by a similar equation

$$\dot{Q}_{avP} = \frac{B_{Pu}^{u} \cdot N_{HM}^{0} \cdot E_f}{\tau}. \tag{3.93}$$

The direct fission product yield fraction (Y_{FD}) at the end of the time interval can be obtained from the sum of the yield from each isotope according to equation (3.4)

$$Y_{FD} = \frac{\gamma_{23}B_{23}^{u} + \gamma_{25}B_{25}^{u} + \gamma_{49}B_{49}^{u} + \gamma_{41}B_{41}^{u}}{B_T^{u}}. \tag{3.94}$$

Similarly for the cumulative fission yield fraction the result is obtained from equation (3.5)

$$Y_{FC} = \frac{\Gamma_{23}B_{23}^{u} + \Gamma_{25}B_{25}^{u} + \Gamma_{49}B_{49}^{u} + \Gamma_{41}B_{41}^{u}}{B_T^{u}}. \tag{3.95}$$

Stated more simply, Y_{FD} and Y_{FC} is the average number of fission product atoms produced per fission (during the time interval) for direct and cumulative yields respectively.

3.2.3 Activation Product Source

The general equations for activation product production from the fission product, and destruction from absorption and decay are given by

$$\frac{dN_p}{dt} = -\phi\sigma_{c,p}N_p - \lambda_p N_p + W_{\tau,D} \tag{3.96}$$

and

$$\frac{dN_A}{dt} = -\phi\sigma_{c,A}N_A - \lambda_A N_A + y_{A,p}\phi\sigma_{c,p}N_p, \tag{3.97}$$

where the subscripts p and A refer to fission product and activation product respectively, and the other parameters are described in the previous two sections. These two equations form a set of coupled differential equations, which can be solved by solving the first equation and then substituting this solution in the second.

Starting by factorising on the right hand side of equation (3.96) and rearranging to get all N_p terms on the left hand side

$$\frac{dN_p}{dt} + \left(\phi\sigma_{c,p} + \lambda_p\right)N_p = W_{\tau,D} \tag{3.98}$$

and multiplying out by an integrating factor $e^{(\phi\sigma_{c,p}+\lambda_p)t}$

$$e^{(\phi\sigma_{c,p}+\lambda_p)t}\frac{dN_p}{dt}+\left(\phi\sigma_{c,p}+\lambda_p\right)e^{(\phi\sigma_{c,p}+\lambda_p)t}N_p=W_{\tau,D}e^{(\phi\sigma_{c,p}+\lambda_p)t} \tag{3.99}$$

then noting the left hand side can be expressed as a single differential gives

$$\frac{d\left(e^{(\phi\sigma_{c,p}+\lambda_p)t}N_p\right)}{dt}=W_{\tau,D}e^{(\phi\sigma_{c,p}+\lambda_p)t}. \tag{3.100}$$

Rearranging this equation

$$d\left(e^{(\phi\sigma_{c,p}+\lambda_p)t}N_p\right)=W_{\tau,D}e^{(\phi\sigma_{c,p}+\lambda_p)t}dt \tag{3.101}$$

and integrating both sides from $t=0$ to $t=t$

$$\int_{t=0}^{t=t}d\left(e^{(\phi\sigma_{c,p}+\lambda_p)t}N_p\right)=\int_0^t W_{\tau,D}e^{(\phi\sigma_{c,p}+\lambda_p)t}dt \tag{3.102}$$

$$e^{(\phi\sigma_{c,p}+\lambda_p)t}N_p(t)-N_p(0)=\frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}\left(e^{(\phi\sigma_{c,p}+\lambda_p)t}-1\right) \tag{3.103}$$

and finally rearranging and simplifying yields the time dependent fission product inventory equation

$$N_p(t)=\left(N_p(0)-\frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}\right)e^{-(\phi\sigma_{c,p}+\lambda_p)t}+\frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}. \tag{3.104}$$

Substituting this solution into equation (3.97) and moving the N_A terms to the left hand side and factorising

$$\frac{dN_A}{dt}+\left(\phi\sigma_{c,A}+\lambda_A\right)N_A=y_{A,p}\phi\sigma_{c,p}\left(N_p(0)-\frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}\right)e^{-(\phi\sigma_{c,p}+\lambda_p)t}+\frac{y_{A,p}\phi\sigma_{c,p}W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p} \tag{3.105}$$

multiplying both sides by the integrating factor $e^{(\phi\sigma_{c,A}+\lambda_A)t}$

$$\begin{aligned}&e^{(\phi\sigma_{c,A}+\lambda_A)t}\frac{dN_A}{dt}+\left(\phi\sigma_{c,A}+\lambda_A\right)e^{(\phi\sigma_{c,A}+\lambda_A)t}N_A\\&=y_{A,p}\phi\sigma_{c,p}\left(N_p(0)-\frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}\right)e^{(-\phi\sigma_{c,p}-\lambda_p+\phi\sigma_{c,A}+\lambda_A)t}+\frac{y_{A,p}\phi\sigma_{c,p}W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}e^{(\phi\sigma_{c,A}+\lambda_A)t}\end{aligned} \tag{3.106}$$

and noting that the left hand side can be expressed as a differential

$$\begin{aligned}\frac{d\left(N_Ae^{(\phi\sigma_{c,A}+\lambda_A)t}\right)}{dt}&=y_{A,p}\phi\sigma_{c,p}\left(N_p(0)-\frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}\right)e^{(-\phi\sigma_{c,p}-\lambda_p+\phi\sigma_{c,A}+\lambda_A)t}+\\&\frac{y_{A,p}\phi\sigma_{c,p}W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}e^{(\phi\sigma_{c,A}+\lambda_A)t}\end{aligned} \tag{3.107}$$

rearranging this equation

$$\begin{aligned}d\left(N_Ae^{(\phi\sigma_{c,A}+\lambda_A)t}\right)&=\left(y_{A,p}\phi\sigma_{c,p}\left(N_p(0)-\frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}\right)e^{(-\phi\sigma_{c,p}-\lambda_p+\phi\sigma_{c,A}+\lambda_A)t}+\right.\\&\left.\frac{y_{A,p}\phi\sigma_{c,p}W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}e^{(\phi\sigma_{c,A}+\lambda_A)t}\right)dt\end{aligned} \tag{3.108}$$

and integrating from $t=0$ to $t=t$

$$\int_{t=0}^{t=t} d\left(N_A e^{\left(\phi\sigma_{c,A}+\lambda_A\right)t}\right) = \int_0^t \left(y_{A,p}\phi\sigma_{c,p}\left(N_p(0) - \frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}\right) e^{\left(-\phi\sigma_{c,p}-\lambda_p+\phi\sigma_{c,A}+\lambda_A\right)t} + \frac{y_{A,p}\phi\sigma_{c,p}W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p} e^{\left(\phi\sigma_{c,A}+\lambda_A\right)t} \right) dt \tag{3.109}$$

yielding

$$N_A(t)e^{\left(\phi\sigma_{c,A}+\lambda_A\right)t} - N_A(0) = \frac{y_{A,p}\phi\sigma_{c,p}W_{\tau,D}}{\left(\phi\sigma_{c,A}+\lambda_A\right)\left(\phi\sigma_{c,p}+\lambda_p\right)}\left(e^{\left(\phi\sigma_{c,A}+\lambda_A\right)t} - 1\right) + \frac{y_{A,p}\phi\sigma_{c,p}}{\phi\sigma_{c,A}+\lambda_A-\phi\sigma_{c,p}-\lambda_p}\left(N_p(0) - \frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}\right)\left(e^{\left(-\phi\sigma_{c,p}-\lambda_p+\phi\sigma_{c,A}+\lambda_A\right)t} - 1\right) \tag{3.110}$$

and rearranging to yield the activation product inventory at the end of the timestep

$$N_A(t) = N_A(0)e^{-\left(\phi\sigma_{c,A}+\lambda_A\right)t} + \frac{y_{A,p}\phi\sigma_{c,p}W_{\tau,D}}{\left(\phi\sigma_{c,A}+\lambda_A\right)\left(\phi\sigma_{c,p}+\lambda_p\right)}\left(1 - e^{-\left(\phi\sigma_{c,A}+\lambda_A\right)t}\right) + \frac{y_{A,p}\phi\sigma_{c,p}}{\phi\sigma_{c,A}+\lambda_A-\phi\sigma_{c,p}-\lambda_p}\left(N_p(0) - \frac{W_{\tau,D}}{\phi\sigma_{c,p}+\lambda_p}\right)\left(e^{\left(-\phi\sigma_{c,p}-\lambda_p\right)t} - e^{-\left(\phi\sigma_{c,A}+\lambda_A\right)t}\right) \tag{3.111}$$

If it is assumed that the fission product does not decay ($\lambda_p = 0$ for stable fission product, as is usually the case), this equation can be written more simply as

$$N_A(t) = N_A(0)e^{-\left(\phi\sigma_{c,A}+\lambda_A\right)t} + \frac{y_{A,p}W_{\tau,D}}{\left(\phi\sigma_{c,A}+\lambda_A\right)}\left(1 - e^{-\left(\phi\sigma_{c,A}+\lambda_A\right)t}\right) + \frac{y_{A,p}\phi\sigma_{c,p}}{\phi\sigma_{c,A}+\lambda_A-\phi\sigma_{c,p}}\left(N_p(0) - \frac{W_{\tau,D}}{\phi\sigma_{c,p}}\right)\left(e^{-\phi\sigma_{c,p}t} - e^{-\left(\phi\sigma_{c,A}+\lambda_A\right)t}\right), \tag{3.112}$$

and further assuming no initial inventory of fission or activation product, it becomes

$$N_A(t) = y_{A,p}W_{\tau,D}\left(\frac{\left(1 - e^{-\left(\phi\sigma_{c,A}+\lambda_A\right)t}\right)}{\left(\phi\sigma_{c,A}+\lambda_A\right)} - \frac{\left(e^{-\phi\sigma_{c,p}t} - e^{-\left(\phi\sigma_{c,A}+\lambda_A\right)t}\right)}{\phi\sigma_{c,A}+\lambda_A-\phi\sigma_{c,p}}\right). \tag{3.113}$$

These are very similar to the formulae used in GETTER, but an anomaly [3], [4] exists in obtaining the exact formula when it comes to activation product inventory calculations. These can be resolved by adjustments to the source code, or verification of the correctness of code, both tasks falling outside the scope of this work.

3.2.4 Estimations of Nuclide Inventory

It is frequently required to estimate nuclide inventory from constant production rates and changing production rates of the isotope. For example, the case of activation product production varies over a timestep, as the mother product concentration increases over the timestep. In most cases, GETTER uses a constant production rate over a timestep, as calculated by equations such as (3.7) and (3.6), this is especially true for fission products. Sometimes it also assumes a linearly increasing production rate, where it uses an interpolation between the production rate at the start and end of a timestep, especially relevant for activation products. This section discusses the simplistic formulae used to calculate the inventory changes by such production rates.

3.2.4.1 Inventory change for constant production rate – no initial concentration given

Assuming a constant production rate R(atoms.s^{-1}) for production of an isotope with decay constant λ, over a timestep of length τ, the balance equation for nuclide production and loss can be written as

$$\frac{dN}{dt} = R - \lambda N \tag{3.114}$$

where $N = N(t)$ is the number of atoms (of the isotope) produced and still living since the beginning of the timestep, i.e. $N(0) = 0$ as the initial condition.

Rearranging this equation so that all terms containing N are moved to the left hand side

$$\frac{dN}{dt} + \lambda N = R, \tag{3.115}$$

followed by multiplying both sides with the integrating factor $e^{\lambda t}$

$$e^{\lambda t}\frac{dN}{dt} + \lambda N e^{\lambda t} = R e^{\lambda t}, \tag{3.116}$$

and noticing that the left hand side can be expressed as a single differential

$$\frac{d\left(Ne^{\lambda t}\right)}{dt} = R e^{\lambda t}, \tag{3.117}$$

which after rearrangement yields

$$d\left(Ne^{\lambda t}\right) = R e^{\lambda t} dt, \tag{3.118}$$

to be integrated on both sides from $t = 0$ to $t = \tau$

$$\int_{t=0}^{t=\tau} d\left(Ne^{\lambda t}\right) = R\int_{t=0}^{t=\tau} e^{\lambda t} dt, \tag{3.119}$$

yielding the equation (after applying the initial condition of no initial concentration)

$$N(\tau)e^{\lambda\tau} = \frac{R}{\lambda}\left(e^{\lambda\tau} - 1\right), \tag{3.120}$$

dividing this by the exponential finally gives the solution for inventory of isotope produced since the start of the timestep and still living at the end of the timestep as

$$N(\tau) = \frac{R}{\lambda}\left(1 - e^{-\lambda\tau}\right), \tag{3.121}$$

where the coefficient of inventory change (from the rate of production) is given by

$$\alpha_I = \frac{\left(1 - e^{-\lambda\tau}\right)}{\lambda}.$$

3.2.4.2 Inventory change for constant production rate – initial concentration given

Following a similar procedure as in the previous section, except using a known initial concentration given by $N(0)=N_0$ in equation (3.119) yields,

$$N(\tau)e^{\lambda\tau}-N_0=\frac{R}{\lambda}\left(e^{\lambda\tau}-1\right), \tag{3.122}$$

dividing this by the exponential finally gives the solution for inventory of isotope still living at the end of the timestep as

$$N(\tau)=\frac{R}{\lambda}\left(1-e^{-\lambda\tau}\right)+N_0e^{-\lambda\tau}. \tag{3.123}$$

3.2.4.3 Inventory change for linearly increasing production rate (initial and final rate given)

For this case it is assumed that the isotope production rate increases linearly from R_0 at time $t=0$, to R_τ at $t=\tau$, hence

$$R(t)=\left(\frac{R_\tau-R_0}{\tau}\right)t+R_0, \tag{3.124}$$

and the balance equation for isotope inventory may be written as

$$\frac{dN}{dt}=\left(\frac{R_\tau-R_0}{\tau}\right)t+R_0-\lambda N, \tag{3.125}$$

where once again, $N=N(t)$ is the number of atoms (of the isotope) produced and still living since the beginning of the timestep, i.e. $N(0)=0$ as the initial condition. Rearranging by moving all terms containing N to the left hand side

$$\frac{dN}{dt}+\lambda N=\left(\frac{R_\tau-R_0}{\tau}\right)t+R_0, \tag{3.126}$$

followed by multiplying both sides by an integrating factor $e^{\lambda t}$

$$\frac{dN}{dt}e^{\lambda t}+\lambda Ne^{\lambda t}=\left(\frac{R_\tau-R_0}{\tau}\right)te^{\lambda t}+R_0e^{\lambda t}, \tag{3.127}$$

and noting that the left hand side can be expressed as a single differential

$$\frac{d\left(Ne^{\lambda t}\right)}{dt}=\left(\frac{R_\tau-R_0}{\tau}\right)te^{\lambda t}+R_0e^{\lambda t}, \tag{3.128}$$

which after rearrangement yields

$$d\left(Ne^{\lambda t}\right)=\left(\left(\frac{R_\tau-R_0}{\tau}\right)te^{\lambda t}+R_0e^{\lambda t}\right)dt. \tag{3.129}$$

Integrating both sides of this equation from $t=0$ to $t=\tau$,

$$\int_{t=0}^{t=\tau}d\left(Ne^{\lambda t}\right)=\int_{t=0}^{t=\tau}\left(\left(\frac{R_\tau-R_0}{\tau}\right)te^{\lambda t}+R_0e^{\lambda t}\right)dt, \tag{3.130}$$

where the integral of the first bracketed term on the right hand side is obtained from a table of integrals [22], [23], and also applying the initial condition $N(0) = 0$, yields

$$N(\tau)e^{\lambda\tau} = \left(\frac{R_\tau - R_0}{\tau}\right)\left(\frac{e^{\lambda\tau}}{\lambda^2}(\lambda\tau - 1) + \frac{1}{\lambda^2}\right) + R_0\left(\frac{e^{\lambda t} - 1}{\lambda}\right). \tag{3.131}$$

Dividing both sides of this equation by the integrating factor,

$$N(\tau) = \left(\frac{R_\tau - R_0}{\tau}\right)\left(\frac{1}{\lambda^2}(\lambda\tau - 1) + \frac{e^{-\lambda\tau}}{\lambda^2}\right) + R_0\left(\frac{1 - e^{-\lambda\tau}}{\lambda}\right), \tag{3.132}$$

followed by expanding the term in brackets of the first term

$$N(\tau) = \left(\frac{R_\tau - R_0}{\tau}\right)\left(\frac{\tau}{\lambda} - \frac{1}{\lambda^2} + \frac{e^{-\lambda\tau}}{\lambda^2}\right) + R_0\left(\frac{1 - e^{-\lambda\tau}}{\lambda}\right), \tag{3.133}$$

and factorising within this bracket gives

$$N(\tau) = \left(\frac{R_\tau - R_0}{\lambda\tau}\right)\left(\tau - \left(\frac{1 - e^{-\lambda t}}{\lambda}\right)\right) + R_0\left(\frac{1 - e^{-\lambda t}}{\lambda}\right), \tag{3.134}$$

where multiplying out the first term

$$N(\tau) = \left(\frac{R_\tau - R_0}{\lambda}\right) - \left(\frac{R_\tau - R_0}{\lambda\tau}\right)\left(\frac{1 - e^{-\lambda\tau}}{\lambda}\right) + R_0\left(\frac{1 - e^{-\lambda\tau}}{\lambda}\right), \tag{3.135}$$

and factorising the last two terms gives

$$N(\tau) = \left(\frac{R_\tau - R_0}{\lambda}\right) + \left(\frac{1 - e^{-\lambda\tau}}{\lambda}\right)\left(R_0 - \frac{R_\tau - R_0}{\lambda\tau}\right), \tag{3.136}$$

which is the form of the isotope inventory equation (produced during a timestep, and still surviving) at the end of a timestep, for linearly increasing production rate, as used in GETTER. It is important to note that such an equation is not only restricted to application over an entire timestep, but it could be used for smaller integral or discrete timesteps as well.

3.2.4.4 Inventory change for linearly increasing release rate (initial and average rate given)

Consider the case of a given initial release rate (R_0), and average rate (R_{av}) of isotope release (from coated particle, sphere, etc.) over a timestep τ, where the initial inventory $N(0) = 0$. The linear rate dependence as a function of time can be written as

$$R(t) = mt + R_0, \tag{3.137}$$

where m represents the gradient of the release rate. The balance equation for the average release rate can be written as

$$\frac{dN}{dt} = R_{av} - \lambda N, \tag{3.138}$$

which is the same form as equation (3.114), and hence has the same form of solution as in equation (3.121)

$$N(\tau)=\frac{R_{av}}{\lambda}\left(1-e^{-\lambda\tau}\right). \tag{3.139}$$

For the increasing release rate, the balance equation can be written as

$$\frac{dN}{dt}=mt+R_0-\lambda N\,, \tag{3.140}$$

which can be solved in a similar manner to the previous section, and has solution

$$N(\tau)=\frac{m}{\lambda}\left(\tau-\left(\frac{1-e^{-\lambda\tau}}{\lambda}\right)\right)+R_0\left(\frac{1-e^{-\lambda\tau}}{\lambda}\right). \tag{3.141}$$

Solving for the gradient m by substituting this equation into the average rate equation (3.139)

$$m=\left(R_{av}-R_0\right)\frac{\left(1-e^{-\lambda\tau}\right)}{\left(\tau-\left(\dfrac{1-e^{-\lambda\tau}}{\lambda}\right)\right)}\,, \tag{3.142}$$

is the rate of change of the release rate over the timestep, and so the time dependence of the rate of release can be written as

$$R(t)=\left(R_{av}-R_0\right)\frac{\left(1-e^{-\lambda\tau}\right)}{\left(\tau-\left(\dfrac{1-e^{-\lambda\tau}}{\lambda}\right)\right)}t+R_0\,. \tag{3.143}$$

3.2.5 Burnup in Contamination

Heavy metal content of the fuel element contamination differs from that in the coated particles, for example, the enrichment is closer to that of natural uranium. In order to calculate the burnup in the contamination, one could apply the formulae derived section 3.2.1.3 to the contamination heavy metal inventory. However, a simpler method exists, which requires less computing resources, but is less accurate. This technique involves using the coated particle burnup and factoring this with the heavy metal content of the contamination, as described in more detail in the sub-sections below. In this section, fuel refers purely to the heavy metal in the UO_2 kernels, and contamination to the heavy metal outside of the UO_2 kernels, i.e. in the matrix graphite.

3.2.5.1 Burnup in uranium based fuel

For fuel and contamination based only on uranium 235 and 238 (plutonium produced only as a product of burnup), the Bateman equation for ^{235}U (3.31) can be re-expressed as

$$\frac{dN_{25F}}{dt}=-\left(\phi\sigma_{c,25}+\phi\sigma_{f,25}\right)N_{25F} \tag{3.144}$$

where the production from activation of ^{234}U has been removed. The subscript F has been added to illustrate that this refers to the fuel inventory, and subscript C will be used for the contamination inventory. Solution of this differential equation is done via the method of integrating factors outlined in the previous section, yielding

$$N_{25F}(t) = N_{25F}(0)e^{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})t}, \tag{3.145}$$

which is similar for the contamination

$$N_{25C}(t) = N_{25C}(0)e^{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})t} \tag{3.146}$$

and so for the burnup (FIMA) of ^{235}U in the fuel, substituting (3.145) in (3.82)

$$B^{u}_{25F}(t) = \frac{\int_0^t \phi\sigma_{f,25}\left(N_{25F}(0)e^{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})t}\right)dt}{N^{0}_{HMF}}, \tag{3.147}$$

and integrating

$$B^{u}_{25F}(t) = \frac{\phi\sigma_{f,25}}{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})N^{0}_{HMF}}\left(e^{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})t}-1\right)N_{25F}(0), \tag{3.148}$$

similarly for the contamination

$$B^{u}_{25C}(t) = \frac{\phi\sigma_{f,25}}{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})N^{0}_{HMC}}\left(e^{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})t}-1\right)N_{25C}(0). \tag{3.149}$$

For an equal timestep size, the two equations above (for fuel and contamination) have a common factor containing the fluxes, cross-sections and timestep size, so letting

$$k_{25} = \frac{\phi\sigma_{f,25}}{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})N^{0}_{HMF}}\left(e^{-(\phi\sigma_{c,25}+\phi\sigma_{f,25})t}-1\right), \tag{3.150}$$

these become

$$B^{u}_{25F}(t) = k_{25}\frac{N_{25F}(0)}{N^{0}_{HMF}} \tag{3.151}$$

$$B^{u}_{25C}(t) = k_{25}\frac{N_{25C}(0)}{N^{0}_{HMC}} \tag{3.152}$$

Similar equations can apply for the burnup from the other fissile isotopes, although this is not entirely correct, because their Bateman equations have production terms. This is an anomaly in GETTER. The extent of the correctness of this assumption needs to be assessed, however, the derivation will be presented here. So the equations for burnup of ^{239}Pu

$$B^{u}_{49F}(t) = k_{49}\frac{N_{28F}(0)}{N^{0}_{HMF}} \tag{3.153}$$

$$B^{u}_{49C}(t) = k_{49}\frac{N_{28C}(0)}{N^{0}_{HMC}} \tag{3.154}$$

and ^{241}Pu

$$B^{u}_{41F}(t) = k_{41}\frac{N_{28F}(0)}{N^{0}_{HMF}} \tag{3.155}$$

$$B^{u}_{41C}(t) = k_{41}\frac{N_{28C}(0)}{N^{0}_{HMC}} \tag{3.156}$$

where the same precursor (^{238}U) was used as the source nuclide. The multiplicative constants in the contamination equations can be eliminated by substitution of the fuel burnup equations, yielding

$$B_{25C}^{u}(t)=\frac{B_{25F}^{u}(t)N_{HMF}^{0}}{N_{25F}(0)}\cdot\frac{N_{25C}(0)}{N_{HMC}^{0}}, \tag{3.157}$$

$$B_{49C}^{u}(t)=\frac{B_{49F}^{u}(t)N_{HMF}^{0}}{N_{28F}(0)}\cdot\frac{N_{28C}(0)}{N_{HMC}^{0}}, \text{ and} \tag{3.158}$$

$$B_{41C}^{u}(t)=\frac{B_{41F}^{u}(t)N_{HMF}^{0}}{N_{28F}(0)}\cdot\frac{N_{28C}(0)}{N_{HMC}^{0}}. \tag{3.159}$$

The fissions per initial atom in the fuel and contamination are given by

$$B_{TF}^{u}=B_{25F}^{u}+B_{49F}^{u}+B_{41F}^{u} \tag{3.160}$$

and

$$B_{TC}^{u}=B_{25C}^{u}+B_{49C}^{u}+B_{41C}^{u} \tag{3.161}$$

respectively. The ratio of burnup between contamination and fuel is given by

$$B_{r}=\frac{B_{TC}^{u}}{B_{TF}^{u}} \tag{3.162}$$

which can be expanded by substitution of (3.151) to (3.161)

$$B_{r}=\frac{\frac{B_{25F}^{u}(t)N_{HMF}^{0}}{N_{25F}(0)}\cdot\frac{N_{25C}(0)}{N_{HMC}^{0}}+\frac{B_{49F}^{u}(t)N_{HMF}^{0}}{N_{28F}(0)}\cdot\frac{N_{28C}(0)}{N_{HMC}^{0}}+\frac{B_{41F}^{u}(t)N_{HMF}^{0}}{N_{28F}(0)}\cdot\frac{N_{28C}(0)}{N_{HMC}^{0}}}{B_{TF}^{u}} \tag{3.163}$$

and simplification by factorisation

$$B_{r}=\frac{\frac{B_{25F}^{u}(t)N_{25C}(0)}{N_{25F}(0)}+\frac{B_{49F}^{u}(t)N_{28C}(0)}{N_{28F}(0)}+\frac{B_{41F}^{u}(t)N_{28C}(0)}{N_{28F}(0)}}{B_{TF}^{u}}\cdot\frac{N_{HMF}^{0}}{N_{HMC}^{0}} \tag{3.164}$$

Letting the ratio of ^{235}U to ^{238}U in the fuel and contamination be a_F and a_C respectively, and substituting this into equation (3.164) yields

$$B_{r}=\frac{\frac{B_{25F}^{u}(t)a_{C}N_{28C}(0)}{a_{F}N_{28F}(0)}+\frac{B_{49F}^{u}(t)N_{28C}(0)}{N_{28F}(0)}+\frac{B_{41F}^{u}(t)N_{28C}(0)}{N_{28F}(0)}}{B_{TF}^{u}}\cdot\frac{N_{HMF}^{0}}{N_{HMC}^{0}}, \tag{3.165}$$

which can be factorised to

$$B_{r}=\frac{B_{25F}^{u}(t)\frac{a_{C}}{a_{F}}+B_{49F}^{u}(t)+B_{41F}^{u}(t)}{B_{TF}^{u}}\cdot\frac{N_{HMF}^{0}N_{28C}(0)}{N_{HMC}^{0}N_{28F}(0)}. \tag{3.166}$$

Now for fuel composed only of ^{235}U and ^{238}U, it is given that the initial composition is described by

$$N_{HMF}^{0}=N_{25F}(0)+N_{28F}(0) \tag{3.167}$$

and

$$N^0_{HMC} = N_{25C}(0) + N_{28C}(0) \tag{3.168}$$

for the fuel and contamination respectively. Once again using the ratios a_f and a_c in these equations gives

$$N^0_{HMF} = a_F N_{28F}(0) + N_{28F}(0), \tag{3.169}$$

and

$$N^0_{HMC} = a_C N_{28C}(0) + N_{28C}(0), \tag{3.170}$$

which can be factorised to

$$N^0_{HMF} = N_{28F}(0)(a_F + 1), \tag{3.171}$$

and

$N^0_{HMC} = N_{28C}(0)(a_C + 1)$. Substituting these two equations into (3.166) and cancelling common factors

$$B_r = \frac{B^u_{25F}(t)\frac{a_C}{a_F} + B^u_{49F}(t) + B^u_{41F}(t)}{B^u_{TF}} \cdot \frac{(a_F + 1)}{(a_C + 1)} \tag{3.172}$$

which gives the ratio of FIMA in contamination to FIMA in fuel based on enrichments ratios and fuel burnup.

3.2.6 Fission Product Recoil

Consider recoil in a sphere of radius r_a with a uniform fission rate density of $w_{p,n}$. Assume the fission products are emitted isotropically, and have an average stopping distance (or recoil range) of l_n in the sphere's material. For a fission occurring at a distance r from the centre of the sphere, the fraction leaving the sphere is given by the ratio of the surface area of the recoil sphere (radius l_n) outside the fission sphere (of radius r_a), to the total area of the fission sphere (see Figure 4); more simply stated

$$\varepsilon(r) = \frac{A_{out}}{A_{tot}}. \tag{3.173}$$

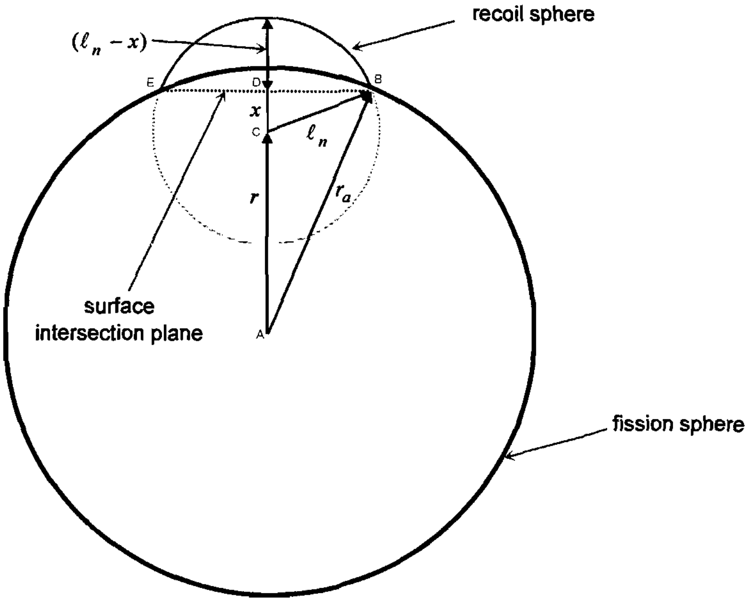


Figure 4: Diagram showing geometry of recoil modelling

The surface area of the recoil sphere outside the fission sphere is equivalent to the surface area of the spherical cap defined by the plane of intersection of the two sphere surfaces (along line BDE), namely,

$$A_{out} = 2\pi \ell_n (\ell_n - x) \tag{3.174}$$

where x is the distance between the surface intersection plane and the centre of the recoil sphere. Proof of this well known relation [24] can be demonstrated using the surface area of revolution integration technique [22].

Solution of x in terms of r, r_a and l_n can be done by applying Pythagoras' Theorem to triangle ABD and CDB to yield

$$(x+r)^2 + DB^2 = r_a^2 \text{, and} \tag{3.175}$$

$$x^2 + DB^2 = \ell_n^2, \tag{3.176}$$

respectively. Substitution of (3.175) into (3.176) and solving for x gives the result

$$x = \frac{r_a^2 - \ell_n^2 - r^2}{2r}. \tag{3.177}$$

Substituting this into equation (3.174) and then into (3.173) yields the area ratio as

$$\varepsilon(r) = \frac{2\pi \ell_n \left(\ell_n - \frac{r_a^2 - \ell_n^2 - r^2}{2r} \right)}{4\pi \ell_n^2}, \tag{3.178}$$

which can be simplified to [10]

$$\varepsilon(r) = \frac{1}{2} - \frac{r_a^2 - \ell_n^2 - r^2}{4 r_a r}. \tag{3.179}$$

For a spherical shell volume element at radius r in the fission sphere, where fission product production rate density is given by $w_{p,n}$, the rate of fission product nuclei leaving the fission sphere by recoil from this volume element is described by

$$dW = w_{p,n} \cdot 4\pi r^2 \cdot \varepsilon(r) \cdot dr \, . \tag{3.180}$$

Integrating this over the entire volume from $r = r_a - \ell_n$ to $r = r_a$, where the recoil range is sufficient to escape the fission sphere, yields the net rate of nuclei leaving the fission sphere

$$W_{R,n} = \int dW \, . \tag{3.181}$$

Substituting (3.180) into this

$$\begin{aligned} W_{R,n} &= \int_{r_a-\ell_n}^{r_a} w_{p,n} \cdot 4\pi r^2 \cdot \varepsilon(r) \cdot dr \\ &= 4\pi\, w_{p,n} \int_{r_a-\ell_n}^{r_a} r^2 \left(\frac{1}{2} - \frac{r_a^2 - \ell_n^2 - r^2}{4 r_a r} \right) dr \end{aligned} \tag{3.182}$$

and carrying out the integration (many lengthy steps) yields the rate of fission product leaving the fission sphere via recoil loss

$$W_{R,n} = w_{p,n} \pi \left(\ell_n r_a^2 - \frac{\ell_n^3}{12} \right). \tag{3.183}$$

The fractional release from the sphere is then given by

$$F_{R,n} = \frac{W_{R,n}}{w_{p,n} V_n} = \frac{W_{R,n}}{W_{p,n}} \tag{3.184}$$

where V_n is the volume of the sphere (or spherical shell) in which the production rate density $w_{p,n}$ is occurring, from a total production rate of $W_{p,n} = w_{p,n} V_n$. It is important to note that this fractional release is only dependent on the geometric factors of sphere radius and recoil range, namely

$$F_{R,n} = \frac{\pi}{V_n} \left(\ell_n r_a^2 - \frac{\ell_n^3}{12} \right), \tag{3.185}$$

where the volume of the sphere can be expressed in terms of the radius, yielding

$$F_{R,n} = \frac{\pi}{\frac{4}{3} \pi r_a^3} \left(\ell_n r_a^2 - \frac{\ell_n^3}{12} \right) \tag{3.186}$$

which after simplification gives the fractional yield from a sphere as

$$F_{R,n} = \frac{3\ell_n}{4 r_a} - \frac{\ell_n^3}{16 r_a^3} \, . \tag{3.187}$$

This can also be done rather simplistically for the case of a spherical shell, provided that

- the thickness of the shell $\delta r = r_a - r_i$ is greater than about twice the recoil range, and
- recoil loss from the inner part of the shell is neglected.

GETTER uses such an approximation for the shell layers of the coated particle, where recoil ranges are of the order of 10 to 15 µm, and layer thickness are greater than 30µm, however, the second condition has not been justified, especially between the silicon carbide and outer pyrocarbon layer. This is an anomaly that needs to be resolved.

Continuing with the case of a spherical shell, the only difference will be the term corresponding to the volume of production would have to be that of the shell, so

$$F_{R,n,s}=\frac{\pi}{\frac{4}{3}\pi\left(r_a^{\ 3}-r_i^{\ 3}\right)}\left(\ell_n r_a^2-\frac{\ell_n^3}{12}\right) \tag{3.188}$$

and

$$F_{R,n,s}=\frac{W_{R,n}}{W_{p,n,s}} \tag{3.189}$$

where the extra subscript s was introduced to refer specifically to the special condition of a shell. This can be simplified to yield the shell fractional release formula (remembering the assumed provisions above)

$$F_{R,n,s}=\frac{3}{4\left(r_a^{\ 3}-r_i^{\ 3}\right)}\left(\ell_n r_a^2-\frac{\ell_n^3}{12}\right) \tag{3.190}$$

3.2.6.1 Source rate density for kernel

As discussed earlier in Table 2, fission product source contributions for the kernel come from fission in the kernel; whereas loss occurs by fission product recoil from the surface of the kernel. For a coated particle fission product production rate $W_{p,cp}$, with contamination fraction C_T in the pyrocarbon layers, the production rate of fission product in the kernel is given by

$$W_{p,k}=W_{p,cp}(1-C_T), \tag{3.191}$$

by subtraction of the recoil rate from the kernel, the net source rate of fission product in the kernel is therefore

$$W_{s,k}=W_{p,cp}\left(1-C_T\right)-W_{R,k}, \tag{3.192}$$

and dividing this by the volume of the kernel gives the source rate density of fission product in the kernel

$$w_{s,k}=\frac{W_{p,cp}\left(1-C_T\right)-W_{R,k}}{V_k}. \tag{3.193}$$

Using equation (3.184) for the kernel gives the fractional release for the kernel as

$$F_{R,k}=\frac{W_{R,k}}{W_{p,k}}=\frac{3\ell_k}{4r_k}-\frac{\ell_k^3}{16r_k^{\ 3}} \tag{3.194}$$

which can be substituted for $W_{R,k}$ in equation (3.193) to yield

$$w_{s,k}=\frac{W_{p,cp}\left(1-C_T\right)-F_{R,k}W_{p,k}}{V_k} \tag{3.195}$$

followed by substituting equation (3.191) into this

$$w_{s,k} = \frac{W_{p,cp}(1-C_T) - F_{R,k}W_{p,cp}(1-C_T)}{V_k} \tag{3.196}$$

and after some factorisation and simplification gives the source rate density for the kernel based on the total coated particle production rate, contamination and geometric fractional release factor

$$w_{s,k} = \frac{W_{p,cp}(1-C_T)(1-F_{R,k})}{V_k} \tag{3.197}$$

3.2.6.2 Source rate density for inner pyrocarbon/buffer layer

GETTER models the inner pyrocarbon layer and buffer layer as a single layer of the coated particle. This is not entirely correct, as these have rather different properties, with regards to density and fission product migration. This anomaly needs to be resolved, by using the correct fractional release formulae for a shell, or verifying that difference is negligible.

For the inner pyrocarbon layer, the source of fission product is twofold, namely from fission production in the contamination (where the contamination fraction is given by C_{ip})

$$W_{p,ip} = W_{p,cp}C_{ip}, \tag{3.198}$$

and recoil from the kernel into the pyrocarbon layer $W_{R,k}$. Loss mechanisms from the inner and outer wall are not taken into account here, and therefore this is an anomaly that needs to be resolved. The source rate in the inner pyrocarbon is given by

$$W_{s,ip} = W_{p,cp}C_{ip} + W_{R,k} \tag{3.199}$$

and dividing by the volume of the inner pyrocarbon shell (V_{ip}) gives the source rate density in the inner pyrocarbon layer

$$w_{s,ip} = \frac{W_{p,cp}C_{ip} + W_{R,k}}{V_{ip}}. \tag{3.200}$$

Substituting (3.194) and (3.191) into this, for $W_{R,k}$, and factorising yields the net fission product source rate density in the inner pyrocarbon layer

$$w_{s,ip} = \frac{W_{p,cp}(C_{ip} + F_{R,k}(1-C_T))}{V_{ip}} \tag{3.201}$$

3.2.6.3 Source rate density for the silicon carbide layer

It is assumed that no heavy metal contamination exists in the silicon carbide layer, and that the only source of fission product is recoil from the inner pyrocarbon layer (shell). Hence the source rate of fission product in the silicon carbide layer is given by

$$W_{s,sc} = W_{R,ip}, \tag{3.202}$$

where the inner pyrocarbon recoil rate $W_{R,ip}$ was used. Dividing this by the volume of the silicon carbide shell (V_{sc}) yields the source rate density of fission product in the silicon carbide shell

$$w_{s,sc} = \frac{W_{R,ip}}{V_{sc}}. \tag{3.203}$$

The fractional recoil release from the inner pyrocarbon shell is obtained by using (3.189)

$$F_{R,ip,s} = \frac{W_{R,ip}}{W_{p,ip,s}} = \frac{3}{4\left(r_{ip}^{\ 3} - r_k^{\ 3}\right)}\left(\ell_{ip} r_{ip}^2 - \frac{\ell_{ip}^3}{12}\right) \tag{3.204}$$

and substituting this into (3.203) gives

$$w_{s,sc} = \frac{F_{R,ip,s} W_{p,ip,s}}{V_{sc}} \tag{3.205}$$

which can be expanded by substitution of the inner pyrocarbon production rate, namely equation (3.198), to yield the fission product source rate density in the silicon carbide layer

$$w_{s,sc} = \frac{F_{R,ip,s} W_{p,cp} C_{ip}}{V_{sc}}. \tag{3.206}$$

3.2.6.4 Source rate density for outer pyrocarbon layer

The source rate of fission product for the outer pyrocarbon layer is made up of production from the contamination, and loss via recoil from the surface

$$W_{s,op} = W_{p,op,s} - W_{R,op}, \tag{3.207}$$

which can be transformed to the source rate density by dividing by the volume of the outer pyrocarbon layer (shell)

$$w_{s,op} = \frac{W_{p,op,s} - W_{R,op}}{V_{op}} \tag{3.208}$$

Production from the contamination is proportional to the total production from the coated particle, with the proportionality constant being the fraction of heavy metal in the outer pyrocarbon layer C_{op}, so

$$W_{p,op,s} = W_{p,cp} C_{op}, \tag{3.209}$$

and the recoil rate can be given in terms of the recoil fraction from a shell (3.189), namely

$$F_{R,op,s} = \frac{W_{R,op}}{W_{p,op,s}} = \frac{3}{4\left(r_{op}^{\ 3} - r_{sc}^{\ 3}\right)}\left(\ell_{op} r_{op}^2 - \frac{\ell_{op}^3}{12}\right) \tag{3.210}$$

When these two equations are substituted into (3.208) the result is

$$w_{s,op} = \frac{W_{p,cp} C_{op} - F_{R,op,s} W_{p,op,s}}{V_{op}} \tag{3.211}$$

and once again substituting (3.209) into this and factorising gives the fission product source rate in the outer pyrocarbon layer

$$w_{s,op} = \frac{W_{p,cp} C_{op} \left(1 - F_{R,op,s}\right)}{V_{op}} \tag{3.212}$$

3.2.7 Gas Precursor Contribution

Derivation of equation (3.10) for the gas precursor release over birth rate in matrix grains and/or pores was illustrated elsewhere [15]. This report also deals with the derivation of the gas precursor concentrations in the grains and/or pores, namely equation (3.11). These equations are used to calculate the rate of formation of the daughter fission product from the parent gas precursor fraction (indirect yield) that migrates through the fuel element.

3.2.8 Heat Transport

For calculating temperatures in the fuel sphere, analytical solutions of the heat diffusion equation (3.15) are used for discretized spherical shells. Steady state conditions and spherical symmetry are assumed, and so a one dimensional shell solution in radial co-ordinate r is determined for different regions of the sphere, namely the fuel free and fuel zone.

3.2.8.1 Fuel free zone

Consider a spherical shell in the fuel free zone, with known outer temperature (T_o at r_o in Figure 5) and heat flux, and wherein the thermal conductivity and heat generation rate is constant.

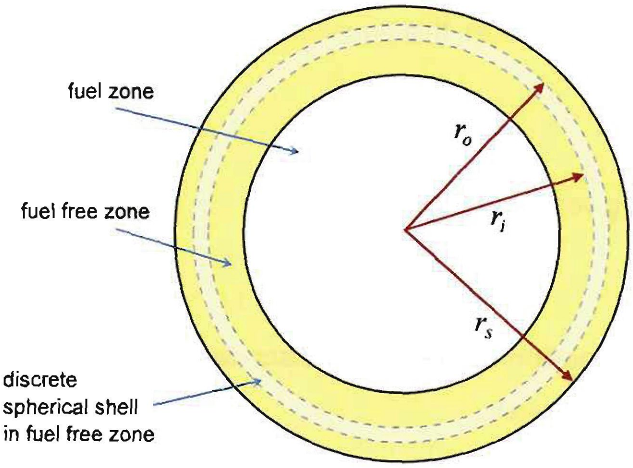


Figure 5: Diagram illustrating discrete spherical shell in fuel free zone

For the fuel-free zone, with constant volumetric heat generation rate given by $\bar{q}_{ffz}$, the steady state heat diffusion equation has the form

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\left(k_m\frac{dT}{dr}\right)\right) + \bar{q}_{ffz} = 0, \tag{3.213}$$

with boundary conditions of known discrete shell outer temperature and heat flux, namely

$$T(r_o) = T_o, \tag{3.214}$$

$$-k_m A_o \left.\frac{dT}{dr}\right|_{r=r_o} = \dot{Q}(r_o) \tag{3.215}$$

where A_o is the discrete spherical shell outer surface area, and $\dot{Q}(r_o)$ is the total power of the sphere up to radius r_o, i.e. the power produced by gamma heating from r_o to r_s is not included. If $\dot{Q}_g$ is the total gamma heating power produced from the fuel sphere, and $\dot{Q}_f$ the total sphere fission power originating from fissions in the fuel zone, then assuming uniform gamma heating throughout the sphere yields

$$\dot{Q}(r_o) = \dot{Q}_f + \dot{Q}_g \frac{r_o^3}{r_s^3}, \tag{3.216}$$

and

$$\bar{q}_{ffz} = \frac{\dot{Q}_g}{\frac{4}{3}\pi r_s^3}. \tag{3.217}$$

By rearranging (3.213)

$$\frac{d}{dr}\left(r^2\left(k_m \frac{dT}{dr}\right)\right) = -\bar{q}_{ffz} r^2, \tag{3.218}$$

and integrating over r yields

$$r^2\left(k_m \frac{dT}{dr}\right) = \frac{-\bar{q}_{ffz} r^3}{3} + C_1, \tag{3.219}$$

where C_1 is an arbitrary constant of integration. Assuming the conductivity is constant in the discrete shell (i.e. no radial dependence), this equation can be rearranged

$$\frac{dT}{dr} = \frac{-\bar{q}_{ffz} r}{3k_m} + \frac{C_1}{k_m r^2}, \tag{3.220}$$

and integrated over r again gives the general solution

$$T(r) = \frac{-\bar{q}_{ffz} r^2}{6k_m} - \frac{C_1}{k_m r} + C_2. \tag{3.221}$$

Applying the first boundary condition of the known discrete shell outer surface temperature, namely equation (3.214) into this gives

$$T_o = \frac{-\bar{q}_{ffz} r_o^2}{6k_m} - \frac{C_1}{k_m r_o} + C_2, \tag{3.222}$$

and the second boundary condition (3.215) can most easily be applied by substitution into (3.220), yielding

$$-k_m A_o \left(\frac{-\bar{q}_{ffz} r_o}{3k_m} + \frac{C_1}{k_m r_o^2}\right) = \dot{Q}(r_o) \tag{3.223}$$

noting that $A_o = 4\pi r_o^2$, the area of the discrete spherical shell outer surface, this may be simplified and solved for C_1,

$$-k_m 4\pi r_o^2\left(\frac{-\bar{\dot q}_{ffz} r_o}{3k_m}+\frac{C_1}{k_m r_o^2}\right)=\dot Q(r_o) \tag{3.224}$$

$$4\pi\left(\frac{\bar{\dot q}_{ffz} r_o^3}{3}-C_1\right)=\dot Q(r_o) \tag{3.225}$$

$$C_1=-\frac{\dot Q(r_o)}{4\pi}+\frac{\bar{\dot q}_{ffz} r_o^3}{3} \tag{3.226}$$

Substituting this into (3.222)

$$T_s=\frac{-\bar{\dot q}_{ffz} r_o^2}{6k_m}+\frac{1}{k_m r_o}\left(\frac{\dot Q(r_o)}{4\pi}-\frac{\bar{\dot q}_{ffz} r_o^3}{3}\right)+C_2 \tag{3.227}$$

and solving for C_2

$$C_2=\frac{\bar{\dot q}_{ffz} r_o^2}{6k_m}-\frac{1}{k_m r_o}\left(\frac{\dot Q(r_o)}{4\pi}-\frac{\bar{\dot q}_{ffz} r_o^3}{3}\right)+T_o \tag{3.228}$$

Finally substituting solutions for C_1 and C_2 into the general solution (3.221) yields

$$T(r)=\frac{-\bar{\dot q}_{ffz} r^2}{6k_m}-\frac{1}{k_m r}\left(\frac{\dot Q(r_o)}{4\pi}-\frac{\bar{\dot q}_{ffz} r_o^3}{3}\right)+\frac{\bar{\dot q}_{ffz} r_o^2}{6k_m}-\frac{1}{k_m r_o}\left(\frac{\dot Q(r_o)}{4\pi}-\frac{\bar{\dot q}_{ffz} r_o^3}{3}\right)+T_o \tag{3.229}$$

and simplifying this gives the radial temperature distribution in the fuel free zone

$$T(r)=\frac{\bar{\dot q}_{ffz}\left(r_o^2-r^2\right)}{6k_m}+\frac{1}{k_m}\left(\frac{\dot Q(r_o)}{4\pi}-\frac{\bar{\dot q}_{ffz} r_o^3}{3}\right)\left(\frac{1}{r}-\frac{1}{r_o}\right)+T_o. \tag{3.230}$$

Substituting the power density in the fuel free zone (3.217) and sphere power (3.216) into this yields

$$T(r)=\frac{\dot Q_g\left(r_o^2-r^2\right)}{8\pi r_s^3 k_m}+\frac{1}{k_m}\left(\frac{\left(\dot Q_f+\dot Q_g\frac{r_o^3}{r_s^3}\right)}{4\pi}-\frac{\dot Q_g r_o^3}{4\pi r_s^3}\right)\left(\frac{1}{r}-\frac{1}{r_o}\right)+T_o \tag{3.231}$$

which can be simplified to

$$T(r)=\frac{1}{4\pi k_m}\left(\frac{\dot Q_g\left(r_o^2-r^2\right)}{2r_s^3}+\dot Q_f\left(\frac{1}{r}-\frac{1}{r_o}\right)\right)+T_o, \tag{3.232}$$

and so for the inner surface of the discrete spherical shell, the temperature is given by

$$T_i=T(r_i)=\frac{1}{4\pi k_m}\left(\frac{\dot Q_g\left(r_o^2-r_i^2\right)}{2r_s^3}+\dot Q_f\left(\frac{1}{r_i}-\frac{1}{r_o}\right)\right)+T_o. \tag{3.233}$$

3.2.8.2 Fuel zone

The spatial temperature distribution for the fuel zone is determined in a similar manner to that of the fuel free zone, with the exception that the fuel zone has a modified power density and flux boundary condition.

Consider a discrete spherical shell (see Figure 6) in the fuel zone with known outer surface temperature (T_{fo} at r_{fo}) and wherein the thermal conductivity and power generation rate (fission and gamma heating) is constant.

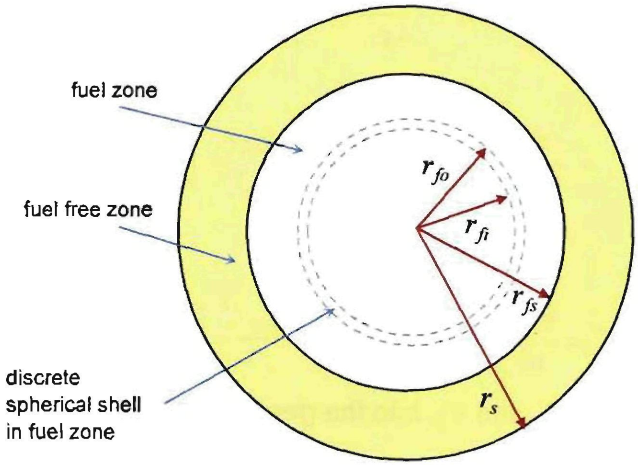


Figure 6: Diagram illustrating discrete spherical shell in fuel zone

For a uniform power density ($\dot{q}_{fz}$) in the fuel zone, the heat diffusion equation in the fuel zone has the form

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\left(k_m\frac{dT_f}{dr}\right)\right)+\dot{q}_{fz}=0 \tag{3.234}$$

with boundary conditions of known discrete shell outer temperature and heat flux, namely

$$T_f(r_{fo})=T_{fo}\,, \tag{3.235}$$

$$-k_m A_{fo}\left.\frac{dT_f}{dr}\right|_{r=r_{fo}}=\dot{Q}_f(r_{fo}) \tag{3.236}$$

where A_{fo} is the discrete spherical shell outer surface area, and $\dot{Q}_f\left(r_{fo}\right)$ is the total power of the sphere up to radius r_{fo}, i.e.

$$\dot{Q}_f\left(r_{fo}\right)=\tfrac{4}{3}\pi r_{fo}^3\dot{q}_{fz} \tag{3.237}$$

If $\dot{Q}_g$ is the total gamma heating power produced from the fuel sphere, and $\dot{Q}_f$ the total sphere fission power originating from fissions in the fuel zone, then for uniform power generation throughout the sphere

$$\dot{q}_{fz} = \frac{\dot{Q}_g}{\frac{4}{3}\pi r_s^3} + \frac{\dot{Q}_f}{\frac{4}{3}\pi r_{fs}^3} \tag{3.238}$$

where it is implied that fission heating takes place only in the fuel zone.

Rearranging the heat diffusion equation (3.234) in the fuel zone

$$\frac{d}{dr}\left(r^2\left(k_m \frac{dT_f}{dr}\right)\right) = -\dot{q}_{fz} r^2 \tag{3.239}$$

and integrating once over r yields

$$r^2\left(k_m \frac{dT_f}{dr}\right) = -\dot{q}_{fz}\frac{r^3}{3} + C_3 \tag{3.240}$$

where C_3 is an arbitrary constant of integration. Rearranging this

$$\frac{dT_f}{dr} = -\frac{\dot{q}_{fz} r}{3k_m} + \frac{C_3}{k_m r^2} \tag{3.241}$$

and integrating once more over r yields the general solution of the radial temperature in the fuel zone

$$T_f(r) = -\frac{\dot{q}_{fz} r^2}{6k_m} - \frac{C_3}{k_m r} + C_4 . \tag{3.242}$$

Applying the first boundary condition (3.235) to this solution yields

$$T_f(r_{fo}) = T_{fo} = -\frac{\dot{q}_{fz} r_{fo}^2}{6k_m} - \frac{C_3}{k_m r_{fo}} + C_4 \tag{3.243}$$

and the second boundary condition (3.236) can be most easily applied using (3.241) to give

$$-k_m A_{fo}\left(-\frac{\dot{q}_{fz} r_{fo}}{3k_m} + \frac{C_3}{k_m r_{fo}^2}\right) = \dot{Q}_f(r_{fo}) \tag{3.244}$$

which can be simplified substituting equation (3.237) into it and rearranging to solve for C_3

$$C_3 = \frac{\dot{q}_{fz} r_{fo}^3}{3} - \frac{\frac{4}{3}\pi r_{fo}^5 \dot{q}_{fz}}{A_{fo}} \tag{3.245}$$

and substituting $A_{fo} = 4\pi r_{fo}^2$ into this results in

$$C_3 = 0 , \tag{3.246}$$

So by substituting this into (3.243) to and rearranging to solve for C_4

$$C_4 = \frac{\dot{q}_{fz} r_{fo}^2}{6k_m} + T_{fo} \tag{3.247}$$

which when substituted into the general solution (3.242) gives the particular solution

$$T_f(r) = -\frac{\dot{q}_{fz} r^2}{6k_m} + \frac{\dot{q}_{fz} r_{fo}^2}{6k_m} + T_{fo} , \tag{3.248}$$

and after some simplifications gives the solution

$$T_f(r) = \frac{\dot{q}_{fz}}{6k_m}\left(r_{fo}^2 - r^2\right) + T_{fo} . \tag{3.249}$$

Hence for the temperature at the inner surface (at $r = r_{fi}$) of the discrete shell

$$T_{fi} = T_f(r_{fi}) = \frac{\dot{q}_{fz}}{6k_m}\left(r_{fo}^2 - r_{fi}^2\right) + T_{fo}. \tag{3.250}$$

For the special case of the innermost shell $r_{fi} = 0$, the equation for the centre temperature is given by

$$T_{fi,in} = \frac{\dot{q}_{fz}}{6k_m} r_{fo,in}^2 + T_{fo,in}, \tag{3.251}$$

where $r_{fo,in}$ is the radius of the innermost spherical shell (which is actually a sphere), and $T_{fo,in}$ the temperature on the surface of this innermost "shell".

3.2.8.2.1 Fuel zone - volumetric average temperature

The volumetric average temperature of a spherical shell from $r = r_{fi}$ to r_{fo}, with temperature distribution $T_f(r)$, is given by

$$\overline{T}_{f,sh} = \frac{\int_{r_{fi}}^{r_{fo}} T_f(r)\,dV}{\int_{r_{fi}}^{r_{fo}} dV} \tag{3.252}$$

where the volume element dV can be expressed as

$$dV = 4\pi r^2 dr \tag{3.253}$$

because $T_f(r)$ is assumed to be independent of polar or azimuthal co-ordinate, so the equation becomes

$$\overline{T}_{f,sh} = \frac{\int_{r_{fi}}^{r_{fo}} T_f(r) 4\pi r^2 dr}{\int_{r_{fi}}^{r_{fo}} 4\pi r^2 dr}. \tag{3.254}$$

Cancelling the common factor of 4π between numerator and denominator, integrating the denominator, and substituting the temperature distribution for a spherical shell (equation (3.249)) into this

$$\overline{T}_{f,sh} = \frac{\int_{r_{fi}}^{r_{fo}} \left(\frac{\dot{q}_{fz}}{6k_m}\left(r_{fo}^2 - r^2\right) + T_{fo} \right) r^2 dr}{\frac{r_{fo}^3 - r_{fi}^3}{3}}, \tag{3.255}$$

and multiplying out the integrand

$$\bar{T}_{f,sh} = \frac{\int_{r_{fi}}^{r_{fo}} \left(\frac{\dot{q}_{fz}}{6k_m} r_{fo}^2 r^2 - \frac{\dot{q}_{fz}}{6k_m} r^4 + T_{fo} r^2 \right) dr}{\frac{r_{fo}^3 - r_{fi}^3}{3}} \tag{3.256}$$

which can now be integrated to yield

$$\bar{T}_{f,sh} = \frac{\frac{\dot{q}_{fz}}{6k_m} r_{fo}^2 \left(\frac{r_{fo}^3 - r_{fi}^3}{3} \right) - \frac{\dot{q}_{fz}}{6k_m} \left(\frac{r_{fo}^5 - r_{fi}^5}{5} \right) + T_{fo} \left(\frac{r_{fo}^3 - r_{fi}^3}{3} \right)}{\frac{r_{fo}^3 - r_{fi}^3}{3}} \tag{3.257}$$

where inverting the denominator and simplifying finally gives the volumetric average temperature for a fuel zone spherical shell

$$\bar{T}_{f,sh} = \frac{\dot{q}_{fz}}{6k_m} r_{fo}^2 - \frac{\dot{q}_{fz}}{10k_m} \left(\frac{r_{fo}^5 - r_{fi}^5}{r_{fo}^3 - r_{fi}^3} \right) + T_{fo} . \tag{3.258}$$

For the case that the spherical shell represents the innermost shell (i.e. central spherical shell), $r_{fi} = 0$, and this equation becomes

$$\bar{T}_{f,sh,in} = \frac{\dot{q}_{fz}}{6k_m} r_{fo}^2 - \frac{\dot{q}_{fz}}{10k_m} r_{fo}^2 + T_{fo} \tag{3.259}$$

which can be simplified by adding like terms gives the volumetric average temperature of the innermost shell as

$$\bar{T}_{f,sh,in} = \frac{\dot{q}_{fz}}{15k_m} r_{fo,in}^2 + T_{fo,in} . \tag{3.260}$$

It must be noted that for the innermost shell, equation (3.251) can be substituted into this to replace $r_{fo,in}^2$, giving the volumetric average temperature as a function of the centre temperature and innermost shell outer temperature

$$\bar{T}_{f,sh,in} = \frac{2}{5}\left(T_{fi,in} - T_{fo,in}\right) + T_{fo,in} . \tag{3.261}$$

There is an anomaly in GETTER as it uses the above equation for the non-innermost shells of the temperature zones as well. The correct formula to use for these zones is equation (3.258).

3.2.8.3 Graphite cup (calotte) surrounding the fuel sphere

In the case of irradiation experiments in a materials test reactor, the fuel sphere is usually encapsulated in a graphite cup, also referred to in the code as a calotte (German origin), which can be approximated to be a thin spherical shell. Even though this is not the case, i.e. the calotte is spherically hollow inside and cylindrical on the outside, GETTER uses the model of a spherical shell cup to calculate the temperatures in the cup. This is an anomaly that needs to be resolved by modelling the correct cup geometry.

In the materials test reactor, the fuel sphere surface temperature is given by thermocouples placed on the surface, and hence this value need not be calculated as in the case of a pebble in the pebble bed reactor. It is also assumed that the gamma heating density in the graphite cup is the same as that of the fuel free zone, a reasonable assumption as the densities and material types are rather well matched. It is also assumed that the temperature gradient and dimension of the graphite cup is small enough not to change the conductivity significantly, and hence a constant conductivity is assumed throughout the graphite cup.

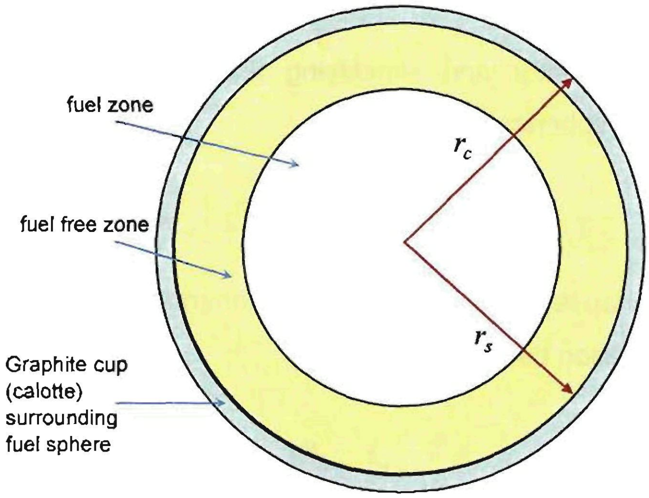


Figure 7: Diagram illustrating graphite cup surrounding fuel sphere

Hence the heat diffusion equation for the graphite cup, with a constant volumetric heat generation rate $\bar{q}_c$, is given by

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\left(k_m\frac{dT_{cp}}{dr}\right)\right)+\bar{q}_c=0 \qquad (3.262)$$

with boundary conditions of known inner surface temperature and heat flux, namely

$$T_{cp}(r_s)=T_{cp,s} \qquad (3.263)$$

$$-k_mA_c\left.\frac{dT_{cp}}{dr}\right|_{r=r_c}=\dot{Q}(r_c) \qquad (3.264)$$

where A_c is the surface area of the outer surface of the cup (at r_c), and $\dot{Q}(r_c)$ is the total power generated by the sphere (fission and gamma heating) and graphite cup. Using the previous definition of $\dot{Q}_g$ as the total gamma heating power produced from the fuel sphere, and assuming that the gamma power density in the fuel zone and fuel free zone is the same as that of the cup (an anomaly still to be proved), then the power density in the fuel free zone can be written as

$$\bar{q}_c=\bar{q}_{ffz}=\frac{\dot{Q}_g}{\frac{4}{3}\pi r_s^3}, \qquad (3.265)$$

and the total gamma power from the graphite cup $\left(\dot{Q}_{g,c}\right)$ is therefore

$$\dot{Q}_{g,c}=\frac{\dot{Q}_g}{\frac{4}{3}\pi r_s^3}\cdot\tfrac{4}{3}\pi\left(r_c^3-r_s^3\right) \tag{3.266}$$

which can be written more simply as

$$\dot{Q}_{g,c}=\frac{\dot{Q}_g}{r_s^3}\left(r_c^3-r_s^3\right). \tag{3.267}$$

Another useful variable is the total power from the sphere $\dot{Q}_T$, which can be written as the sum of the fission power in the fuel zone $\dot{Q}_f$, the gamma power in the sphere $\dot{Q}_g$, namely

$$\dot{Q}_T=\dot{Q}_f+\dot{Q}_g. \tag{3.268}$$

Hence the total power generated by the cup and the sphere can be written as

$$\dot{Q}(r_c)=\dot{Q}_T+\dot{Q}_{g,c}, \tag{3.269}$$

where the power from the graphite cup can be re-expressed using equation (3.267)

$$\dot{Q}(r_c)=\dot{Q}_T+\frac{\dot{Q}_g}{r_s^3}\left(r_c^3-r_s^3\right) \tag{3.270}$$

and the boundary condition for heat flux (equation (3.264)) becomes

$$-k_m A_c\left.\frac{dT_{cp}}{dr}\right|_{r=r_c}=\dot{Q}_T+\frac{\dot{Q}_g}{r_s^3}\left(r_c^3-r_s^3\right) \tag{3.271}$$

where the area $A_c=4\pi r_c^2$ can be substituted into this to give

$$-k_m 4\pi r_c^2\left.\frac{dT_{cp}}{dr}\right|_{r=r_c}=\dot{Q}_T+\frac{\dot{Q}_g}{r_s^3}\left(r_c^3-r_s^3\right), \tag{3.272}$$

and after some simplification and rearrangement, the boundary condition becomes

$$\left.\frac{dT_{cp}}{dr}\right|_{r=r_c}=-\frac{\dot{Q}_T}{4\pi r_c^2 k_m}-\frac{\dot{Q}_g}{4\pi r_c^2 k_m r_s^3}\left(r_c^3-r_s^3\right). \tag{3.273}$$

Returning to the differential equation (3.262), and substituting the cup power density (3.265) into this

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\left(k_m\frac{dT_{cp}}{dr}\right)\right)+\frac{\dot{Q}_g}{\frac{4}{3}\pi r_s^3}=0, \tag{3.274}$$

and rearranging

$$\frac{d}{dr}\left(r^2\left(k_m\frac{dT_{cp}}{dr}\right)\right)=-\frac{\dot{Q}_g}{\frac{4}{3}\pi r_s^3}r^2, \tag{3.275}$$

followed by integrating both sides with respect to r yields

$$r^2\left(k_m\frac{dT_{cp}}{dr}\right)=-\frac{\dot{Q}_g}{\frac{4}{3}\pi r_s^3}\frac{r^3}{3}+C_1, \tag{3.276}$$

where C_1 is a constant of integration. Dividing both sides of this equation by $r^2 k_m$, and noting that k_m was assumed to be a constant through the graphite cup, gives a first order differential equation

$$\frac{dT_{cp}}{dr} = -\frac{\dot{Q}_g}{4\pi k_m r_s^3} r + \frac{C_1}{r^2 k_m}, \tag{3.277}$$

which at the outer surface of the graphite cup, $r = r_c$, can be expressed as

$$\left.\frac{dT_{cp}}{dr}\right|_{r=r_c} = -\frac{\dot{Q}_g}{4\pi k_m r_s^3} r_c + \frac{C_1}{r_c^2 k_m}. \tag{3.278}$$

Substituting this equation into the heat flux boundary condition (3.273)

$$-\frac{\dot{Q}_g}{4\pi k_m r_s^3} r_c + \frac{C_1}{r_c^2 k_m} = -\frac{\dot{Q}_T}{4\pi r_c^2 k_m} - \frac{\dot{Q}_g}{4\pi r_c^2 k_m r_s^3}\left(r_c^3 - r_s^3\right), \tag{3.279}$$

followed by rearranging and simplifying yields the solution for the integration constant as

$$C_1 = \frac{\dot{Q}_g}{4\pi} - \frac{\dot{Q}_T}{4\pi}, \tag{3.280}$$

which can be substituted into the differential equation (3.277) to give

$$\frac{dT_{cp}}{dr} = -\frac{\dot{Q}_g}{4\pi k_m r_s^3} r + \frac{1}{r^2 k_m}\left(\frac{\dot{Q}_g}{4\pi} - \frac{\dot{Q}_T}{4\pi}\right). \tag{3.281}$$

This equation can be integrated with respect to r to yield the temperature distribution within the graphite cup

$$T_{cp}(r) = -\frac{\dot{Q}_g}{8\pi k_m r_s^3} r^2 - \frac{1}{r k_m}\left(\frac{\dot{Q}_g}{4\pi} - \frac{\dot{Q}_T}{4\pi}\right) + C_2, \tag{3.282}$$

save for an integration constant C_2, which can be determined by use of the inner surface temperature boundary condition (3.263)

$$T_{cp}(r_s) = T_{cp,s} = -\frac{\dot{Q}_g}{8\pi k_m r_s} - \frac{1}{r_s k_m}\left(\frac{\dot{Q}_g}{4\pi} - \frac{\dot{Q}_T}{4\pi}\right) + C_2, \tag{3.283}$$

which upon rearrangement yields the integration constant as

$$C_2 = T_{cp,s} + \frac{\dot{Q}_g}{8\pi k_m r_s} + \frac{1}{r_s k_m}\left(\frac{\dot{Q}_g}{4\pi} - \frac{\dot{Q}_T}{4\pi}\right). \tag{3.284}$$

Substituting this constant into the solution (3.282) gives the temperature distribution in the graphite cup as

$$T_{cp}(r) = -\frac{\dot{Q}_g}{8\pi k_m r_s^3} r^2 - \frac{1}{r k_m}\left(\frac{\dot{Q}_g}{4\pi} - \frac{\dot{Q}_T}{4\pi}\right) + T_{cp,s} + \frac{\dot{Q}_g}{8\pi k_m r_s} + \frac{1}{r_s k_m}\left(\frac{\dot{Q}_g}{4\pi} - \frac{\dot{Q}_T}{4\pi}\right), \tag{3.285}$$

or more simply (after some algebra)

$$T_{cp}(r) = T_{cp,s} + \frac{\dot{Q}_g}{8\pi k_m r_s^3}\left(r_s^2 - r^2\right) + \frac{1}{4\pi k_m}\left(\frac{1}{r_s} - \frac{1}{r}\right)\left(\dot{Q}_g - \dot{Q}_T\right). \tag{3.286}$$

For the temperature at the outer surface of the graphite cup, i.e. at $r = r_c$, this equation yields

$$T_{cp}(r_c) = T_{cp,s} + \frac{\dot{Q}_g}{8\pi k_m r_s^3}\left(r_s^2 - r_c^2\right) + \frac{1}{4\pi k_m}\left(\frac{1}{r_s} - \frac{1}{r_c}\right)\left(\dot{Q}_g - \dot{Q}_T\right), \tag{3.287}$$

which can be multiplied out and simplified to give the surface temperature of the graphite cup as

$$T_{cp}(r_c) = T_{cp,s} + \frac{\dot{Q}_g}{4\pi k_m r_s^3}\left(\frac{3}{2}r_s^3 - \frac{r_c^2}{2} - \frac{r_s^3}{r_c}\right) + \frac{\dot{Q}_T}{4\pi k_m}\left(\frac{1}{r_c} - \frac{1}{r_s}\right). \tag{3.288}$$

3.2.9 Time dependent concentration and numerical solution of the diffusion equation

Assuming the fission/activation product concentration has a spatial dependence only in the radial direction, i.e. no azimuthal or polar dependence, the diffusion equation (3.26) can be simplified to

$$\frac{\partial c_n}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left(D_n(r)\frac{\partial c_n}{\partial r}\right)\right) + w_{p,n}(r) - \lambda c_n, \tag{3.289}$$

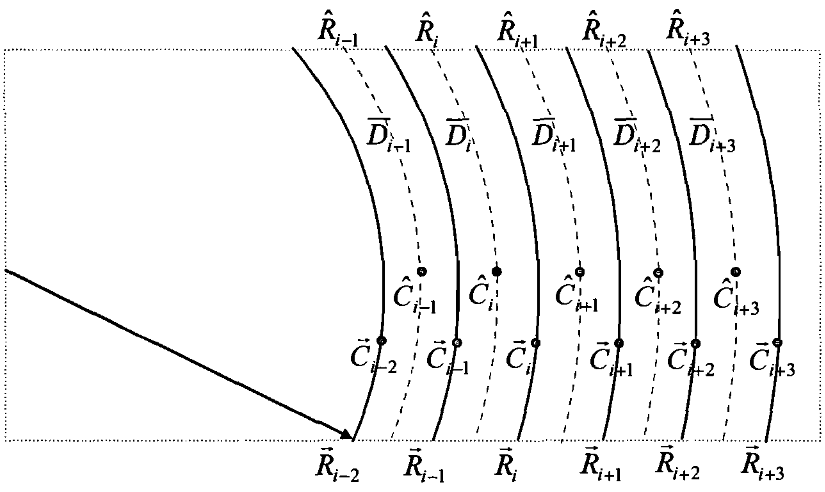
where spatial diffusion coefficient (D_n) and production rate $(w_{p,n})$ have a radial spatial dependence. For the purpose of simplicity in this section, the subscripts p and n will be dropped, and capital $C\ (= c)$ will be used, yielding the equation

$$\frac{\partial C}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\left(D(r)\frac{\partial C}{\partial r}\right)\right) + w(r) - \lambda C. \tag{3.290}$$

Analytical solution of this equation cannot been found, primarily because the diffusion coefficient and production rate do not have known analytical forms. Hence a numerical solution is sought, with many possible discretizations schemes possible. A discussion is given of two similar schemes, both involving Crank-Nicholson solution of the second order partial differential equation, but from slightly different perspectives. The first presents a direct discretization of the differential equation (3.290), and the second uses Fick's first law and conservation of mass. These approaches have previously been used and are also summarised in an early Dragon Project report of the software code FIPDIG [25].

3.2.9.1 Finite difference approach

Consider a section of the discrete spherical shells, where indexes for the diffusion coefficient, production rate and concentration are assigned as shown in Figure 8.



KEY
$\vec{R}_i$ = radius at outer surface of mesh zone i,
$\hat{R}_i$ = radius at centre of mesh zone i,
$\vec{C}_i$ = concentration at outer surface of mesh zone i,
$\hat{C}_i$ = concentration at centre of mesh zone i,
$\overline{D}_i$ = average diffusion coefficient in mesh zone i.

Figure 8: Diagram illustrating indexing of discrete spherical shells.

Carrying out the outer derivative spatial (radial) discretization for the generalised mesh zone i yields

$$\frac{\partial \hat{C}_i}{\partial t} = \frac{1}{\hat{R}_i^2} \frac{\left(\vec{R}_i^2 \vec{D}_i \left.\frac{\partial C}{\partial r}\right|_i - \vec{R}_{i-1}^2 \vec{D}_{i-1} \left.\frac{\partial C}{\partial r}\right|_{i-1} \right)}{\vec{R}_i - \vec{R}_{i-1}} + w_i - \lambda \hat{C}_i, \qquad (3.291)$$

where

$\vec{D}_i$ = effective diffusion coefficient on the outer surface of mesh zone i,

$\left.\frac{\partial C}{\partial r}\right|_i$ = gradient of concentration at outer surface of mesh zone i, and

w_i = average production rate density of fission/activation product in mesh zone i.

The effective diffusion coefficient on the outer surface can be determined by using conservation of mass (i.e. flow rate of material from the inner part of mesh zone boundary must equal the flow rate from the outer part), namely for the outer boundary of mesh zone i

$$-\overline{D}_i \frac{\vec{C}_i - \hat{C}_i}{\vec{R}_i - \hat{R}_i} = -\overline{D}_{i+1} \frac{\hat{C}_{i+1} - \vec{C}_i}{\hat{R}_{i+1} - \vec{R}_i} = -\vec{D}_i \frac{\hat{C}_{i+1} - \hat{C}_i}{\hat{R}_{i+1} - \hat{R}_i}. \qquad (3.292)$$

Taking the left side equation

$$-\overline{D}_i \frac{\vec{C}_i - \hat{C}_i}{\vec{R}_i - \hat{R}_i} = -\overline{D}_{i+1} \frac{\hat{C}_{i+1} - \vec{C}_i}{\hat{R}_{i+1} - \vec{R}_i} \tag{3.293}$$

and solving for $\vec{C}_i$ by first simplifying and rearranging

$$\overline{D}_i \left(\vec{C}_i - \hat{C}_i\right)\left(\hat{R}_{i+1} - \vec{R}_i\right) = \overline{D}_{i+1}\left(\hat{C}_{i+1} - \vec{C}_i\right)\left(\vec{R}_i - \hat{R}_i\right) \tag{3.294}$$

then multiplying out

$$\overline{D}_i \vec{C}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) - \overline{D}_i \hat{C}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) = \overline{D}_{i+1} \hat{C}_{i+1} \left(\vec{R}_i - \hat{R}_i\right) - \overline{D}_{i+1} \vec{C}_i \left(\vec{R}_i - \hat{R}_i\right) \tag{3.295}$$

and gathering $\vec{C}_i$ terms on the left hand side

$$\overline{D}_i \vec{C}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1} \vec{C}_i \left(\vec{R}_i - \hat{R}_i\right) = \overline{D}_{i+1} \hat{C}_{i+1} \left(\vec{R}_i - \hat{R}_i\right) + \overline{D}_i \hat{C}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) \tag{3.296}$$

taking out a common factor of $\vec{C}_i$, and dividing through by the remaining factor yields

$$\vec{C}_i = \frac{\overline{D}_{i+1} \hat{C}_{i+1} \left(\vec{R}_i - \hat{R}_i\right) + \overline{D}_i \hat{C}_i \left(\hat{R}_{i+1} - \vec{R}_i\right)}{\overline{D}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1} \left(\vec{R}_i - \hat{R}_i\right)}. \tag{3.297}$$

Now (3.292) can be used to solve for the effective diffusion coefficient $\vec{D}_i$ by substituting (3.297) into the right hand equation of (3.292)

$$-\overline{D}_{i+1} \frac{\hat{C}_{i+1} - \dfrac{\overline{D}_{i+1} \hat{C}_{i+1} \left(\vec{R}_i - \hat{R}_i\right) + \overline{D}_i \hat{C}_i \left(\hat{R}_{i+1} - \vec{R}_i\right)}{\overline{D}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1} \left(\vec{R}_i - \hat{R}_i\right)}}{\hat{R}_{i+1} - \vec{R}_i} = -\vec{D}_i \frac{\hat{C}_{i+1} - \hat{C}_i}{\hat{R}_{i+1} - \hat{R}_i} \tag{3.298}$$

and simplifying the numerator on the left hand side by finding a common denominator

$$-\overline{D}_{i+1} \frac{\dfrac{\hat{C}_{i+1}\left(\overline{D}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1} \left(\vec{R}_i - \hat{R}_i\right)\right) - \overline{D}_{i+1} \hat{C}_{i+1} \left(\vec{R}_i - \hat{R}_i\right) - \overline{D}_i \hat{C}_i \left(\hat{R}_{i+1} - \vec{R}_i\right)}{\overline{D}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1} \left(\vec{R}_i - \hat{R}_i\right)}}{\hat{R}_{i+1} - \vec{R}_i} = -\vec{D}_i \frac{\hat{C}_{i+1} - \hat{C}_i}{\hat{R}_{i+1} - \hat{R}_i} \tag{3.299}$$

and multiplying out

$$-\overline{D}_{i+1} \frac{\dfrac{\hat{C}_{i+1} \overline{D}_i \hat{R}_{i+1} - \hat{C}_{i+1} \overline{D}_i \vec{R}_i + \hat{C}_{i+1} \overline{D}_{i+1} \vec{R}_i - \hat{C}_{i+1} \overline{D}_{i+1} \hat{R}_i - \overline{D}_{i+1} \hat{C}_{i+1} \vec{R}_i + \overline{D}_{i+1} \hat{C}_{i+1} \hat{R}_i - \overline{D}_i \hat{C}_i \hat{R}_{i+1} + \overline{D}_i \hat{C}_i \vec{R}_i}{\overline{D}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1} \left(\vec{R}_i - \hat{R}_i\right)}}{\hat{R}_{i+1} - \vec{R}_i}$$

$$= -\vec{D}_i \frac{\hat{C}_{i+1} - \hat{C}_i}{\hat{R}_{i+1} - \hat{R}_i}$$

…(3.300)

thereafter removing additive inverses

$$-\overline{D}_{i+1} \frac{\dfrac{\hat{C}_{i+1} \overline{D}_i \hat{R}_{i+1} - \hat{C}_{i+1} \overline{D}_i \vec{R}_i - \hat{C}_i \overline{D}_i \hat{R}_{i+1} + \hat{C}_i \overline{D}_i \vec{R}_i}{\overline{D}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1} \left(\vec{R}_i - \hat{R}_i\right)}}{\hat{R}_{i+1} - \vec{R}_i} = -\vec{D}_i \frac{\hat{C}_{i+1} - \hat{C}_i}{\hat{R}_{i+1} - \hat{R}_i} \tag{3.301}$$

and factorising the numerator

$$-\overline{D}_{i+1} \frac{\dfrac{\hat{C}_{i+1} \overline{D}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) - \hat{C}_i \overline{D}_i \left(\hat{R}_{i+1} - \vec{R}_i\right)}{\overline{D}_i \left(\hat{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1} \left(\vec{R}_i - \hat{R}_i\right)}}{\hat{R}_{i+1} - \vec{R}_i} = -\vec{D}_i \frac{\hat{C}_{i+1} - \hat{C}_i}{\hat{R}_{i+1} - \hat{R}_i} \tag{3.302}$$

Removing a common factor from the numerator and cancelling with the denominator

$$-\bar{D}_{i+1}\frac{\hat{C}_{i+1}\bar{D}_i-\hat{C}_i\bar{D}_i}{\bar{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\bar{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)}=-\vec{D}_i\frac{\hat{C}_{i+1}-\hat{C}_i}{\hat{R}_{i+1}-\hat{R}_i} \tag{3.303}$$

Once again factorising the numerator

$$-\bar{D}_{i+1}\frac{\bar{D}_i\left(\hat{C}_{i+1}-\hat{C}_i\right)}{\bar{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\bar{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)}=-\vec{D}_i\frac{\hat{C}_{i+1}-\hat{C}_i}{\hat{R}_{i+1}-\hat{R}_i} \tag{3.304}$$

And simplifying by dividing through by common factors

$$\frac{\bar{D}_{i+1}\bar{D}_i}{\bar{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\bar{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)}=\vec{D}_i\frac{1}{\hat{R}_{i+1}-\hat{R}_i} \tag{3.305}$$

Rearranging this gives the effective diffusion coefficient at the outer boundary of mesh zone i

$$\vec{D}_i=\frac{\bar{D}_{i+1}\bar{D}_i\left(\hat{R}_{i+1}-\hat{R}_i\right)}{\bar{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\bar{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)}. \tag{3.306}$$

Similarly, for the inner boundary of mesh zone i the diffusion coefficient may be found

$$\vec{D}_{i-1}=\frac{\bar{D}_i\bar{D}_{i-1}\left(\hat{R}_i-\hat{R}_{i-1}\right)}{\bar{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\bar{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)}. \tag{3.307}$$

Substituting these into equation (3.291)

$$\begin{aligned}\frac{\partial\hat{C}_i}{\partial t}=\frac{1}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\Bigg[&\vec{R}_i^2\left(\frac{\bar{D}_{i+1}\bar{D}_i\left(\hat{R}_{i+1}-\hat{R}_i\right)}{\bar{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\bar{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)}\right)\left|\frac{\partial C}{\partial r}\right|_i-\\ &\vec{R}_{i-1}^2\left(\frac{\bar{D}_i\bar{D}_{i-1}\left(\hat{R}_i-\hat{R}_{i-1}\right)}{\bar{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\bar{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)}\right)\left|\frac{\partial C}{\partial r}\right|_{i-1}\Bigg]+w_i-\lambda\hat{C}_i\end{aligned} \tag{3.308}$$

and discretising the inner gradient of the concentration

$$\begin{aligned}\frac{\partial\hat{C}_i}{\partial t}=\frac{1}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\Bigg[&\vec{R}_i^2\left(\frac{\bar{D}_{i+1}\bar{D}_i\left(\hat{R}_{i+1}-\hat{R}_i\right)}{\bar{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\bar{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)}\right)\left(\frac{\hat{C}_{i+1}-\hat{C}_i}{\hat{R}_{i+1}-\hat{R}_i}\right)-\\ &\vec{R}_{i-1}^2\left(\frac{\bar{D}_i\bar{D}_{i-1}\left(\hat{R}_i-\hat{R}_{i-1}\right)}{\bar{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\bar{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)}\right)\left(\frac{\hat{C}_i-\hat{C}_{i-1}}{\hat{R}_i-\hat{R}_{i-1}}\right)\Bigg]+w_i-\lambda\hat{C}_i\end{aligned} \tag{3.309}$$

which can be simplified by cancelling common factors across numerators and denominators

$$\begin{aligned}\frac{\partial\hat{C}_i}{\partial t}=\frac{1}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\Bigg[&\vec{R}_i^2\left(\frac{\bar{D}_{i+1}\bar{D}_i\left(\hat{C}_{i+1}-\hat{C}_i\right)}{\bar{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\bar{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)}\right)-\\ &\vec{R}_{i-1}^2\left(\frac{\bar{D}_i\bar{D}_{i-1}\left(\hat{C}_i-\hat{C}_{i-1}\right)}{\bar{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\bar{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)}\right)\Bigg]+w_i-\lambda\hat{C}_i\end{aligned}. \tag{3.310}$$

Applying the time discretization and using average concentrations on the right hand side, as per Crank-Nicholson technique

$$\begin{aligned}\frac{\hat{C}_i^{j+1}-\hat{C}_i^j}{\Delta t}=\frac{1}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}&\left[\vec{R}_i^2\left(\frac{\overline{D}_{i+1}\overline{D}_i\left(\frac{\hat{C}_{i+1}^{j+1}+\hat{C}_{i+1}^j}{2}-\frac{\hat{C}_i^{j+1}+\hat{C}_i^j}{2}\right)}{\overline{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)}\right)-\right.\\ &\left.\vec{R}_{i-1}^2\left(\frac{\overline{D}_i\overline{D}_{i-1}\left(\frac{\hat{C}_i^{j+1}+\hat{C}_i^j}{2}-\frac{\hat{C}_{i-1}^{j+1}+\hat{C}_{i-1}^j}{2}\right)}{\overline{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)}\right)\right]+w_i-\lambda\left(\frac{\hat{C}_i^{j+1}+\hat{C}_i^j}{2}\right)\end{aligned} \qquad (3.311)$$

Multiplying out by Δt and simplifying

$$\begin{aligned}\hat{C}_i^{j+1}-\hat{C}_i^j=\frac{1}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}&\left[\vec{R}_i^2\left(\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\left(\hat{C}_{i+1}^{j+1}+\hat{C}_{i+1}^j-\hat{C}_i^{j+1}-\hat{C}_i^j\right)}{2\left(\overline{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)\right)}\right)-\right.\\ &\left.\vec{R}_{i-1}^2\left(\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\left(\hat{C}_i^{j+1}+\hat{C}_i^j-\hat{C}_{i-1}^{j+1}-\hat{C}_{i-1}^j\right)}{2\left(\overline{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)\right)}\right)\right]+w_i\Delta t-\lambda\left(\hat{C}_i^{j+1}+\hat{C}_i^j\right)\frac{\Delta t}{2}\end{aligned} \qquad (3.312)$$

and rearranging to move all $j+1$ terms to the left hand side, and all j terms to the right hand side and factorising

$$\begin{aligned}&\left(1+\lambda\frac{\Delta t}{2}+\frac{\vec{R}_i^2}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\frac{\Delta t\overline{D}_{i+1}\overline{D}_i}{2\left(\overline{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)\right)}+\right.\\ &\left.\frac{\vec{R}_{i-1}^2}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\frac{\Delta t\overline{D}_i\overline{D}_{i-1}}{2\left(\overline{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)\right)}\right)\hat{C}_i^{j+1}-\\ &\frac{\vec{R}_i^2}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\frac{\Delta t\overline{D}_{i+1}\overline{D}_i}{2\left(\overline{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)\right)}\hat{C}_{i+1}^{j+1}-\\ &\frac{\vec{R}_{i-1}^2}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\frac{\Delta t\overline{D}_i\overline{D}_{i-1}}{2\left(\overline{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)\right)}\hat{C}_{i-1}^{j+1}\\ =\;&\left(1-\lambda\frac{\Delta t}{2}-\frac{\vec{R}_i^2}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\frac{\Delta t\overline{D}_{i+1}\overline{D}_i}{2\left(\overline{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)\right)}-\right.\\ &\left.\frac{\vec{R}_{i-1}^2}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\frac{\Delta t\overline{D}_i\overline{D}_{i-1}}{2\left(\overline{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)\right)}\right)\hat{C}_i^j+\\ &\frac{\vec{R}_i^2}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\frac{\Delta t\overline{D}_{i+1}\overline{D}_i}{2\left(\overline{D}_i\left(\hat{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\hat{R}_i\right)\right)}\hat{C}_{i+1}^j+\\ &\frac{\vec{R}_{i-1}^2}{\hat{R}_i^2\left(\vec{R}_i-\vec{R}_{i-1}\right)}\frac{\Delta t\overline{D}_i\overline{D}_{i-1}}{2\left(\overline{D}_{i-1}\left(\hat{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\hat{R}_{i-1}\right)\right)}\hat{C}_{i-1}^j+w_i\Delta t\end{aligned} \qquad (3.313)$$

Letting the coefficients of $\hat{C}_{i-1}^{j+1}$, $\hat{C}_i^{j+1}$ and $\hat{C}_{i+1}^{j+1}$ be equal to A_i, G_i, and H_i respectively, this equation then becomes

$$G_i\hat{C}_i^{j+1}+H_i\hat{C}_{i+1}^{j+1}+A_i\hat{C}_{i-1}^{j+1}=\left(2-G_i\right)\hat{C}_i^j-H_i\hat{C}_{i+1}^j-A_i\hat{C}_{i-1}^j+w_i\Delta t \qquad (3.314)$$

where it may be noted that

$$G_i = 1 + \lambda\frac{\Delta t}{2} - H_i - A_i \, . \tag{3.315}$$

Letting the right hand side of equation (3.314) equal K_i^j gives the general form as

$$G_i\hat{C}_i^{j+1} + H_i\hat{C}_{i+1}^{j+1} + A_i\hat{C}_{i-1}^{j+1} = K_i^j \tag{3.316}$$

The boundary condition at the centre of the sphere is given by the requirement of symmetry, in that the gradient of the concentration at the centre of the sphere be equal to zero, and is basically a Neumann boundary condition [23] as the gradient is specified. In discrete form this may be stated as

$$-D(0)\left|\frac{\partial C}{\partial r}\right|_0 = -\vec{D}_0\frac{\vec{C}_0 - \hat{C}_1}{\vec{R}_0 - \hat{R}_1} = 0 \, , \tag{3.317}$$

where the subscript 0 refers to the sphere centre position, namely at $r = \vec{R}_0 = 0$.

This may be used in the discrete equation for the first mesh zone of the sphere, namely equation (3.308) for the first mesh zone

$$\begin{aligned}\frac{\partial\hat{C}_1}{\partial t} = \frac{1}{\hat{R}_1^2\left(\vec{R}_1 - \vec{R}_0\right)}\Bigg\{ & \vec{R}_1^2\left(\frac{\overline{D}_2\overline{D}_1\left(\hat{R}_2 - \hat{R}_1\right)}{\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)}\right)\left|\frac{\partial C}{\partial r}\right|_1 - \\ & \vec{R}_0^2\left(\frac{\overline{D}_1\overline{D}_0\left(\hat{R}_1 - \hat{R}_0\right)}{\overline{D}_0\left(\hat{R}_1 - \vec{R}_0\right) + \overline{D}_1\left(\vec{R}_0 - \hat{R}_0\right)}\right)\left|\frac{\partial C}{\partial r}\right|_0\Bigg\} + w_1 - \lambda\hat{C}_1\end{aligned} \, , \tag{3.318}$$

and substituting (3.317) into this results in

$$\frac{\partial\hat{C}_1}{\partial t} = \frac{1}{\hat{R}_1^2\left(\vec{R}_1 - \vec{R}_0\right)}\vec{R}_1^2\left(\frac{\overline{D}_2\overline{D}_1\left(\hat{R}_2 - \hat{R}_1\right)}{\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)}\right)\left|\frac{\partial C}{\partial r}\right|_1 + w_1 - \lambda\hat{C}_1 \tag{3.319}$$

which be simplified completely discretized by applying similar techniques as for equation (3.308) through (3.313) above to yield

$$\begin{aligned}&\left(1 + \frac{\lambda\Delta t}{2} + \frac{\vec{R}_1^2}{\hat{R}_1^2\left(\vec{R}_1 - \vec{R}_0\right)}\frac{\Delta t\overline{D}_2\overline{D}_1}{2\left(\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\right)\hat{C}_1^{j+1} - \\ &\frac{\vec{R}_1^2}{\hat{R}_1^2\left(\vec{R}_1 - \vec{R}_0\right)}\frac{\Delta t\overline{D}_2\overline{D}_1}{2\left(\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\hat{C}_2^{j+1} \\ &\quad = \left(1 - \frac{\lambda\Delta t}{2} - \frac{\vec{R}_1^2}{\hat{R}_1^2\left(\vec{R}_1 - \vec{R}_0\right)}\frac{\Delta t\overline{D}_2\overline{D}_1}{2\left(\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\right)\hat{C}_1^j + \\ &\qquad \frac{\vec{R}_1^2}{\hat{R}_1^2\left(\vec{R}_1 - \vec{R}_0\right)}\frac{\Delta t\overline{D}_2\overline{D}_1}{2\left(\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\hat{C}_2^j + w_1\Delta t\end{aligned} \tag{3.320}$$

where $\vec{R}_0 = 0$ has been used. Letting the coefficient of $\hat{C}_1^{j+1}$ and $\hat{C}_2^{j+1}$ be equal to G_1 and H_1 respectively, yields

$$G_1\hat{C}_1^{j+1} + H_1\hat{C}_2^{j+1} = \left(2 - G_1\right)\hat{C}_1^j - H_1\hat{C}_2^j + w_1\Delta t \, , \tag{3.321}$$

where $G_1 = \left(1 + \frac{\lambda\Delta t}{2} + H_1\right)$. Finally, setting the right hand side equal to K_1^j gives

$$G_1\hat{C}_1^{j+1} + H_1\hat{C}_2^{j+1} = K_1^j \qquad (3.322)$$

For the outer surface, two boundary conditions are possible, that of a constant surface concentration, or that of a constant outer concentration resulting in a mass transfer rate governed by the evapouration constant. These are discussed further.

3.2.9.1.1 Constant surface concentration boundary condition

At the surface of the sphere (i.e. at $r = R_b = r_s$), a Dirichlet boundary condition is applied in that the concentration is specified and fixed at all times, namely

$$C(R_b) = \vec{C}_b, \qquad (3.323)$$

where the index b refers to the outermost mesh zone of the sphere. Defining a radial position midway between $\hat{R}_b$ and $\vec{R}_b$ as $\hat{\vec{R}}_b$, and treating this as the mesh zone surface between $\hat{C}_b$ and $\vec{C}_b$ yields (using equation (3.291) and Figure 9)

$$\frac{\partial \hat{C}_b}{\partial t} = \frac{1}{\hat{R}_b^2}\frac{\left(\hat{\vec{R}}_b^2\overline{D}_b\left\|\frac{\partial C}{\partial r}\right\|_b - \vec{R}_{b-1}^2\vec{D}_{b-1}\left|\frac{\partial C}{\partial r}\right|_{b-1}\right)}{\hat{\vec{R}}_b - \vec{R}_{b-1}} + w_b - \lambda\hat{C}_b, \qquad (3.324)$$

where

$\left\|\frac{\partial C}{\partial r}\right\|_b$ is the gradient of the concentration at radial position $\hat{\vec{R}}_b$.

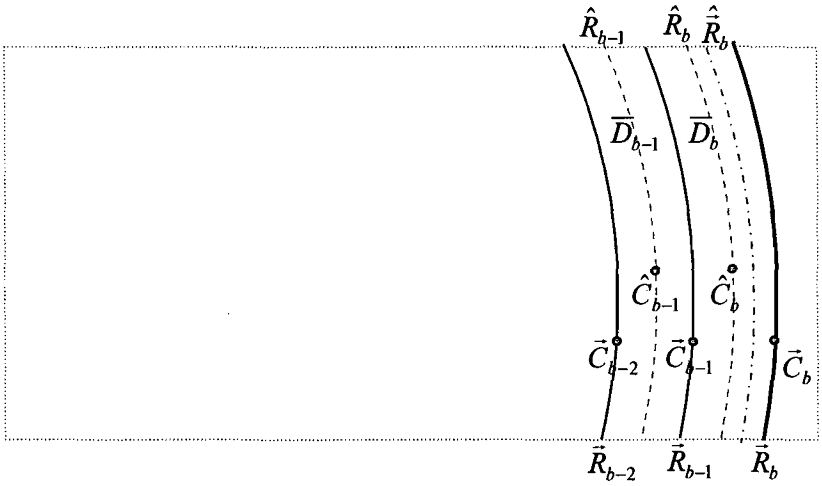


Figure 9: Diagram illustrating indexing near boundary mesh zone

Using the mesh zone boundary diffusion coefficient equation (3.307) for $\vec{D}_{b-1}$, equation (3.324) becomes

$$\frac{\partial \hat{C}_b}{\partial t} = \frac{1}{\hat{R}_b^2} \frac{\left(\hat{\vec{R}}_b^2 \overline{D}_b \left\| \frac{\partial C}{\partial r} \right\|_b - \vec{R}_{b-1}^2 \left(\frac{\overline{D}_b \overline{D}_{b-1} \left(\hat{R}_b - \hat{R}_{b-1} \right)}{\overline{D}_{b-1} \left(\hat{R}_b - \vec{R}_{b-1} \right) + \overline{D}_b \left(\vec{R}_{b-1} - \hat{R}_{b-1} \right)} \right) \left| \frac{\partial C}{\partial r} \right|_{b-1} \right)}{\hat{\vec{R}}_b - \vec{R}_{b-1}} + w_b - \lambda \hat{C}_b , \tag{3.325}$$

and discretising the inner concentration gradients

$$\begin{aligned} \frac{\partial \hat{C}_b}{\partial t} = \frac{1}{\hat{R}_b^2 \left(\hat{\vec{R}}_b - \vec{R}_{b-1} \right)} \Bigg\{ & \hat{\vec{R}}_b^2 \overline{D}_b \left(\frac{\vec{C}_b - \hat{C}_b}{\vec{R}_b - \hat{R}_b} \right) - \\ & \vec{R}_{b-1}^2 \left(\frac{\overline{D}_b \overline{D}_{b-1} \left(\hat{R}_b - \hat{R}_{b-1} \right)}{\overline{D}_{b-1} \left(\hat{R}_b - \vec{R}_{b-1} \right) + \overline{D}_b \left(\vec{R}_{b-1} - \hat{R}_{b-1} \right)} \right) \left(\frac{\hat{C}_b - \hat{C}_{b-1}}{\hat{R}_b - \hat{R}_{b-1}} \right) \Bigg\} + w_b - \lambda \hat{C}_b \end{aligned} \tag{3.326}$$

which can be simplified slightly by cancelling common factors between numerator and denominator

$$\begin{aligned} \frac{\partial \hat{C}_b}{\partial t} = \frac{1}{\hat{R}_b^2 \left(\hat{\vec{R}}_b - \vec{R}_{b-1} \right)} \Bigg\{ & \hat{\vec{R}}_b^2 \overline{D}_b \left(\frac{\vec{C}_b - \hat{C}_b}{\vec{R}_b - \hat{R}_b} \right) - \quad . \\ & \vec{R}_{b-1}^2 \left(\frac{\overline{D}_b \overline{D}_{b-1} \left(\hat{C}_b - \hat{C}_{b-1} \right)}{\overline{D}_{b-1} \left(\hat{R}_b - \vec{R}_{b-1} \right) + \overline{D}_b \left(\vec{R}_{b-1} - \hat{R}_{b-1} \right)} \right) \Bigg\} + w_b - \lambda \hat{C}_b \end{aligned} \tag{3.327}$$

Applying the time discretization and using average concentrations on the right hand side, as per Crank-Nicholson technique

$$\begin{aligned} \frac{\hat{C}_b^{j+1} - \hat{C}_b^j}{\Delta t} = \frac{1}{\hat{R}_b^2 \left(\hat{\vec{R}}_b - \vec{R}_{b-1} \right)} \Bigg\{ & \hat{\vec{R}}_b^2 \overline{D}_b \left(\frac{\vec{C}_b^{j+1} + \vec{C}_b^j - \hat{C}_b^{j+1} - \hat{C}_b^j}{2 \left(\vec{R}_b - \hat{R}_b \right)} \right) - \\ & \vec{R}_{b-1}^2 \left(\frac{\overline{D}_b \overline{D}_{b-1} \left(\hat{C}_b^{j+1} + \hat{C}_b^j - \hat{C}_{b-1}^{j+1} - \hat{C}_{b-1}^j \right)}{2 \left(\overline{D}_{b-1} \left(\hat{R}_b - \vec{R}_{b-1} \right) + \overline{D}_b \left(\vec{R}_{b-1} - \hat{R}_{b-1} \right) \right)} \right) \Bigg\} + w_b - \lambda \left(\frac{\hat{C}_b^{j+1} + \hat{C}_b^j}{2} \right) \end{aligned} \tag{3.328}$$

multiplying out by Δt and simplifying

$$\begin{aligned} \hat{C}_b^{j+1} - \hat{C}_b^j = & \frac{\Delta t \hat{\vec{R}}_b^2 \overline{D}_b}{\hat{R}_b^2} \left(\frac{\vec{C}_b^{j+1} + \vec{C}_b^j - \hat{C}_b^{j+1} - \hat{C}_b^j}{2 \left(\hat{\vec{R}}_b - \vec{R}_{b-1} \right) \left(\vec{R}_b - \hat{R}_b \right)} \right) - \\ & \frac{\Delta t \vec{R}_{b-1}^2}{\hat{R}_b^2} \left(\frac{\overline{D}_b \overline{D}_{b-1} \left(\hat{C}_b^{j+1} + \hat{C}_b^j - \hat{C}_{b-1}^{j+1} - \hat{C}_{b-1}^j \right)}{2 \left(\hat{\vec{R}}_b - \vec{R}_{b-1} \right) \left(\overline{D}_{b-1} \left(\hat{R}_b - \vec{R}_{b-1} \right) + \overline{D}_b \left(\vec{R}_{b-1} - \hat{R}_{b-1} \right) \right)} \right) + \\ & \Delta t w_b - \frac{\Delta t \lambda}{2} \left(\hat{C}_b^{j+1} + \hat{C}_b^j \right) \end{aligned} \tag{3.329}$$

noting that $\vec{C}_b^j = \vec{C}_b^{j+1} = \vec{C}_b$ as per boundary condition, and rearranging to move all non-boundary $j+1$ terms to the left hand side, and all j terms to the right hand side and factorising

$$\begin{aligned}
&\left\{1+\frac{\Delta t\lambda}{2}+\left(\frac{\Delta t\hat{\vec{R}}_b^2\overline{D}_b}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\vec{R}_b-\hat{R}_b\right)}\right)+\right.\\
&\left.\left(\frac{\Delta t\vec{R}_{b-1}^2\overline{D}_b\overline{D}_{b-1}}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\right\}\hat{C}_b^{j+1}-\\
&\left(\frac{\Delta t\vec{R}_{b-1}^2\overline{D}_b\overline{D}_{b-1}}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\hat{C}_{b-1}^{j+1}\\
&=\left\{1-\frac{\Delta t\lambda}{2}-\left(\frac{\Delta t\hat{\vec{R}}_b^2\overline{D}_b}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\vec{R}_b-\hat{R}_b\right)}\right)-\right.\\
&\left.\left(\frac{\Delta t\vec{R}_{b-1}^2\overline{D}_b\overline{D}_{b-1}}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\right\}\hat{C}_b^{j}+\\
&\left(\frac{\Delta t\vec{R}_{b-1}^2\overline{D}_b\overline{D}_{b-1}}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\hat{C}_{b-1}^{j}+\\
&\Delta tw_b+\left(\frac{\Delta t\hat{\vec{R}}_b^2\overline{D}_b}{\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\vec{R}_b-\hat{R}_b\right)}\right)\vec{C}_b
\end{aligned}\tag{3.330}$$

Letting the coefficients of $\hat{C}_{b-1}^{j+1}$ and $\hat{C}_b^{j+1}$ be equal to A_b and G_b respectively, this equation then becomes

$$A_b\hat{C}_{b-1}^{j+1}+G_b\hat{C}_b^{j+1}=\left(2-G_b\right)\hat{C}_b^j-A_b\hat{C}_{b-1}^j+\Delta tw_b+\left(\frac{\Delta t\hat{\vec{R}}_b^2\overline{D}_b}{\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\vec{R}_b-\hat{R}_b\right)}\right)\vec{C}_b \tag{3.331}$$

and setting the right hand side equal to K_b^j yields

$$A_b\hat{C}_{b-1}^{j+1}+G_b\hat{C}_b^{j+1}=K_b^j\,. \tag{3.332}$$

Finally, the equations for the inner boundary (3.322), general mesh zone (3.316), and outer boundary (3.332) form a set of simultaneous equations, which can be cast into matrix form as

$$\begin{pmatrix} G_1 & H_1 & 0 & 0 & \cdots & \cdots & 0 \\ A_2 & G_2 & H_2 & 0 & \cdots & \cdots & 0 \\ 0 & A_3 & G_3 & H_3 & \cdots & \cdots & 0 \\ \vdots & 0 & \ddots & \ddots & \ddots & \cdots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & 0 \\ \vdots & \vdots & \vdots & 0 & A_{b-1} & G_{b-1} & H_{b-1} \\ 0 & 0 & \cdots & \cdots & 0 & A_b & G_b \end{pmatrix} \begin{pmatrix} \hat{C}_1^{j+1} \\ \hat{C}_2^{j+1} \\ \hat{C}_3^{j+1} \\ \vdots \\ \vdots \\ \hat{C}_{b-1}^{j+1} \\ \hat{C}_b^{j+1} \end{pmatrix} = \begin{pmatrix} K_1^j \\ K_2^j \\ K_3^j \\ \vdots \\ \vdots \\ K_{b-1}^j \\ K_b^j \end{pmatrix}. \qquad (3.333)$$

The elements on the right hand side of the equation are known from the initial and boundary conditions for the first time step ($j = 0$ to $j = 1$), and the elements in the leftmost tri-diagonal matrix are known from diffusion and geometric data of the system, and so this equation can be solved for concentration at the end of the timestep ($j = 1$) by using the Crout Factorisation for Tridiagonal Linear Systems algorithm [26]. These new concentration values can then be used as the initial values for the following timestep and so forth; hence a complete numerical solution of concentration profile as a function of time is achieved.

The first step in the Gauss-Jordan elimination of a tri-diagonal matrix is known as forward elimination, in which the lower triangular elements are eliminated by subtraction of multiplies of the upper row, i.e.

$$A_2' = A_2 - \frac{A_2}{G_1} G_1 = 0 \qquad (3.334)$$

$$G_2' = G_2 - \frac{A_2}{G_1} H_1 \qquad (3.335)$$

$$H_2' = H_2 - \frac{A_2}{G_1} \cdot 0 = H_2 \qquad (3.336)$$

$$K_2'^j = K_2^j - \frac{A_2}{G_1} K_1^j \qquad (3.337)$$

Or more generally

$$A_i' = 0 \quad \forall \quad 2 \le i \le b \qquad (3.338)$$

$$G_i' = G_i - \frac{A_i}{G_{i-1}} H_{i-1} \quad \forall \quad 2 \le i \le b \qquad (3.339)$$

$$H_i' = H_i \quad \forall \quad 1 \le i \le b-1 \qquad (3.340)$$

$$K_i'^j = K_i^j - \frac{A_i}{G_{i-1}} K_{i-1}^j \quad \forall \quad 2 \le i \le b \qquad (3.341)$$

This step of forward elimination reduces the matrix equation to the upper triangular form

$$\begin{pmatrix} G_1' & H_1 & 0 & 0 & \cdots & \cdots & 0 \\ 0 & G_2' & H_2 & 0 & \cdots & \cdots & 0 \\ 0 & 0 & G_3' & H_3 & \cdots & \cdots & 0 \\ \vdots & 0 & \ddots & \ddots & \ddots & \cdots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & 0 \\ \vdots & \vdots & \vdots & 0 & 0 & G_{b-1}' & H_{b-1} \\ 0 & 0 & \cdots & \cdots & 0 & 0 & G_b' \end{pmatrix} \begin{pmatrix} \hat{C}_1^{j+1} \\ \hat{C}_2^{j+1} \\ \hat{C}_3^{j+1} \\ \vdots \\ \vdots \\ \hat{C}_{b-1}^{j+1} \\ \hat{C}_b^{j+1} \end{pmatrix} = \begin{pmatrix} K_1'^j \\ K_2'^j \\ K_3'^j \\ \vdots \\ \vdots \\ K_{b-1}'^j \\ K_b'^j \end{pmatrix} \tag{3.342}$$

Following this, is the step of backward substitution where the solutions are determined by substituting solutions of concentrations from the last element to the first,

$$\hat{C}_b^{j+1} = \frac{K_b'^j}{G_b'} \tag{3.343}$$

$$\hat{C}_{b-1}^{j} = \left(K_{b-1}'^j - H_{b-1}\hat{C}_b^{j+1}\right) / G_{b-1}' \tag{3.344}$$

In general

$$\hat{C}_i^{j+1} = \left(K_i'^j - H_i\hat{C}_{i+1}^{j+1}\right) / G_i' \quad \forall \quad 1 \le i \le b-1 \tag{3.345}$$

gives the solution of the concentration profile for each successive timestep.

3.2.9.1.2 Mass transfer at surface boundary condition

For a given concentration $\left(C_{b+1}^j\right)$ of diffusant beyond the surface, the mass transfer at the surface (of the sphere) can be given by the relation [17], [18]

$$J_b = h_c\left(\vec{C}_b - C_{b+1}^j\right) \tag{3.346}$$

where

h_c = mass transfer coefficient,

J_b = flux of mass transfer at the boundary.

For conservation of mass, this flux must equal the flux flowing out of the surface from the outer mesh zone, namely

$$J_b = -\bar{D}_b\left(\frac{\hat{C}_b - \vec{C}_b}{\hat{R}_b - \vec{R}_b}\right) = h_c\left(\vec{C}_b - C_{b+1}^j\right), \tag{3.347}$$

where it can be solved for $\vec{C}_b$ by first multiplying out on both sides

$$-\hat{C}_b\left(\frac{\bar{D}_b}{\hat{R}_b - \vec{R}_b}\right) + \vec{C}_b\left(\frac{\bar{D}_b}{\hat{R}_b - \vec{R}_b}\right) = h_c\vec{C}_b - h_c C_{b+1}^j \tag{3.348}$$

and then moving all the $\vec{C}_b$ terms to the left hand side

$$\vec{C}_b\left(\frac{\bar{D}_b}{\hat{R}_b - \vec{R}_b}\right) - h_c\vec{C}_b = -h_c C_{b+1}^j + \hat{C}_b\left(\frac{\bar{D}_b}{\hat{R}_b - \vec{R}_b}\right), \tag{3.349}$$

followed by factorising the common factor of $\vec{C}_b$ on the left hand side,

$$\vec{C}_b\left(\left(\frac{\overline{D}_b}{\hat{R}_b-\vec{R}_b}\right)-h_c\right)=-h_c C^{j}_{b+1}+\hat{C}_b\left(\frac{\overline{D}_b}{\hat{R}_b-\vec{R}_b}\right), \tag{3.350}$$

and dividing through by the coefficient of $\vec{C}_b$,

$$\vec{C}_b=\frac{\hat{C}_b\left(\frac{\overline{D}_b}{\hat{R}_b-\vec{R}_b}\right)-h_c C^{j}_{b+1}}{\left(\left(\frac{\overline{D}_b}{\hat{R}_b-\vec{R}_b}\right)-h_c\right)}, \tag{3.351}$$

which can be simplified by multiplying out by the denominator to finaly yield

$$\vec{C}_b=\frac{\hat{C}_b\overline{D}_b-h_c C^{j}_{b+1}\left(\hat{R}_b-\vec{R}_b\right)}{\overline{D}_b-h_c\left(\hat{R}_b-\vec{R}_b\right)} \tag{3.352}$$

Substituting this into equation (3.327), which represents the discretized diffusion equation for the outermost mesh zone,

$$\begin{aligned}\frac{\partial\hat{C}_b}{\partial t}=\frac{1}{\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)}&\left(\hat{\vec{R}}_b^2\overline{D}_b\left(\frac{\frac{\hat{C}_b\overline{D}_b-h_c C^{j}_{b+1}\left(\hat{R}_b-\vec{R}_b\right)}{\overline{D}_b-h_c\left(\hat{R}_b-\vec{R}_b\right)}-\hat{C}_b}{\vec{R}_b-\hat{R}_b}\right)-\right.\\&\left.\vec{R}_{b-1}^2\left(\frac{\overline{D}_b\overline{D}_{b-1}\left(\hat{C}_b-\hat{C}_{b-1}\right)}{\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)}\right)\right)+w_b-\lambda\hat{C}_b\end{aligned} \tag{3.353}$$

and simplifying by reducing the fractional component in the double fraction,

$$\begin{aligned}\frac{\partial\hat{C}_b}{\partial t}=\frac{1}{\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)}&\left(\hat{\vec{R}}_b^2\overline{D}_b\left(\frac{\hat{C}_b\overline{D}_b-h_c C^{j}_{b+1}\left(\hat{R}_b-\vec{R}_b\right)-\hat{C}_b\overline{D}_b+\hat{C}_b h_c\left(\hat{R}_b-\vec{R}_b\right)}{\left(\vec{R}_b-\hat{R}_b\right)\left(\overline{D}_b-h_c\left(\hat{R}_b-\vec{R}_b\right)\right)}\right)-\right.\\&\left.\vec{R}_{b-1}^2\left(\frac{\overline{D}_b\overline{D}_{b-1}\left(\hat{C}_b-\hat{C}_{b-1}\right)}{\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)}\right)\right)+w_b-\lambda\hat{C}_b\end{aligned} \tag{3.354}$$

and then gathering like terms in the numerator that has been reduced, and cancelling common factors

$$\begin{aligned}\frac{\partial\hat{C}_b}{\partial t}=\frac{1}{\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)}&\left(\hat{\vec{R}}_b^2\overline{D}_b\left(\frac{h_c\left(C^{j}_{b+1}-\hat{C}_b\right)}{\overline{D}_b-h_c\left(\hat{R}_b-\vec{R}_b\right)}\right)-\right.\\&\left.\vec{R}_{b-1}^2\left(\frac{\overline{D}_b\overline{D}_{b-1}\left(\hat{C}_b-\hat{C}_{b-1}\right)}{\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)}\right)\right)+w_b-\lambda\hat{C}_b\end{aligned} \tag{3.355}$$

Applying the time discretization and using average concentrations on the right hand side, as per Crank-Nicholson technique

$$\begin{aligned}\frac{\hat{C}_b^{j+1}-\hat{C}_b^{j}}{\Delta t}=\frac{1}{\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)}&\left(\hat{\vec{R}}_b^2\overline{D}_b\left(\frac{h_c\left(C_{b+1}^{j+1}+C_{b+1}^{j}-\hat{C}_b^{j+1}-\hat{C}_b^{j}\right)}{2\left(\overline{D}_b-h_c\left(\hat{R}_b-\vec{R}_b\right)\right)}\right)-\right.\\&\left.\vec{R}_{b-1}^2\left(\frac{\overline{D}_b\overline{D}_{b-1}\left(\hat{C}_b^{j+1}+\hat{C}_b^{j}-\hat{C}_{b-1}^{j+1}-\hat{C}_{b-1}^{j}\right)}{2\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\right)+w_b-\frac{\lambda}{2}\left(\hat{C}_b^{j+1}+\hat{C}_b^{j}\right)\end{aligned}\tag{3.356}$$

multiplying out by Δt and simplifying

$$\begin{aligned}\hat{C}_b^{j+1}-\hat{C}_b^{j}=\frac{\Delta t}{\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)}&\left(\hat{\vec{R}}_b^2\overline{D}_b\left(\frac{h_c\left(C_{b+1}^{j+1}+C_{b+1}^{j}-\hat{C}_b^{j+1}-\hat{C}_b^{j}\right)}{2\left(\overline{D}_b-h_c\left(\hat{R}_b-\vec{R}_b\right)\right)}\right)-\right.\\&\left.\vec{R}_{b-1}^2\left(\frac{\overline{D}_b\overline{D}_{b-1}\left(\hat{C}_b^{j+1}+\hat{C}_b^{j}-\hat{C}_{b-1}^{j+1}-\hat{C}_{b-1}^{j}\right)}{2\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\right)+w_b\Delta t-\frac{\Delta t\lambda}{2}\left(\hat{C}_b^{j+1}+\hat{C}_b^{j}\right)\end{aligned}\tag{3.357}$$

noting that $C_{b+1}^{j}=C_{b+1}^{j+1}=C_{b+1}^{j}$ as per boundary condition, and rearranging to move all non-boundary $j+1$ terms to the left hand side, and all j terms to the right hand side and factorising

$$\begin{aligned}&\left(1+\frac{\Delta t\lambda}{2}+\left(\frac{\Delta t h_c\hat{\vec{R}}_b^2\overline{D}_b}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_b-h_c\left(\hat{R}_b-\vec{R}_b\right)\right)}\right)+\right.\\&\left.\left(\frac{\Delta t\vec{R}_{b-1}^2\overline{D}_b\overline{D}_{b-1}}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\right)\hat{C}_b^{j+1}-\\&\left(\frac{\Delta t\vec{R}_{b-1}^2\overline{D}_b\overline{D}_{b-1}}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\hat{C}_{b-1}^{j+1}=\\&\left(1-\frac{\Delta t\lambda}{2}-\left(\frac{\Delta t h_c\hat{\vec{R}}_b^2\overline{D}_b}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_b-h_c\left(\hat{R}_b-\vec{R}_b\right)\right)}\right)-\right.\\&\left.\left(\frac{\Delta t\vec{R}_{b-1}^2\overline{D}_b\overline{D}_{b-1}}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\right)\hat{C}_b^{j}+\\&\left(\frac{\Delta t\vec{R}_{b-1}^2\overline{D}_b\overline{D}_{b-1}}{2\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_{b-1}\left(\hat{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\hat{R}_{b-1}\right)\right)}\right)\hat{C}_{b-1}^{j}+\\&w_b\Delta t+\left(\frac{\Delta t\hat{\vec{R}}_b^2\overline{D}_b h_c}{\hat{R}_b^2\left(\hat{\vec{R}}_b-\vec{R}_{b-1}\right)\left(\overline{D}_b-h_c\left(\hat{R}_b-\vec{R}_b\right)\right)}\right)C_{b+1}^{j}\end{aligned}\tag{3.358}$$

Letting the coefficients of $\hat{C}_{b-1}^{j+1}$ and $\hat{C}_b^{j+1}$ be equal to A_b and $\overline{G}_b$ respectively, this equation then becomes

$$\overline{G}_b\hat{C}_b^{j+1} + A_b\hat{C}_{b-1}^{j+1} = \left(2-\overline{G}_b\right)\hat{C}_b^j - A_b\hat{C}_{b-1}^j + \Delta t w_b + \left(\frac{\Delta t\hat{\vec{R}}_b^2\overline{D}_b h_c}{\hat{R}_b^2\left(\hat{\vec{R}}_b - \vec{R}_{b-1}\right)\left(\overline{D}_b - h_c\left(\hat{R}_b - \vec{R}_b\right)\right)}\right)C_{b+1}^j \qquad (3.359)$$

and setting the right hand side equal to $\overline{K}_b^j$ yields

$$A_b\hat{C}_{b-1}^{j+1} + \overline{G}_b\hat{C}_b^{j+1} = \overline{K}_b^j\,. \qquad (3.360)$$

Finally, the equations for the inner boundary (3.322), general mesh zone (3.316), and outer boundary (3.332) form a set of simultaneous equations, which can be cast into matrix form as

$$\begin{pmatrix} G_1 & H_1 & 0 & 0 & \cdots & \cdots & 0 \\ A_2 & G_2 & H_2 & 0 & \cdots & \cdots & 0 \\ 0 & A_3 & G_3 & H_3 & \cdots & \cdots & 0 \\ \vdots & 0 & \ddots & \ddots & \ddots & \cdots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & 0 \\ \vdots & \vdots & \vdots & 0 & A_{b-1} & G_{b-1} & H_{b-1} \\ 0 & 0 & \cdots & \cdots & 0 & A_b & \overline{G}_b \end{pmatrix} \begin{pmatrix} \hat{C}_1^{j+1} \\ \hat{C}_2^{j+1} \\ \hat{C}_3^{j+1} \\ \vdots \\ \vdots \\ \hat{C}_{b-1}^{j+1} \\ \hat{C}_b^{j+1} \end{pmatrix} = \begin{pmatrix} K_1^j \\ K_2^j \\ K_3^j \\ \vdots \\ \vdots \\ K_{b-1}^j \\ \overline{K}_b^j \end{pmatrix}. \qquad (3.361)$$

The elements on the right hand side of the equation are known from the initial and boundary conditions for the first time step ($j=0$ to $j=1$), and the elements in the leftmost tri-diagonal matrix are known from diffusion and geometric data of the system, and so this equation can be solved for concentration at the end of the timestep ($j=1$) by using the Crout Factorisation for Tridiagonal Linear Systems algorithm [26]. These new concentration values can then be used as the initial values for the following timestep and so forth; hence a complete numerical solution of concentration profile as a function of time is achieved.

The first step in the Gauss-Jordan elimination of a tri-diagonal matrix is known as forward elimination, in which the lower triangular elements are eliminated by subtraction of multiplies of the upper row, i.e.

$$A_2' = A_2 - \frac{A_2}{G_1}G_1 = 0 \qquad (3.362)$$

$$G_2' = G_2 - \frac{A_2}{G_1}H_1 \qquad (3.363)$$

$$H_2' = H_2 - \frac{A_2}{G_1}\cdot 0 = H_2 \qquad (3.364)$$

$$K_2'^j = K_2^j - \frac{A_2}{G_1}K_1^j \qquad (3.365)$$

Or more generally

$$A_i' = 0 \quad \forall \quad 2 \le i \le b \qquad (3.366)$$

$$G'_i = G_i - \frac{A_i}{G_{i-1}} H_{i-1} \quad \forall \quad 2 \le i \le b \tag{3.367}$$

$$H'_i = H_i \quad \forall \quad 1 \le i \le b-1 \tag{3.368}$$

$$K'^j_i = K^j_i - \frac{A_i}{G_{i-1}} K^j_{i-1} \quad \forall \quad 2 \le i \le b \tag{3.369}$$

This step of forward elimination reduces the matrix equation to the upper triangular form

$$\begin{pmatrix} G'_1 & H_1 & 0 & 0 & \cdots & \cdots & 0 \\ 0 & G'_2 & H_2 & 0 & \cdots & \cdots & 0 \\ 0 & 0 & G'_3 & H_3 & \cdots & \cdots & 0 \\ \vdots & 0 & \ddots & \ddots & \ddots & \cdots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & 0 \\ \vdots & \vdots & \vdots & 0 & 0 & G'_{b-1} & H_{b-1} \\ 0 & 0 & \cdots & \cdots & 0 & 0 & \overline{G'_b} \end{pmatrix} \begin{pmatrix} \hat{C}_1^{j+1} \\ \hat{C}_2^{j+1} \\ \hat{C}_3^{j+1} \\ \vdots \\ \vdots \\ \hat{C}_{b-1}^{j+1} \\ \hat{C}_b^{j+1} \end{pmatrix} = \begin{pmatrix} K'^j_1 \\ K'^j_2 \\ K'^j_3 \\ \vdots \\ \vdots \\ K'^j_{b-1} \\ \overline{K'^j_b} \end{pmatrix} \tag{3.370}$$

Following this, is the step of backward substitution where the solutions are determined by substituting solutions of concentrations from the last element to the first,

$$\hat{C}_b^{j+1} = \frac{\overline{K'^j_b}}{\overline{G'_b}} \tag{3.371}$$

$$\hat{C}^j_{b-1} = \left(K'^j_{b-1} - H_{b-1}\hat{C}_b^{j+1}\right)/G'_{b-1} \tag{3.372}$$

In general

$$\hat{C}_i^{j+1} = \left(K'^j_i - H_i\hat{C}_{i+1}^{j+1}\right)/G'_i \quad \forall \quad 1 \le i \le b-1 \tag{3.373}$$

gives the solution of the concentration profile for each successive timestep.

3.2.9.2 Mass balance approach

The time dependent diffusion equation (3.26) may be integrated over a volume to yield

$$\int \left(\frac{\partial c_n}{\partial t} - w_{p,n} + \lambda c_n \right) dV = \int \left(\nabla \bullet \left(D_n \nabla c_n \right) \right) dV \tag{3.374}$$

where the subscripts p, n can be dropped and capital $C\,(=c)$ used for simplicity this section it becomes

$$\int \left(\frac{\partial C}{\partial t} - w + \lambda C \right) dV = \int \left(\nabla \bullet \left(D \nabla C \right) \right) dV \tag{3.375}$$

and applying the Divergence Theorem [22], [23], [27] to the right hand side of this equation transforms the volume integral into a surface integral

$$\int \left(\frac{\partial C}{\partial t} - w + \lambda C \right) dV = \int \left(D \nabla C \right) \bullet d\mathbf{S} . \tag{3.376}$$

Applying this to a finite volume element (or mesh zone) ΔV_i, with directed surface elements $\Delta \mathbf{S}_\mathrm{k}$, this can be approximated as

$$\left(\frac{\partial \overline{C}_i}{\partial t} - w_i + \lambda \overline{C}_i \right) \Delta V_i = \sum_{k \text{ surfaces}} \left(\left(D \nabla C \right)_k \bullet \Delta \mathbf{S}_\mathrm{k} \right) \tag{3.377}$$

where

$\overline{C}_i$ = average concentration in volume element i,

$(D\nabla C)|_k$ = product of diffusion coefficient and gradient of concentration at surface k.

The flux is defined as

$$\phi = -D\nabla C \qquad (3.378)$$

and so (3.377) can be more intuitively as

$$\left(\frac{\partial \overline{C}_i}{\partial t} - w_i + \lambda \overline{C}_i\right)\Delta V_i = -\sum_{k\ \text{surfaces}} (\boldsymbol{\phi}_\mathbf{k} \bullet \Delta \mathbf{S}_\mathbf{k}) \qquad (3.379)$$

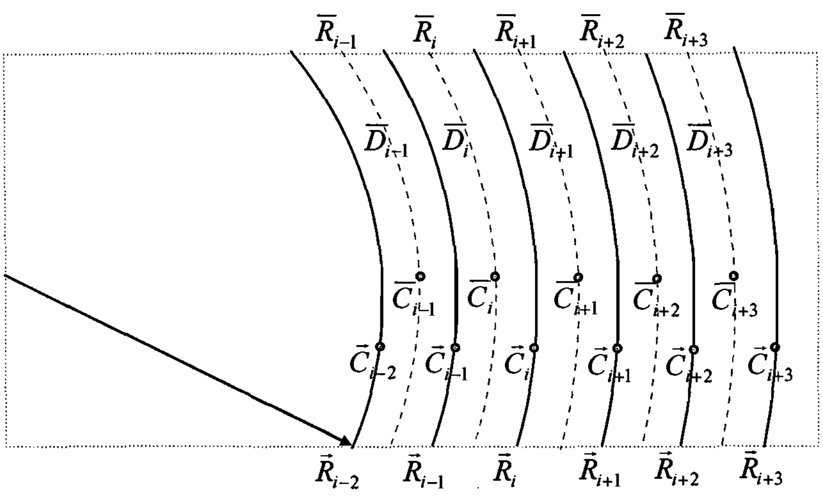
where the right hand side is the sum of the total number of fission/activation product entering/leaving the volume element ΔV_i (which is bounded by surfaces $\Delta \mathbf{S}_k$).

For the case of spherical volume elements with spherical symmetry (i.e. no polar and azimuthal dependence of concentration of diffusing species) indexing is slightly different to the finite difference case, and is shown in Figure 10. Using this, equation (3.377) can be written as

$$\left(\frac{\partial \overline{C}_i}{\partial t} - w_i + \lambda \overline{C}_i\right)\Delta V_i = \left(D\frac{\partial C}{\partial r}\right)\bigg|_i \Delta S_i - \left(D\frac{\partial C}{\partial r}\right)\bigg|_{i-1} \Delta S_{i-1} \qquad (3.380)$$

where

ΔS_i = area of spherical surface at radius $\vec{R}_i$.



KEY
$\vec{R}_i$ = radius at outer surface of mesh zone i,
$\overline{R}_i$ = radius at average concentration in mesh zone i,
$\vec{C}_i$ = concentration at outer surface of mesh zone i,
$\overline{C}_i$ = average concentration of mesh zone i,
$\overline{D}_i$ = average diffusion coefficient in mesh zone i.

Figure 10: Diagram illustrating indexing of discrete spherical shells for mass balance numerical solution

Discretising the gradients at the surfaces can be done using gradients across the positions of the average concentration

$$\left(\frac{\partial \overline{C}_i}{\partial t} - w_i + \lambda \overline{C}_i\right)\Delta V_i = \vec{D}_i\left(\frac{\overline{C}_{i+1} - \overline{C}_i}{\overline{R}_{i+1} - \overline{R}_i}\right)\mathit{\Delta} S_i - \vec{D}_{i-1}\left(\frac{\overline{C}_i - \overline{C}_{i-1}}{\overline{R}_i - \overline{R}_{i-1}}\right)\mathit{\Delta} S_{i-1} \tag{3.381}$$

where the surface diffusion coefficients from equations (3.306) and (3.307) can be used to yield

$$\begin{aligned}\left(\frac{\partial \overline{C}_i}{\partial t} - w_i + \lambda \overline{C}_i\right)\Delta V_i = {} & \frac{\overline{D}_{i+1}\overline{D}_i\left(\overline{R}_{i+1} - \overline{R}_i\right)}{\overline{D}_i\left(\overline{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1}\left(\vec{R}_i - \overline{R}_i\right)}\left(\frac{\overline{C}_{i+1} - \overline{C}_i}{\overline{R}_{i+1} - \overline{R}_i}\right)\mathit{\Delta} S_i - \\ & \frac{\overline{D}_i\overline{D}_{i-1}\left(\overline{R}_i - \overline{R}_{i-1}\right)}{\overline{D}_{i-1}\left(\overline{R}_i - \vec{R}_{i-1}\right) + \overline{D}_i\left(\vec{R}_{i-1} - \overline{R}_{i-1}\right)}\left(\frac{\overline{C}_i - \overline{C}_{i-1}}{\overline{R}_i - \overline{R}_{i-1}}\right)\mathit{\Delta} S_{i-1}\end{aligned} \tag{3.382}$$

where cancelling common factors gives

$$\left(\frac{\partial \overline{C}_i}{\partial t} - w_i + \lambda \overline{C}_i\right)\Delta V_i = \frac{\overline{D}_{i+1}\overline{D}_i\left(\overline{C}_{i+1} - \overline{C}_i\right)\mathit{\Delta} S_i}{\overline{D}_i\left(\overline{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1}\left(\vec{R}_i - \overline{R}_i\right)} - \frac{\overline{D}_i\overline{D}_{i-1}\left(\overline{C}_i - \overline{C}_{i-1}\right)\mathit{\Delta} S_{i-1}}{\overline{D}_{i-1}\left(\overline{R}_i - \vec{R}_{i-1}\right) + \overline{D}_i\left(\vec{R}_{i-1} - \overline{R}_{i-1}\right)} \tag{3.383}$$

by applying discretization of the time differential, and using Crank-Nicholson averages for the concentrations,

$$\begin{aligned}\left(\left(\frac{\overline{C}_i^{\,j+1} - \overline{C}_i^{\,j}}{\Delta t}\right) - w_i + \lambda\left(\frac{\overline{C}_i^{\,j+1} + \overline{C}_i^{\,j}}{2}\right)\right)\Delta V_i = {} & \frac{\overline{D}_{i+1}\overline{D}_i\left(\overline{C}_{i+1}^{\,j+1} + \overline{C}_{i+1}^{\,j} - \overline{C}_i^{\,j+1} - \overline{C}_i^{\,j}\right)\mathit{\Delta} S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1} - \vec{R}_i\right) + \overline{D}_{i+1}\left(\vec{R}_i - \overline{R}_i\right)\right)} - \\ & \frac{\overline{D}_i\overline{D}_{i-1}\left(\overline{C}_i^{\,j+1} + \overline{C}_i^{\,j} - \overline{C}_{i-1}^{\,j+1} - \overline{C}_{i-1}^{\,j}\right)\mathit{\Delta} S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i - \vec{R}_{i-1}\right) + \overline{D}_i\left(\vec{R}_{i-1} - \overline{R}_{i-1}\right)\right)}\end{aligned} \tag{3.384}$$

Multiplying out by Δt

$$\left(\overline{C}_i^{\,j+1}-\overline{C}_i^{\,j}\right)\Delta V_i-\Delta t w_i\Delta V_i+\Delta t\lambda\left(\frac{\overline{C}_i^{\,j+1}+\overline{C}_i^{\,j}}{2}\right)\Delta V_i=\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\left(\overline{C}_{i+1}^{\,j+1}+\overline{C}_{i+1}^{\,j}-\overline{C}_i^{\,j+1}-\overline{C}_i^{\,j}\right)\Delta S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}-\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\left(\overline{C}_i^{\,j+1}+\overline{C}_i^{\,j}-\overline{C}_{i-1}^{\,j+1}-\overline{C}_{i-1}^{\,j}\right)\Delta S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\tag{3.385}$$

and expanding

$$\begin{aligned}&\Delta V_i\overline{C}_i^{\,j+1}-\Delta V_i\overline{C}_i^{\,j}-\Delta t w_i\Delta V_i+\frac{\Delta V_i\Delta t\lambda}{2}\overline{C}_i^{\,j+1}+\frac{\Delta V_i\Delta t\lambda}{2}\overline{C}_i^{\,j}=\\&\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\Delta S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\overline{C}_{i+1}^{\,j+1}+\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\Delta S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\overline{C}_{i+1}^{\,j}-\\&\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\Delta S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\overline{C}_i^{\,j+1}-\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\Delta S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\overline{C}_i^{\,j}-\\&\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\Delta S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\overline{C}_i^{\,j+1}-\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\Delta S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\overline{C}_i^{\,j}+\\&\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\Delta S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\overline{C}_{i-1}^{\,j+1}+\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\Delta S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\overline{C}_{i-1}^{\,j}\end{aligned}\tag{3.386}$$

and rearranging to move all $j+1$ terms to the left hand side, and all j terms to the right hand side and factorising common factors of concentration

$$\begin{aligned}&\left(\Delta V_i+\frac{\Delta V_i\Delta t\lambda}{2}+\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\Delta S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}+\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\Delta S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\right)\overline{C}_i^{\,j+1}\\&-\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\Delta S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\overline{C}_{i+1}^{\,j+1}-\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\Delta S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\overline{C}_{i-1}^{\,j+1}\\&=\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\Delta S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\overline{C}_{i+1}^{\,j}+\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\Delta S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\overline{C}_{i-1}^{\,j}+\Delta t w_i\Delta V_i+\\&\left(\Delta V_i-\frac{\Delta V_i\Delta t\lambda}{2}-\frac{\Delta t\overline{D}_{i+1}\overline{D}_i\Delta S_i}{2\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}-\frac{\Delta t\overline{D}_i\overline{D}_{i-1}\Delta S_{i-1}}{2\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\right)\overline{C}_i^{\,j}\end{aligned}\tag{3.387}$$

Further noting that $\Delta S_i=4\pi\vec{R}_i^2$, and substituting this into the above, with simplification gives

$$\begin{aligned}&\left(\Delta V_i+\frac{\Delta V_i\Delta t\lambda}{2}+\frac{\Delta t\overline{D}_i\overline{D}_{i-1}2\pi\vec{R}_{i-1}^2}{\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}+\frac{\Delta t\overline{D}_{i+1}\overline{D}_i2\pi\vec{R}_i^2}{\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\right)\overline{C}_i^{\,j+1}\\&-\frac{\Delta t\overline{D}_{i+1}\overline{D}_i2\pi\vec{R}_i^2}{\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\overline{C}_{i+1}^{\,j+1}-\frac{\Delta t\overline{D}_i\overline{D}_{i-1}2\pi\vec{R}_{i-1}^2}{\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\overline{C}_{i-1}^{\,j+1}\\&=\frac{\Delta t\overline{D}_{i+1}\overline{D}_i2\pi\vec{R}_i^2}{\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}\overline{C}_{i+1}^{\,j}+\frac{\Delta t\overline{D}_i\overline{D}_{i-1}2\pi\vec{R}_{i-1}^2}{\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\overline{C}_{i-1}^{\,j}+\Delta t w_i\Delta V_i+\\&\left(\Delta V_i-\frac{\Delta V_i\Delta t\lambda}{2}-\frac{\Delta t\overline{D}_{i+1}\overline{D}_i2\pi\vec{R}_i^2}{\left(\overline{D}_i\left(\overline{R}_{i+1}-\vec{R}_i\right)+\overline{D}_{i+1}\left(\vec{R}_i-\overline{R}_i\right)\right)}-\frac{\Delta t\overline{D}_i\overline{D}_{i-1}2\pi\vec{R}_{i-1}^2}{\left(\overline{D}_{i-1}\left(\overline{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i-1}-\overline{R}_{i-1}\right)\right)}\right)\overline{C}_i^{\,j}\end{aligned}\tag{3.388}$$

Letting the coefficients of $\overline{C}_{i-1}^{\,j+1}, \overline{C}_i^{\,j+1}$, and $\overline{C}_{i+1}^{\,j+1}$ be A_i, G_i, and H_i respectively

$$G_i\overline{C}_i^{\,j+1}+H_i\overline{C}_{i+1}^{\,j+1}+A_i\overline{C}_{i-1}^{\,j+1}=-H_i\overline{C}_{i+1}^{\,j}-A_i\overline{C}_{i-1}^{\,j}+\Delta t w_i\Delta V_i+\left(2\Delta V_i-G_i\right)\overline{C}_i^{\,j}\tag{3.389}$$

and letting the right hand side of this equation equal K_i^j, the general equation for the i'th mesh zone becomes

$$A_i\bar{C}_{i-1}^{j+1} + G_i\bar{C}_i^{j+1} + H_i\bar{C}_{i+1}^{j+1} = K_i^j \tag{3.390}$$

where

$$K_i^j = -H_i\bar{C}_{i+1}^{j} - A_i\bar{C}_{i-1}^{j} + \Delta t w_i \Delta V_i + \left(2\Delta V_i - G_i\right)\bar{C}_i^j . \tag{3.391}$$

The boundary condition at the centre of the sphere (condition of symmetry) for the mass balance conservation is that there is no diffusant flow across the sphere centre, in other words, equation (3.380) has the second term on the right hand side vanish at $i = 1$,

$$\left(\frac{\partial \bar{C}_1}{\partial t} - w_1 + \lambda \bar{C}_1\right)\Delta V_1 = \left(D\frac{\partial C}{\partial r}\right)\bigg|_1 \Delta S_1 \tag{3.392}$$

This equation can be discretised in a similar manner to that used to derive the general equation (3.388) from (3.380) by first discretising the concentration gradient at the surface

$$\left(\frac{\partial \bar{C}_1}{\partial t} - w_1 + \lambda \bar{C}_1\right)\Delta V_1 = \vec{D}_1\left(\frac{\bar{C}_2 - \bar{C}_1}{\bar{R}_2 - \bar{R}_1}\right)\Delta S_1 , \tag{3.393}$$

then using the surface diffusion coefficient from equation (3.306)

$$\left(\frac{\partial \bar{C}_1}{\partial t} - w_1 + \lambda \bar{C}_1\right)\Delta V_1 = \frac{\bar{D}_2\bar{D}_1\left(\hat{R}_2 - \hat{R}_1\right)}{\bar{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \bar{D}_2\left(\vec{R}_1 - \hat{R}_1\right)}\left(\frac{\bar{C}_2 - \bar{C}_1}{\bar{R}_2 - \bar{R}_1}\right)\Delta S_1 \tag{3.394}$$

and cancelling common factors

$$\left(\frac{\partial \bar{C}_1}{\partial t} - w_1 + \lambda \bar{C}_1\right)\Delta V_1 = \frac{\bar{D}_2\bar{D}_1\left(\bar{C}_2 - \bar{C}_1\right)\Delta S_1}{\bar{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \bar{D}_2\left(\vec{R}_1 - \hat{R}_1\right)} \tag{3.395}$$

applying time discretization and using Crank-Nicholson concentration averages

$$\left(\frac{\bar{C}_1^{j+1} - \bar{C}_1^{j}}{\Delta t} - w_1 + \lambda\left(\frac{\bar{C}_1^{j+1} + \bar{C}_1^{j}}{2}\right)\right)\Delta V_1 = \frac{\bar{D}_2\bar{D}_1\left(\bar{C}_2^{j+1} + \bar{C}_2^{j} - \bar{C}_1^{j+1} - \bar{C}_1^{j}\right)\Delta S_1}{2\left(\bar{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \bar{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)} \tag{3.396}$$

multiplying out by Δt

$$\left(\bar{C}_1^{j+1} - \bar{C}_1^{j} - w_1\Delta t + \Delta t\lambda\left(\frac{\bar{C}_1^{j+1} + \bar{C}_1^{j}}{2}\right)\right)\Delta V_1 = \frac{\Delta t\bar{D}_2\bar{D}_1\left(\bar{C}_2^{j+1} + \bar{C}_2^{j} - \bar{C}_1^{j+1} - \bar{C}_1^{j}\right)\Delta S_1}{2\left(\bar{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \bar{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)} \tag{3.397}$$

and expanding

$$\begin{aligned}
&\Delta V_1\bar{C}_1^{j+1} - \Delta V_1\bar{C}_1^{j} - \Delta V_1 w_1\Delta t + \frac{\Delta V_1\lambda\Delta t}{2}\bar{C}_1^{j+1} + \frac{\Delta V_1\lambda\Delta t}{2}\bar{C}_1^{j} \\
&= \frac{\Delta t\bar{D}_2\bar{D}_1\Delta S_1}{2\left(\bar{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \bar{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\bar{C}_2^{j+1} + \frac{\Delta t\bar{D}_2\bar{D}_1\Delta S_1}{2\left(\bar{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \bar{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\bar{C}_2^{j} - \\
&\quad \frac{\Delta t\bar{D}_2\bar{D}_1\Delta S_1}{2\left(\bar{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \bar{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\bar{C}_1^{j+1} - \frac{\Delta t\bar{D}_2\bar{D}_1\Delta S_1}{2\left(\bar{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \bar{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\bar{C}_1^{j}
\end{aligned} \tag{3.398}$$

rearranging to move all $j+1$ terms to the left hand side, and all j terms to the right hand side and factorising common factors of concentration and substituting in the expressions for surface area, namely $\Delta S_i = 4\pi\vec{R}_i^2$,

$$\left(\Delta V_1 + \frac{\Delta V_1 \lambda \Delta t}{2} + \frac{\Delta t \overline{D}_2 \overline{D}_1 2\pi \vec{R}_1^2}{\left(\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\right)\overline{C}_1^{j+1} - \frac{\Delta t \overline{D}_2 \overline{D}_1 2\pi \vec{R}_1^2}{\left(\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\overline{C}_2^{j+1}$$

$$= \left(\Delta V_1 - \frac{\Delta t \overline{D}_2 \overline{D}_1 2\pi \vec{R}_1^2}{\left(\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)} - \frac{\Delta V_1 \lambda \Delta t}{2}\right)\overline{C}_1^{j} + \tag{3.399}$$

$$\frac{\Delta t \overline{D}_2 \overline{D}_1 2\pi \vec{R}_1^2}{\left(\overline{D}_1\left(\hat{R}_2 - \vec{R}_1\right) + \overline{D}_2\left(\vec{R}_1 - \hat{R}_1\right)\right)}\overline{C}_2^{j} + \Delta V_1 w_1 \Delta t$$

letting the coefficients of $\overline{C}_1^{j+1}$ and $\overline{C}_2^{j+1}$ be G_1, and H_1 respectively

$$G_1\overline{C}_1^{j+1} + H_1\overline{C}_2^{j+1} = \left(2\Delta V_1 - G_1\right)\overline{C}_1^{j} - H_1\overline{C}_2^{j} + \Delta V_1 w_1 \Delta t \tag{3.400}$$

letting the right hand side equal to K_1^j yields the discretised equation for the inner boundary condition

$$G_1\overline{C}_1^{j+1} + H_1\overline{C}_2^{j+1} = K_1^j \tag{3.401}$$

where

$$K_1^j = \left(2\Delta V_1 - G_1\right)\overline{C}_1^{j} - H_1\overline{C}_2^{j} + \Delta V_1 w_1 \Delta t\,. \tag{3.402}$$

Once again, as in the case of the finite difference approach of section 3.2.9.1, for the outer surface, two boundary conditions are possible, that of a constant surface concentration, or that of a constant outer concentration resulting in a mass transfer rate governed by the evapouration constant. These are discussed further.

3.2.9.2.1 Constant surface concentration boundary condition

For the outer boundary condition case where the concentration at the surface of the sphere is fixed, namely

$$C(R_b) = \vec{C}_b \tag{3.403}$$

where the index b refers to the outermost mesh zone of the sphere, using equation (3.380) and Figure 11 yields

$$\left(\frac{\partial \overline{C}_b}{\partial t} - w_b + \lambda \overline{C}_b\right)\Delta V_b = \left(D\frac{\partial C}{\partial r}\right)\bigg|_b \Delta S_b - \left(D\frac{\partial C}{\partial r}\right)\bigg|_{b-1} \Delta S_{b-1} \tag{3.404}$$

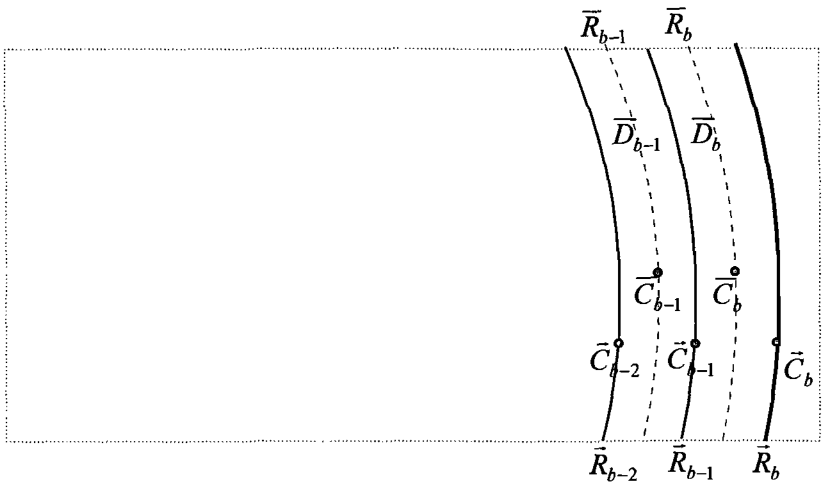


Figure 11: Diagram illustrating boundary condition and indexing at outer edge of sphere for mass balance solution

For the gradient at the surface ΔS_b (i.e. at $\vec{R}_b$), a first order approximation is to use the concentration gradient from the position of average concentration to the fixed surface concentration and so equation (3.404) becomes

$$\left(\frac{\partial\overline{C}_b}{\partial t}-w_b+\lambda\overline{C}_b\right)\Delta V_b=\overline{D}_b\left(\frac{\vec{C}_b-\overline{C}_b}{\vec{R}_b-\overline{R}_b}\right)\mathit{\Delta}S_b-\vec{D}_{b-1}\left(\frac{\overline{C}_b-\overline{C}_{b-1}}{\overline{R}_b-\overline{R}_{b-1}}\right)\mathit{\Delta}S_{b-1} \tag{3.405}$$

by using the mesh surface diffusion coefficient of equation (3.307) for $\vec{D}_{b-1}$

$$\begin{aligned}\left(\frac{\partial\overline{C}_b}{\partial t}-w_b+\lambda\overline{C}_b\right)\Delta V_b=\overline{D}_b\left(\frac{\vec{C}_b-\overline{C}_b}{\vec{R}_b-\overline{R}_b}\right)\mathit{\Delta}S_b-&\\ \frac{\overline{D}_b\overline{D}_{b-1}\left(\overline{R}_b-\overline{R}_{b-1}\right)}{\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)}\left(\frac{\overline{C}_b-\overline{C}_{b-1}}{\overline{R}_b-\overline{R}_{b-1}}\right)\mathit{\Delta}S_{b-1}&\end{aligned} \tag{3.406}$$

and cancelling common factors

$$\left(\frac{\partial\overline{C}_b}{\partial t}-w_b+\lambda\overline{C}_b\right)\Delta V_b=\overline{D}_b\left(\frac{\vec{C}_b-\overline{C}_b}{\vec{R}_b-\overline{R}_b}\right)\mathit{\Delta}S_b-\frac{\overline{D}_b\overline{D}_{b-1}\left(\overline{C}_b-\overline{C}_{b-1}\right)\mathit{\Delta}S_{b-1}}{\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)} \tag{3.407}$$

applying time discretization and using Crank-Nicholson concentration averages and noting that the boundary condition of constant surface concentration requires $\vec{C}_b^{j+1}=\vec{C}_b^j=\vec{C}_b$

$$\begin{aligned}\left(\frac{\overline{C}_b^{j+1}-\overline{C}_b^j}{\Delta t}-w_b+\lambda\left(\frac{\overline{C}_b^{j+1}+\overline{C}_b^j}{2}\right)\right)\Delta V_b=\overline{D}_b\left(\frac{\vec{C}_b-\overline{C}_b^{j+1}-\overline{C}_b^j}{2\left(\vec{R}_b-\overline{R}_b\right)}\right)\mathit{\Delta}S_b-&\\ \frac{\overline{D}_b\overline{D}_{b-1}\left(\overline{C}_b^{j+1}+\overline{C}_b^j-\overline{C}_{b-1}^{j+1}-\overline{C}_{b-1}^j\right)\mathit{\Delta}S_{b-1}}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}&\end{aligned} \tag{3.408}$$

multiplying out by Δt

$$\begin{aligned}\left(\overline{C}_b^{j+1}-\overline{C}_b^j-w_b\Delta t+\lambda\Delta t\left(\frac{\overline{C}_b^{j+1}+\overline{C}_b^j}{2}\right)\right)\Delta V_b=\Delta t\overline{D}_b\left(\frac{\vec{C}_b-\overline{C}_b^{j+1}-\overline{C}_b^j}{2\left(\vec{R}_b-\overline{R}_b\right)}\right)\mathit{\Delta}S_b-&\\ \frac{\Delta t\overline{D}_b\overline{D}_{b-1}\left(\overline{C}_b^{j+1}+\overline{C}_b^j-\overline{C}_{b-1}^{j+1}-\overline{C}_{b-1}^j\right)\mathit{\Delta}S_{b-1}}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}&\end{aligned} \tag{3.409}$$

and expanding

$$\begin{aligned}&\Delta V_b\overline{C}_b^{j+1}-\Delta V_b\overline{C}_b^{j}-\Delta V_b w_b\Delta t+\frac{\Delta V_b\lambda\Delta t}{2}\overline{C}_b^{j+1}+\frac{\Delta V_b\lambda\Delta t}{2}\overline{C}_b^{j}\\&=\frac{\Delta t\overline{D}_b\mathit{\Delta} S_b}{2\left(\vec{R}_b-\overline{R}_b\right)}\vec{C}_b-\frac{\Delta t\overline{D}_b\mathit{\Delta} S_b}{2\left(\vec{R}_b-\overline{R}_b\right)}\overline{C}_b^{j+1}-\frac{\Delta t\overline{D}_b\mathit{\Delta} S_b}{2\left(\vec{R}_b-\overline{R}_b\right)}\overline{C}_b^{j}-\\&\frac{\Delta t\overline{D}_b\overline{D}_{b-1}\mathit{\Delta} S_{b-1}}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_b^{j+1}-\frac{\Delta t\overline{D}_b\overline{D}_{b-1}\mathit{\Delta} S_{b-1}}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_b^{j}+\\&\frac{\Delta t\overline{D}_b\overline{D}_{b-1}\mathit{\Delta} S_{b-1}}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_{b-1}^{j+1}+\frac{\Delta t\overline{D}_b\overline{D}_{b-1}\mathit{\Delta} S_{b-1}}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_{b-1}^{j}\end{aligned}\qquad(3.410)$$

rearranging to move all $j+1$ terms to the left hand side, and all j terms to the right hand side and factorising common factors of concentration together with substitution of the surface area $\Delta S_i=4\pi\vec{R}_i^2$

$$\begin{aligned}&\left(\Delta V_b+\frac{\Delta V_b\lambda\Delta t}{2}+\frac{\Delta t\overline{D}_b 2\pi\vec{R}_b^2}{\left(\vec{R}_b-\overline{R}_b\right)}+\frac{\Delta t\overline{D}_b\overline{D}_{b-1}2\pi\vec{R}_{b-1}^2}{\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\right)\overline{C}_b^{j+1}-\\&\frac{\Delta t\overline{D}_b\overline{D}_{b-1}2\pi\vec{R}_{b-1}^2}{\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_{b-1}^{j+1}\\&=\left(\Delta V_b-\frac{\Delta t\overline{D}_b 2\pi\vec{R}_b^2}{\left(\vec{R}_b-\overline{R}_b\right)}-\frac{\Delta t\overline{D}_b\overline{D}_{b-1}2\pi\vec{R}_{b-1}^2}{\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}-\frac{\Delta V_b\lambda\Delta t}{2}\right)\overline{C}_b^{j}+\\&\frac{\Delta t\overline{D}_b\overline{D}_{b-1}2\pi\vec{R}_{b-1}^2}{\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_{b-1}^{j}+\frac{\Delta t\overline{D}_b 2\pi\vec{R}_b^2}{\left(\vec{R}_b-\overline{R}_b\right)}\vec{C}_b+\Delta V_b w_b\Delta t\end{aligned}\qquad(3.411)$$

letting the coefficients of $\overline{C}_{b-1}^{j+1}$ and $\overline{C}_b^{j+1}$ be A_b, and G_b respectively

$$G_b\overline{C}_b^{j+1}+A_b\overline{C}_{b-1}^{j+1}=\left(2\Delta V_b-G_b\right)\overline{C}_b^{j}-A_b\overline{C}_{b-1}^{j}+\frac{\Delta t\overline{D}_b 2\pi\vec{R}_b^2}{\left(\vec{R}_b-\overline{R}_b\right)}\vec{C}_b+\Delta V_b w_b\Delta t,\qquad(3.412)$$

and letting the right hand side equal K_b^j yields the discrete equation for the boundary mesh zone

$$G_b\overline{C}_b^{j+1}+A_b\overline{C}_{b-1}^{j+1}=K_b^j\qquad(3.413)$$

where

$$K_b^j=\left(2\Delta V_b-G_b\right)\overline{C}_b^{j}-A_b\overline{C}_{b-1}^{j}+\frac{\Delta t\overline{D}_b 2\pi\vec{R}_b^2}{\left(\vec{R}_b-\overline{R}_b\right)}\vec{C}_b+\Delta V_b w_b\Delta t.\qquad(3.414)$$

The set of equations (3.401), (3.390), and (3.413) form a tri-diagonal matrix as in equation (3.333) and can be solved in exactly the same manner to yield the time evolution of the concentration profile in the sphere.

3.2.9.2.2 Mass transfer at surface boundary condition

For boundary codition with a given concentration $\left(C_{b+1}^j\right)$ of diffusant beyond the surface, the mass transfer at the surface (of the sphere) can be given by the relation [17], [18]

$$J_b=h_c\left(\vec{C}_b-C_{b+1}^j\right)\qquad(3.415)$$

where

h_c = mass transfer coefficient,

J_b = flux of mass transfer at the boundary,

As can be seen in Figure 11, the index b refers to the outermost mesh zone of the sphere, and using equation (3.380) together with the transfer rate from the surface given by the equation above yields

$$\left(\frac{\partial\overline{C}_b}{\partial t}-w_b+\lambda\overline{C}_b\right)\Delta V_b=-h_c\left(\vec{C}_b-C^j_{b+1}\right)\mathit{\Delta}S_b-\left(D\frac{\partial C}{\partial r}\right)\bigg|_{b-1}\mathit{\Delta}S_{b-1} \tag{3.416}$$

For conservation of mass, to first approximation, the flux defined in equation (3.415) must equal the flux flowing out of the surface from the outer mesh zone, namely

$$J_b=-\overline{D}_b\left(\frac{\overline{C}_b-\vec{C}_b}{\overline{R}_b-\vec{R}_b}\right)=h_c\left(\vec{C}_b-C^j_{b+1}\right), \tag{3.417}$$

where it can be solved for $\vec{C}_b$ by first multiplying out on both sides

$$-\left(\frac{\overline{D}_b}{\overline{R}_b-\vec{R}_b}\right)\overline{C}_b+\left(\frac{\overline{D}_b}{\overline{R}_b-\vec{R}_b}\right)\vec{C}_b=h_c\vec{C}_b-h_cC^j_{b+1} \tag{3.418}$$

and then moving all the $\vec{C}_b$ terms to the left hand side

$$\left(\frac{\overline{D}_b}{\overline{R}_b-\vec{R}_b}\right)\vec{C}_b-h_c\vec{C}_b=\left(\frac{\overline{D}_b}{\overline{R}_b-\vec{R}_b}\right)\overline{C}_b-h_cC^j_{b+1}, \tag{3.419}$$

followed by factorising the common factor of $\vec{C}_b$ on the left hand side,

$$\left(\left(\frac{\overline{D}_b}{\overline{R}_b-\vec{R}_b}\right)-h_c\right)\vec{C}_b=\left(\frac{\overline{D}_b}{\overline{R}_b-\vec{R}_b}\right)\overline{C}_b-h_cC^j_{b+1}, \tag{3.420}$$

and dividing through by the coefficient of $\vec{C}_b$,

$$\vec{C}_b=\frac{\left(\frac{\overline{D}_b}{\overline{R}_b-\vec{R}_b}\right)\overline{C}_b-h_cC^j_{b+1}}{\left(\left(\frac{\overline{D}_b}{\overline{R}_b-\vec{R}_b}\right)-h_c\right)}, \tag{3.421}$$

which can be simplified by multiplying out by the denominator to finally yield

$$\vec{C}_b=\frac{\overline{D}_b\overline{C}_b-h_cC^j_{b+1}\left(\overline{R}_b-\vec{R}_b\right)}{\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)}. \tag{3.422}$$

Substituting this into the mass transfer diffusion equation for the outermost mesh zone (3.416),

$$\left(\frac{\partial\overline{C}_b}{\partial t}-w_b+\lambda\overline{C}_b\right)\Delta V_b=-h_c\left(\frac{\overline{D}_b\overline{C}_b-h_cC^j_{b+1}\left(\overline{R}_b-\vec{R}_b\right)}{\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)}-C^j_{b+1}\right)\mathit{\Delta}S_b-\left(D\frac{\partial C}{\partial r}\right)\bigg|_{b-1}\mathit{\Delta}S_{b-1} \tag{3.423}$$

and discretising the differential with respect to space on the right hand side

$$\begin{aligned}\left(\frac{\partial\overline{C}_b}{\partial t}-w_b+\lambda\overline{C}_b\right)\Delta V_b=-h_c\left(\frac{\overline{D}_b\overline{C}_b-h_cC_{b+1}^{j}\left(\overline{R}_b-\vec{R}_b\right)}{\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)}-C_{b+1}^{j}\right)\Delta S_b-&\\ \vec{D}_{b-1}\left(\frac{\overline{C}_b-\overline{C}_{b-1}}{\overline{R}_b-\overline{R}_{b-1}}\right)\Delta S_{b-1}&\end{aligned}, \qquad (3.424)$$

further noting that $\vec{D}_{b-1}$ can be re-expressed using equation (3.307)

$$\begin{aligned}\left(\frac{\partial\overline{C}_b}{\partial t}-w_b+\lambda\overline{C}_b\right)\Delta V_b=-h_c\left(\frac{\overline{D}_b\overline{C}_b-h_cC_{b+1}\left(\overline{R}_b-\vec{R}_b\right)}{\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)}-C_{b+1}\right)\Delta S_b-&\\ \frac{\overline{D}_b\overline{D}_{b-1}\left(\overline{R}_b-\overline{R}_{b-1}\right)}{\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)}\left(\frac{\overline{C}_b-\overline{C}_{b-1}}{\overline{R}_b-\overline{R}_{b-1}}\right)\Delta S_{b-1}&\end{aligned} \qquad (3.425)$$

whereupon simplification and cancellation of common factors on the right hand side will yield

$$\left(\frac{\partial\overline{C}_b}{\partial t}-w_b+\lambda\overline{C}_b\right)\Delta V_b=\frac{-h_c\overline{D}_b\left(\overline{C}_b-C_{b+1}^{j}\right)\Delta S_b}{\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)}-\frac{\overline{D}_b\overline{D}_{b-1}\left(\overline{C}_b-\overline{C}_{b-1}\right)\Delta S_{b-1}}{\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)}. \qquad (3.426)$$

Applying time discretization and using Crank-Nicholson averaging for the concentrations, taking into account that C_{b+1} is given as a function of time

$$\begin{aligned}\left(\frac{\overline{C}_b^{\,j+1}-\overline{C}_b^{\,j}}{\Delta t}-w_b+\lambda\left(\frac{\overline{C}_b^{\,j+1}+\overline{C}_b^{\,j}}{2}\right)\right)\Delta V_b=\frac{-h_c\overline{D}_b\left(\overline{C}_b^{\,j+1}+\overline{C}_b^{\,j}-2C_{b+1}^{j}\right)\Delta S_b}{2\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}-&\\ \frac{\overline{D}_b\overline{D}_{b-1}\left(\overline{C}_b^{\,j+1}+\overline{C}_b^{\,j}-\overline{C}_{b-1}^{\,j+1}-\overline{C}_{b-1}^{\,j}\right)\Delta S_{b-1}}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}&\end{aligned} \qquad (3.427)$$

multiplying out by Δt

$$\begin{aligned}\left(\overline{C}_b^{\,j+1}-\overline{C}_b^{\,j}-w_b\Delta t+\lambda\left(\frac{\overline{C}_b^{\,j+1}+\overline{C}_b^{\,j}}{2}\right)\Delta t\right)\Delta V_b=\frac{-h_c\overline{D}_b\left(\overline{C}_b^{\,j+1}+\overline{C}_b^{\,j}-2C_{b+1}^{j}\right)\Delta S_b\Delta t}{2\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}-&\\ \frac{\overline{D}_b\overline{D}_{b-1}\left(\overline{C}_b^{\,j+1}+\overline{C}_b^{\,j}-\overline{C}_{b-1}^{\,j+1}-\overline{C}_{b-1}^{\,j}\right)\Delta S_{b-1}\Delta t}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}&\end{aligned} \qquad (3.428)$$

and once again expanding by multiplying out

$$\begin{aligned}&\overline{C}_b^{\,j+1}\Delta V_b-\overline{C}_b^{\,j}\Delta V_b-w_b\Delta t\Delta V_b+\frac{\lambda\Delta t\Delta V_b}{2}\overline{C}_b^{\,j+1}+\frac{\lambda\Delta t\Delta V_b}{2}\overline{C}_b^{\,j}=\\ &-\frac{h_c\overline{D}_b\Delta S_b\Delta t}{2\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}\overline{C}_b^{\,j+1}-\frac{h_c\overline{D}_b\Delta S_b\Delta t}{2\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}\overline{C}_b^{\,j}+\frac{h_c\overline{D}_b\Delta S_b\Delta t}{\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}C_{b+1}^{j}-\\ &\frac{\overline{D}_b\overline{D}_{b-1}\Delta S_{b-1}\Delta t}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_b^{\,j+1}-\frac{\overline{D}_b\overline{D}_{b-1}\Delta S_{b-1}\Delta t}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_b^{\,j}+\\ &\frac{\overline{D}_b\overline{D}_{b-1}\Delta S_{b-1}\Delta t}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_{b-1}^{\,j+1}+\frac{\overline{D}_b\overline{D}_{b-1}\Delta S_{b-1}\Delta t}{2\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_{b-1}^{\,j}\end{aligned} \qquad (3.429)$$

followed by rearranging to move all $j+1$ terms to the left hand side, and substituting in the surface areas, namely $\Delta S_i=4\pi\vec{R}_i^2$, yields

$$\begin{aligned}
&-\frac{\overline{D}_b\overline{D}_{b-1}2\pi\vec{R}_{b-1}^2\Delta t}{\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_{b-1}^{j+1}+\\
&\left(\frac{h_c\overline{D}_b2\pi\vec{R}_b^2\Delta t}{\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}+\frac{\overline{D}_b\overline{D}_{b-1}2\pi\vec{R}_{b-1}^2\Delta t}{\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}+\Delta V_b+\frac{\lambda\Delta t\Delta V_b}{2}\right)\overline{C}_b^{j+1}=\\
&\frac{\overline{D}_b\overline{D}_{b-1}2\pi\vec{R}_{b-1}^2\Delta t}{\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\overline{C}_{b-1}^{j}+\\
&\left(-\frac{\lambda\Delta t\Delta V_b}{2}+\Delta V_b-\frac{h_c\overline{D}_b2\pi\vec{R}_b^2\Delta t}{\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}-\frac{\overline{D}_b\overline{D}_{b-1}2\pi\vec{R}_{b-1}^2\Delta t}{\left(\overline{D}_{b-1}\left(\overline{R}_b-\vec{R}_{b-1}\right)+\overline{D}_b\left(\vec{R}_{b-1}-\overline{R}_{b-1}\right)\right)}\right)\overline{C}_b^{j}+\\
&w_b\Delta t\Delta V_b+\frac{h_c\overline{D}_b4\pi\vec{R}_b^2\Delta t}{\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}C_{b+1}^{j}
\end{aligned}\qquad(3.430)$$

Letting the coefficients of $\overline{C}_{b-1}^{j+1}$ and $\overline{C}_b^{j+1}$ be, A_b and $\overline{G}_b$ respectively

$$A_b\overline{C}_{b-1}^{j+1}+\overline{G}_b\overline{C}_b^{j+1}=-A_b\overline{C}_{b-1}^{j}+\left(2\Delta V_b-\overline{G}_b\right)\overline{C}_b^{j}+w_b\Delta t\Delta V_b+\frac{h_c\overline{D}_b4\pi\vec{R}_b^2\Delta t}{\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}C_{b+1}^{j},\qquad(3.431)$$

and letting the right hand side equal $\overline{K}_b^j$ yields the discrete equation for the boundary mesh zone, namely

$$A_b\overline{C}_{b-1}^{j+1}+\overline{G}_b\overline{C}_b^{j+1}=\overline{K}_b^j\qquad(3.432)$$

where

$$\overline{K}_b^j=-A_b\overline{C}_{b-1}^{j}+\left(2\Delta V_b-\overline{G}_b\right)\overline{C}_b^{j}+w_b\Delta t\Delta V_b+\frac{h_c\overline{D}_b4\pi\vec{R}_b^2\Delta t}{\left(\overline{D}_b-h_c\left(\overline{R}_b-\vec{R}_b\right)\right)}C_{b+1}^{j}.\qquad(3.433)$$

The set of equations (3.401), (3.390) and (3.432) form a tri-diagonal matrix as in equation (3.361) and can be solved in exactly the same manner to yield the time evolution of the concentration profile in the sphere.

3.2.9.3 GETTER approach

The discretized matrix elements extracted from the code are presented in this section, for comparison with the two approaches described above. For the internal matrix elements, the nomenclature depicted in Figure 8 was used, and the matrix elements are given by

$$\underline{\mathrm{A}}_i=\frac{-\Delta t2\pi\overline{D}_i\overline{D}_{i-1}\left(\vec{R}_i-\vec{R}_{i-2}\right)\vec{R}_{i-1}^2}{\left(\vec{R}_i-\vec{R}_{i-1}\right)\left(\overline{D}_i\left(\vec{R}_{i-1}-\vec{R}_{i-2}\right)+\overline{D}_{i-1}\left(\vec{R}_i-\vec{R}_{i-1}\right)\right)}\qquad(3.434)$$

$$\underline{\mathrm{X}}_i=\frac{-\Delta t2\pi\overline{D}_{i+1}\overline{D}_i\left(\vec{R}_{i+1}-\vec{R}_{i-1}\right)\vec{R}_i^2}{\left(\vec{R}_{i+1}-\vec{R}_i\right)\left(\overline{D}_{i+1}\left(\vec{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i+1}-\vec{R}_i\right)\right)}\qquad(3.435)$$

$$\begin{aligned}
\underline{\mathrm{B}}_i=&\frac{\Delta t2\pi\overline{D}_i\overline{D}_{i-1}\left(\vec{R}_i-\vec{R}_{i-2}\right)\vec{R}_{i-1}^2}{\left(\vec{R}_i-\vec{R}_{i-1}\right)\left(\overline{D}_i\left(\vec{R}_{i-1}-\vec{R}_{i-2}\right)+\overline{D}_{i-1}\left(\vec{R}_i-\vec{R}_{i-1}\right)\right)}+\\
&\frac{-\Delta t2\pi\overline{D}_{i+1}\overline{D}_i\left(\vec{R}_{i+1}-\vec{R}_{i-1}\right)\vec{R}_i^2}{\left(\vec{R}_{i+1}-\vec{R}_i\right)\left(\overline{D}_{i+1}\left(\vec{R}_i-\vec{R}_{i-1}\right)+\overline{D}_i\left(\vec{R}_{i+1}-\vec{R}_i\right)\right)}+\frac{\Delta t\Delta V_i\lambda}{2}+\Delta V_i
\end{aligned}\qquad(3.436)$$

$$\underline{\mathrm{Z}}_i=-\underline{\mathrm{A}}_i\overline{C}_{i-1}^{j}-\underline{\mathrm{X}}_i\overline{C}_{i+1}^{j}+\left(2\Delta V_i-\underline{\mathrm{B}}_i\right)\overline{C}_i^{j}+\Delta V_iw_i\Delta t\qquad(3.437)$$

where the general form of the set of linear equations is given by

$$\underline{\mathrm{A}}_i\overline{C}_{i-1}^{j+1}+\underline{\mathrm{B}}_i\overline{C}_i^{j+1}+\underline{\mathrm{X}}_i\overline{C}_{i+1}^{j+1}=\underline{\mathrm{Z}}_i\qquad(3.438)$$

3.2.9.3.1 Inner boundary condition for the GETTER approach

For the first mesh zone, where the inner boundary condition of zero concentration gradient applies, GETTER has the following matrix elements

$$\underline{\mathrm{A}}_1 = 0 \tag{3.439}$$

$$\underline{\mathrm{X}}_1 = \frac{-\Delta t 2\pi \overline{D}_2 \overline{D}_1 \vec{R}_2 \vec{R}_1^2}{\left(\vec{R}_2 - \vec{R}_1\right)\left(\overline{D}_2 \vec{R}_1 + \overline{D}_1\left(\vec{R}_2 - \vec{R}_1\right)\right)} \tag{3.440}$$

$$\underline{\mathrm{B}}_1 = \frac{\Delta t 2\pi \overline{D}_2 \overline{D}_1 \vec{R}_2 \vec{R}_1^2}{\left(\vec{R}_2 - \vec{R}_1\right)\left(\overline{D}_2 \vec{R}_1 + \overline{D}_1\left(\vec{R}_2 - \vec{R}_1\right)\right)} + \frac{\Delta t \Delta V_1 \lambda}{2} + \Delta V_1 \tag{3.441}$$

$$\underline{\mathrm{Z}}_1 = -\underline{\mathrm{X}}_1 \overline{C}_2^j + \left(2\Delta V_1 - \underline{\mathrm{B}}_1\right)\overline{C}_1^j + \Delta V_1 w_1 \Delta t \tag{3.442}$$

where the equation is given by

$$\underline{\mathrm{B}}_1 \overline{C}_1^{j+1} + \underline{\mathrm{X}}_1 \overline{C}_2^{j+1} = \underline{\mathrm{Z}}_1 \tag{3.443}$$

3.2.9.3.2 Outer boundary condition for the GETTER approach

For the last mesh zone, where the outer boundary condition is applied, GETTER uses

$$\underline{\mathrm{A}}_b = \frac{-\Delta t 2\pi \overline{D}_b \overline{D}_{b-1}\left(\vec{R}_b - \vec{R}_{b-2}\right)\vec{R}_{b-1}^2}{\left(\vec{R}_b - \vec{R}_{b-1}\right)\left(\overline{D}_b\left(\vec{R}_{b-1} - \vec{R}_{b-2}\right) + \overline{D}_{b-1}\left(\vec{R}_b - \vec{R}_{b-1}\right)\right)} \tag{3.444}$$

$$\underline{\mathrm{X}}_b = \frac{-\Delta t \overline{D}_b h_c 4\pi \vec{R}_b^2}{2\overline{\overline{D}}_b + \left(\vec{R}_b - \vec{R}_{b-1}\right)E_z} \tag{3.445}$$

$$\underline{\mathrm{B}}_b = \frac{\Delta t 2\pi \overline{D}_b \overline{D}_{b-1}\left(\vec{R}_b - \vec{R}_{b-2}\right)\vec{R}_{b-1}^2}{\left(\vec{R}_b - \vec{R}_{b-1}\right)\left(\overline{D}_b\left(\vec{R}_{b-1} - \vec{R}_{b-2}\right) + \overline{D}_{b-1}\left(\vec{R}_b - \vec{R}_{b-1}\right)\right)} + \frac{\Delta t \overline{D}_b h_c 4\pi \vec{R}_b^2}{2\overline{\overline{D}}_b + \left(\vec{R}_b - \vec{R}_{b-1}\right)E_z} + \frac{\Delta t \Delta V_b \lambda}{2} + \Delta V_b \tag{3.446}$$

$$\underline{\mathrm{Z}}_b = -\underline{A}_b \overline{C}_{b-1}^j - \underline{X}_b \overline{C}_{b+1}^j + \left(2\Delta V_b - \underline{\mathrm{B}}_b\right)\overline{C}_b^j + \Delta V_b w_b \Delta t \tag{3.447}$$

3.2.9.4 Comparison of approaches and numerical stability of solutions

The set of discrete linear equations derived in section 3.2.9.2, namely the mass balance approach, are very nearly equivalent to those of the GETTER approach, if the radius at average concentration in a mesh zone is taken to be half the distance into the mesh zone, namely

$$\overline{R}_i = \frac{\vec{R}_i + \vec{R}_{i-1}}{2}. \tag{3.448}$$

When applying this, the solutions between the GETTER approach and the mass balance approach differ by a factor of

$$\frac{\vec{R}_i - \vec{R}_{i-2}}{\vec{R}_i - \vec{R}_{i-1}} \neq 2 \tag{3.449}$$

which would be true if mesh spaces were constant. However, this is not always the case in GETTER as different mesh spacings are allowed, especially for the coated particle layers. Several attempts have been made to obtain an expression for the average concentration radius such that the GETTER approach would yield the same result as the mass balance approach, with no real success.

GETTER imposes a condition on the discrete timestep Δt, which is based on keeping the values of concentration positive, in order to prevent oscillations in the numerical solution. However, as it was not possible to derive the exact form of finite difference solution employed by GETTER, verification of this stability condition would be pointless at this stage, and it is left as an anomaly to be resolved, either by implementing the newly derived finite difference solution form discussed here, or by showing that the form used by GETTER is correct.

3.2.10 Volume void per sphere

In order to calculate the volume of void per sphere V_{vps} in a packed bed of porosity ε, simple geometric arguments are used. Assuming a bed of n spheres, each of fixed volume V_s, and the bed having a total volume V_T, which is basically the sum of the total void volume V_v and sphere volume

$$V_T = V_v + nV_s. \tag{3.450}$$

Porosity of the bed being defined as

$$\varepsilon = \frac{V_v}{V_T} \tag{3.451}$$

can be modified by substitution of (3.450) into the denominator to yield

$$\varepsilon = \frac{V_v}{V_v + nV_s} \tag{3.452}$$

where the numerator and denominator on the right hand side can be divided by V_v

$$\varepsilon = \frac{1}{1 + \frac{n}{V_v} V_s} \tag{3.453}$$

and rearranging this to make the volume of void per sphere

$$V_{vps} = \frac{V_v}{n} \tag{3.454}$$

the subject of the formula yields the volume of void per sphere

$$V_{vps} = \frac{V_s \varepsilon}{1 - \varepsilon}. \tag{3.455}$$

3.3 CORRELATIONS

3.3.1 Conductivity in the sphere graphite

Conductivity in the graphite is dependent on four major parameters, namely: the grade of graphite, heat treatment temperature, fast neutron dose, and temperature of graphite. GETTER has the capability to calculate the conductivity using one of two techniques. One being an interpolation of experimental data points, and the other is the well known Kania-Nickel correlation [6] that fits experimental data rather well.

3.3.1.1 Interpolation of experimental data points

Currently, the Brabandt and Theymann data is used as the reference experimental points for the graphite. No reference could be found where this data is presented as to confirm the grade or heat treatment temperature of the graphite; hence this issue is reported as an anomaly. A plot of the correlation behaviour as a function of fast neutron dose (fluence) and temperature is shown in Figure 12 below.

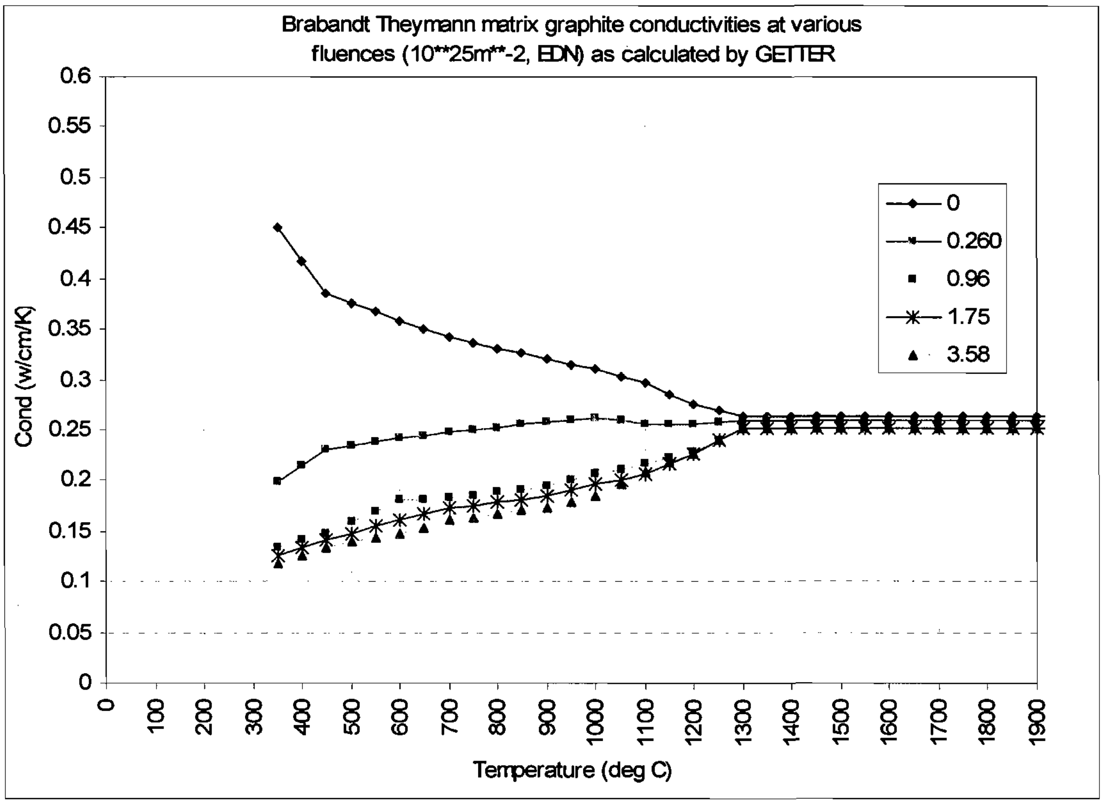


Figure 12: Graphite conductivity according to Brabandt Theymann option in GETTER

3.3.1.2 Kania-Nickel Correlation

According to the report by Kania and Nickel [6], the conductivity of graphite grades A3-3 and A3-27 can be calculated using the equation

$$k_m(T,F) = k_{100}\left[1-\alpha(T-100)e^{\delta T}\right]\left[1-\gamma\left(1-e^{-\beta F}\right)-\varepsilon F\right] \qquad (3.456)$$

where

T = temperature of graphite in °C,

F = fast neutron fluence (or dose) in 10^{25} n.m^{-2} EDN,

k_{100} = thermal conductivity of graphite at 100°C in W.cm^{-1}.K^{-1}, dependent on graphite type,

α = parameter dependent on graphite type (see Table 7) in K^{-1},

δ = parameter dependent on graphite type (see Table 7) in K^{-1},

$$\gamma = 0.940 - 0.604(T/1000), \tag{3.457}$$

$$\beta = 2.960 - 1.955(T/1000), \tag{3.458}$$

$$\varepsilon = 0.043(T/1000) - 0.008(T/1000)^8, \tag{3.459}$$

Table 7: Parameters for use in Kania-Nickel correlation for different graphite types, adapted from [6]

Parameter	A3-3 1800°C Heat Treatment	A3-3 1950°C Heat Treatment	A3-27 1800°C Heat Treatment	A3-27 1950°C Heat Treatment
k_{100} (W.cm^{-1}.K^{-1})	0.508	0.646	0.474	0.622
α (K^{-1})	1.1810 x 10^{-3}	1.4079 x 10^{-3}	9.7556 x 10^{-4}	1.4621 x 10^{-3}
δ (K^{-1})	-7.8453 x 10^{-4}	-9.0739 x 10^{-4}	-6.0360 x 10^{-4}	-9.6050 x 10^{-4}

This correlation (3.456) is correct for the case of matrix graphite that does not contain coated particles or voids, in which case the correlation needs to be modified by an additional factor of

$$F_p = \frac{1-P}{1+0.5P} \tag{3.460}$$

where P is the particle volume loading fraction, typically ~0.1 for 15000 coated particles per fuel zone, hence the complete correlation reads

$$k_m(T,F) = k_{100}\left(1-\alpha(T-100)e^{\delta T}\right)\left(1-\gamma\left(1-e^{-\beta F}\right)-\varepsilon F\right)\left(\frac{1-P}{1+0.5P}\right). \tag{3.461}$$

There is another anomaly in GETTER in that it does not account for the particle loading in the fuel zone when calculating the conductivity of the fuel zone graphite.

3.3.2 Helium Properties

For most cases, GETTER uses the KTA rules [16], [28] to calculate properties of the helium coolant gas that surrounds the pebble. However, some modifications are applied, and these are not justified at present. There are also no checks in place to ensure that correlations are applied within the applicable range. These anomalies need to be resolved.

Applicable range of correlations:

Temperature : $293\text{K} \le T_{He} \le 1773\text{K}$,

Pressure : $1\text{bar} \le p_{He} \le 100\text{bar}$.

3.3.2.1 Mass density

The mass density (ρ_{He}) correlation is given by the KTA rules [28] as

$$\rho_{He} = 48.14\frac{p_{He}}{T_{He}}\left(1+0.4446\frac{p_{He}}{T_{He}^{\ 1.2}}\right)^{-1}, \tag{3.462}$$

where

ρ_{He} = density of Helium in kg.m^{-3},

p_{He} = pressure of Helium in bar,

T_{He} = temperature of Helium in Kelvin (K).

GETTER uses another correlation for calculating the density of Helium, based on the ideal gas equation, namely

$$\hat{\rho}_{He,G} = 0.17623\times 10^{-6}\,p_{He}\left(\frac{273.16}{T_{He}}\right), \tag{3.463}$$

where the subscript G has been added to indicate that the formula is from GETTER, and the tilda to indicate the unit of density this case is kg.cm^{-3}. The ideal gas equation has the general form (for helium)

$$p_{He}V_{He} = n_{He}\underline{R}_i T_{He} \tag{3.464}$$

where

V_{He} = volume of the mass of gas in m^3,

n_{He} = quantity of the gas atoms in moles,

$\underline{R}_i$ = 8.314472 = ideal gas constant in J.mol^{-1}.K^{-1}

$\tilde{p}_{He}$ = pressure of helium in Pa

Rearranging this to obtain the molar density

$$\frac{n_{He}}{V_{He}} = \frac{\tilde{p}_{He}}{\underline{R}_i T_{He}}, \tag{3.465}$$

and multiplying both sides by the molar mass of He ($M_{He} = 4.0026$ g.mol^{-1}) gives the density (in g.m^{-3}) as

$$\tilde{\rho}_{He} = \frac{n_{He}M_{He}}{V_{He}} = \frac{\tilde{p}_{He}M_{He}}{\underline{R}_i T_{He}} \tag{3.466}$$

converting to density to kg.cm^{-3}, and converting pressure to bar requires multiplication by a factor of 1×10^{-4} to give

$$\hat{\rho}_{He,i} = 1\times 10^{-4}\frac{p_{He}M_{He}}{\underline{R}_i T_{He}} \tag{3.467}$$

where the constants for molecular weight and gas constants can be substituted to yield

$$\hat{\rho}_{He,i} = 4.814\times 10^{-5}\frac{p_{He}}{T_{He}} \tag{3.468}$$

which is equivalent to the GETTER equation (3.463).

3.3.2.2 Dynamic viscosity

Calculation of the dynamic viscosity of He is carried out using the correlations from the KTA rules [28] and the original Dragon report [29] , namely

$$\eta_{He} = 3.674 \times 10^{-7} T_{He}^{\ 0.7} \qquad (3.469)$$

where η_{He} is in kg.m^{-1}.s^{-1}.

3.3.2.3 Thermal conductivity

The Dragon report [29] and KTA rules (there is a slight misprint in the German and English version of [28]) gives the thermal conductivity (in W.m^{-1}.K^{-1}) of He related to the pressure and temperature as

$$k_{He} = 2.682 \times 10^{-3}\left(1 + 1.123 \times 10^{-3} p_{He}\right) T^{0.71\left(1-2\times10^{-4} p_{He}\right)}. \qquad (3.470)$$

or

$$k_{He} = 0.144\left(1 + 2.7 \times 10^{-4} p_{He}\right)\left(\frac{T}{T_{00}}\right)^{0.71\left(1-2\times10^{-4} p_{He}\right)} \qquad (3.471)$$

where $T_{00} = 273.15K$, the temperature at 0°C.

GETTER uses almost the same correlation, except that the term $2 \times 10^{-4} p_{He}$ is neglected, probably because it is much smaller than unity for pressure conditions (<100bar) in a typical pebble bed reactor. The GETTER formula is given by

$$k_{He} = 2.682 \times 10^{-3}\left(1 + 1.123 \times 10^{-3} p_{He}\right) T^{0.71} \qquad (3.472)$$

3.3.2.4 Specific Heat

According to the KTA rules [28], the specific heat of He remains unchanged with temperature, at

$$C_{p.He} = 5195 \text{ J.kg}^{-1}\text{.K}^{-1}, \qquad (3.473)$$

which seems to be a reasonable assumption in the operating temperature and pressure regime of the PBMR. An alternative correlation discussed in a PBMR material datasheet [30] is given as

$$C_{p,He} = 5195 - 221.654 T_{He}^{-1.2}\left(10^{-5} \tilde{p}_{He} - 1\right) \qquad (3.474)$$

where, as earlier,

p_{He} = pressure of helium in Pa.

It can easily be shown that second correlation gives results differing by no more than 1% to that given by the first over the PBMR temperature and pressure ranges of operation.

3.3.3 Partial Pressure from Sorption Isotherms

Both Henry and/or Freundlich isotherms may be used to determine the partial pressure (or vapour pressure) of the diffusant in the boundary layer surrounding the sphere [7] for use in equation (3.25). The transition from dominant Henry to dominant Freundlich isotherms occurs at very high surface concentrations (>0.1μmol.g^{-1} [7]), which are rarely attained under normal operation conditions [31].

The partial vapour pressure $p_n(c_s,T)$ of an element n is a function of the surface concentration and temperature, and is calculated as the sum of the Henry ($p_{n,H}(c_s,T)$) and Freundlich isotherm ($p_{n,F}(c_s,T)$) vapour pressure

$$p_n(c_s,T) = p_{n,H}(c_s,T) + p_{n,F}(c_s,T) \tag{3.475}$$

where

$$p_{n,H}(c_s,T) = c_s \exp\left(\left(A_n + \frac{B_n}{T}\right) + \left(D_n - 1 + \frac{E_n}{T}\right)\ln c_t\right), \tag{3.476}$$

$$p_{n,F}(c_s,T) = \exp\left(\left(A_n + \frac{B_n}{T}\right) + \left(D_n + \frac{E_n}{T}\right)\ln c_s\right), \tag{3.477}$$

$$\ln c_t = d_1 - d_2 T. \tag{3.478}$$

The constants A_n, B_n, D_n, E_n, c_t, d_1 and d_2 are empirically determined from experiments [7], and units of the parameters are given as

T = Temperature of surface in K,

$p_{n,H}$ = Henry isotherm vapour pressure in bar,

$p_{n,F}$ = Freundlich isotherm vapour pressure in bar,

B_n, E_n = constants in K,

c_s = concentration on surface in μmol.gC^{-1} (micromole per gram carbon)

d_2 = constant in K^{-1}.

Simplifications of the above formulae may be made by combining expressions containing constants into new constants. This is especially true for the low concentration Henry region, the correlation can be written as

$$p_{n,H}(c_s,T) = c_s \exp\left(F_n + \frac{G_n}{T}\right) \tag{3.479}$$

where

$$F_n = A_n + (D_n - 1)\ln c_t, \tag{3.480}$$

$$G_n = B_n + E_n \ln c_t. \tag{3.481}$$

3.3.4 Nusselt Number

The correlation for calculating the Nusselt number for a pebble bed of spheres, namely equation (3.14), is

$$Nu = 1.27\frac{Pr^{1/3}}{\varepsilon^{1.18}}Re^{0.36} + 0.033\frac{Pr^{1/2}}{\varepsilon^{1.07}}Re^{0.86} \tag{3.14}$$

where the applicable range of parameters are given [16] as

Reynolds number: $100 \le Re \le 10^5$

Void fraction: $0.36 \le \varepsilon \le 0.42$

Diameter ratio: $D/d > 20$ (D = core diameter, d = pebble diameter)

Height of bed: $H > 4d$

It is important to note here that for a core calculation near the wall, this correlation cannot be applied due to the void fraction approaching unity. This correlation was also determined for a cylindrical and not coaxial bed as in the case of the PBMR. Usage of this correlation for pebble bed calculations is therefore an anomaly that needs to be resolved.

The definition of the Reynolds number (Re) for a bed of mass flow rate $\dot{m}$ (in kg.s^{-1}), and cross sectional flow area A (in m^2) is given by the KTA rules [16] as

$$Re = \frac{(\dot{m}/A)d}{\eta_{He}} \tag{3.482}$$

where d is the pebble diameter in meters, and the viscosity is given by equation (3.469).

It must be stated here that GETTER calculates the area from the core radius, assuming a cylindrical core, which is not correct in the case of the PBMR. A possible resolution is to use the effective radius representing an equivalent cross sectional area for the coaxial core.

The Prandtl Number (Pr)

$$Pr = \frac{C_{p,He}\eta_{He}}{k_{He}} \tag{3.483}$$

can be calculated in terms of the Helium properties of specific heat $(C_{p,He})$ in J.kg^{-1}.K^{-1}, dynamic viscosity (η_{He}) in kg.m^{-1}.s^{-1}, and conductivity (k_{He}) in W.m^{-1}.K^{-1}, from equations (3.473), (3.469), and (3.470).

4. PROGRAM FLOW

The algorithm that GETTER employs to implement all the phenomena mentioned above is illustrated in Figure 13.

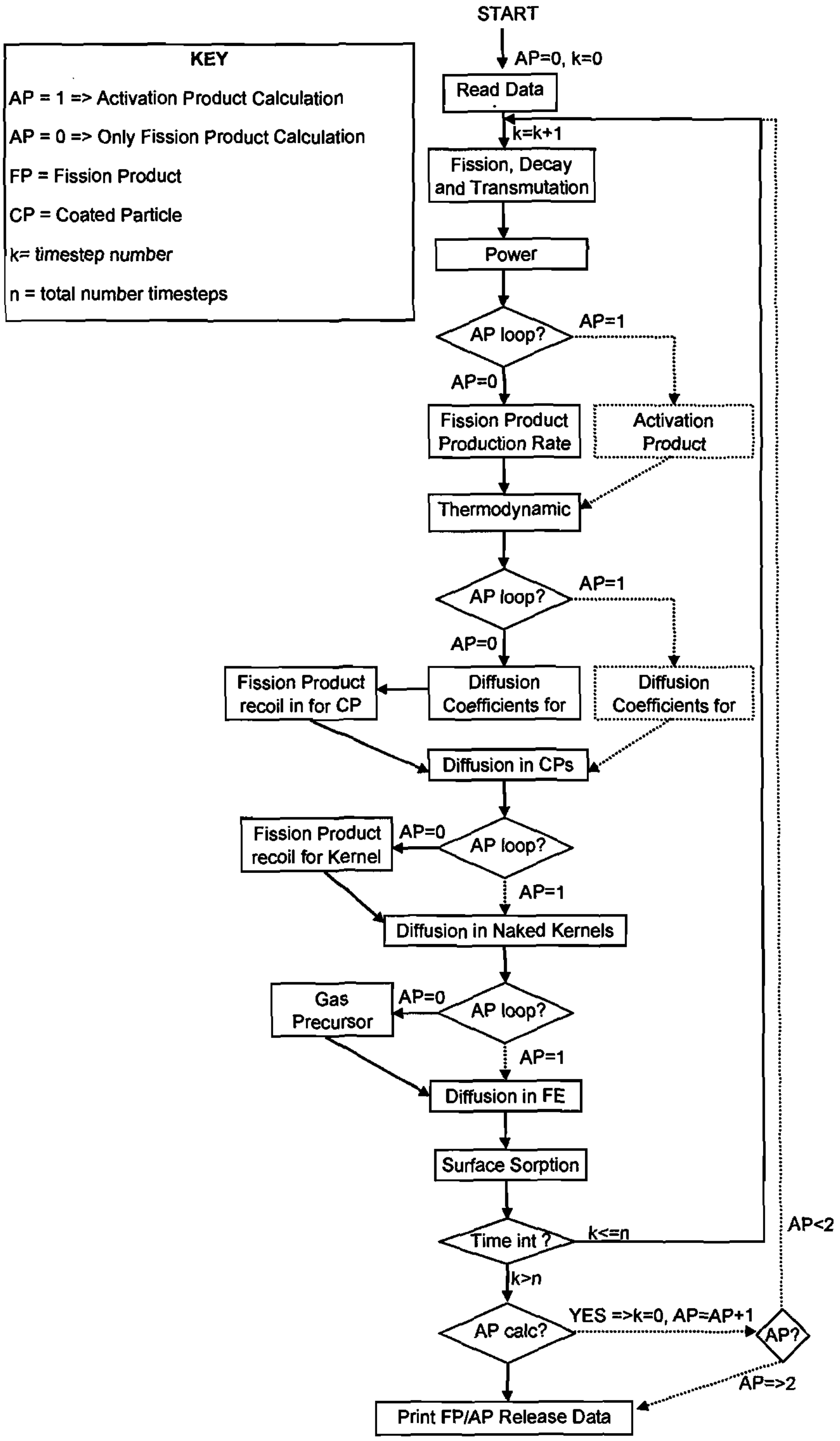


Figure 13: Programme flow of GETTER illustrating implementation of the model phenomena.

5. ANOMALIES

Table 8 lists the anomalies and that were encountered upon reverse engineering of GETTER and extraction of theory. Anomalies with regard to theory implementation or software bugs are covered elsewhere in the implementation report and/or relevant V&V documentation. A record of all anomalies is also kept in the anomaly register [4].

Table 8: List of Anomalies for GETTER Theory

Anomaly Description	Section
Simplification of decay chain needs to be validated to prove it is a justifiable approximation to ignore high absorption cross section nuclides such as ^{233}Th.	3.1.1
Brabandt Theymann data could not be found in literature. Either use other experimental data, or do a comparative study.	3.3.1.1
Particle loading in the fuel zone not accounted for.	3.3.1.2
Formulae for calculation of burnup in contamination based on unqualified assumptions. Rather calculate burnup in contamination using same technique as fuel.	3.2.5.1
KTA rules for heat transfer coefficient are for cylindrical bed, and not coaxial bed. Also not applicable near wall. Obtain new correlations (experiment). Check Reynolds number Area calculation based on cylindrical core in GETTER.	3.3.4
Shell approximation for recoil using the spherical equation needs to be justified with respect to inner recoil losses.	3.2.6.2, 3.2.6.3, 3.2.6.4.
Buffer layer and inner pyrocarbon layer treated as one layer, using pyrocarbon properties. This is not conservative as buffer is much less of a barrier than pyrocarbon.	3.2.6.2
Helium properties from KTA rules modified, and density not that in rules.	3.3.2
Volumetric average temperature for spherical shells in fuel zone not using correct formula.	3.2.8.2.1
Calotte geometry assumed to be spherical shell in code, where it is actually a cylindrical body with a spherically hollowed interior.	3.2.8.3
Gamma heating density in fuel zone, fuel free zone, and graphite cup assumed to be the same.	3.2.8
Activation product inventory formulae in GETTER differ from those derived here.	3.2.3
GETTER discretization of diffusion equation differs from that obtained here. The exact discretization could not be produced, even after two different approaches used in this work.	3.2.9
Gas pressures for diffusant on surface of fuel element incorrectly calculated because of molar mass of diffusant in GETTER formulae. The exact formula in the code could not be reproduced from the theory.	3.3.3

6. CONCLUSIONS

All of the physical laws and correlations used by GETTER have been presented in this dissertation to the extent that the derived equations could be implemented directly into the code, or modified slightly for implementation. The implementation of these into the code is presented as further work in [3], and falls outside the scope of this document.

The anomalies that are presented here form part of the larger scope of anomalies, and exclude those presented upon implementation of the theory, or that of numerical inconsistencies upon code execution. Resolution of these anomalies will probably form part of a newer version of GETTER or justified as negligible or conservative.

7. REFERENCES

The following documents are referenced within this document.

[1] Keshaw, J., "GETTER – A Model for Fission Product Release from Spherical HTR Fuel Elements", HTR2006 conference proceedings No. C00000095, HTR2006, Sandton, South Africa, 2006.

[2] Keshaw, J., "GETTER Theory Description Report", PBMR Doc. No. 026755, Rev. B, 2007.

[3] Keshaw, J., "GETTER Implementation Description", PBMR Doc. No. 056927, Rev. A, 2007.

[4] Keshaw, J., "GETTER Anomaly Register", PBMR Doc. No. 053940, Rev. A, 2007.

[5] Stacey, W. M., "Nuclear Reactor Physics", John Wiley and Sons, Inc., New York, 2001.

[6] Kania, M. J., and Nickel, H., "Performance Assessment of the (Th,U)O_2 HTI-BISO Coated Particle under PNP/HHT Irradiation Conditions," Jül 1685, ISSN 0366-0885, Berichte der Kernforschungsanlage Jülich, 1980.

[7] Verfondern, K (editor), "Fuel Performance and Fission Product Behaviour in Gas Cooled Reactors," IAEA TECDOC 978, International Atomic Energy Agency, Vienna, 1997.

[8] Matzner, D., "PBMR Project Status and the Way Ahead," A04, Proceedings of 2nd International Topical Meeting on High Temperature Reactor Technology, HTR-2004, Beijing, China, 2004.

[9] Röllig, K., "Rechenprogramm GETTER", Westinghouse Reaktor Report No. GBRA 052 477, Westinghouse Reaktor GmbH, Germany, 2001.

[10] Krohn, H., and Finken, R., "FRESCO II: Ein Rechenprogramm zur Berechnung...," Jül Spez 212 ISSN 0343-7639, Kernforschungsanlage Jülich, 1983

[11] National Nuclear Regulator, "Requirements for licensing submissions involving computer software and evaluation models for safety calculations", RD-0016, Rev. 0. National Nuclear Regulator of South Africa, Centurion, 2005.

[12] van der Merwe, H., Clifford, I., "Development of the FIPREX-GETTER Calculation Model and its Application at PBMR", HTR2006 conference proceedings No. C00000073, HTR2006, Sandton, South Africa, 2006.

[13] van der Merwe, H., "Metallic Fission Product Release Calculation Model Report", PBMR Doc. No. T000239, Rev. A, 2005.

[14] Gauld, I. C., Herman, O. W., and Westfall, R. M., "ORIGEN-S: Scale System Module...," NUREG/CR-0200, Rev. 6, Vol. 2, Section F7, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1998

[15] Keshaw, J., "Fission Product Release Short Lived Isotopes – Steady State Release Mathematical Derivation Report", PBMR Doc. No. T000228, Rev. 1, 2005.

[16] Geschäftsstelle des Kerntechnischen Ausschusses beim Bundesamt für Strahlenschutz, "Reactor Core Design of High-Temperature Gas-Cooled Reactors," KTA3102.2, Carl Heymanns Verlag KG, Köln, 1983.

[17] Incropera, F. P., DeWitt, D. P., "Fundamentals of Heat and Mass Transfer", John Wiley and Sons, Inc., New Jersey, 2002.

[18] Bird, R. B., Stewart, W. E., and Lightfoot, E. N., "Transport Phenomena - 2nd Edition", John Wiley and Sons, Inc., New Jersey, 2002.

[19] Mills, A.F., "Heat and Mass transfer", R D Irwin Inc., Chicago, 1995.

[20] Röllig, K., "Release of Rare Fission Gases from Spherical Spheres with Coated Fuel Particles," Nuclear Technology, **35**, 1977.

[21] Lamarsh, J. R., Baratta, A. J., "Introduction to Nuclear Engineering – Third Edition", Prentice-Hall, 2001.

[22] Stewart, J., "Calculus – Second Edition", Brooks/Cole Publishing Company, California, 1991.

[23] Kreyszig, E., "Advanced Engineering Mathematics", John Wiley & Sons, Singapore, 1999.

[24] Weisstein, E. W., "Spherical Cap--A Wolfram Web Resource", http://mathworld.wolfram.com/SphericalCap.html, 2007.

[25] Preinreich, G., "FIPDIG- A One-dimensional Time Dependent Fission Product Diffusion Code", Dragon Project Report No. 565, England, 1968.

[26] Burden, R. L., Faires, J. D., "Numerical Analysis – 8th Edition", Thomson Brooks/Cole, USA,

2005.

[27] Griffiths, D. J., "Introduction to Electrodynamics – Second Edition ", Prentice-Hall, 1989.

[28] Geschäftsstelle des Kerntechnischen Ausschusses beim Bundesamt für Strahlenschutz, "Reactor Core Design of High-Temperature Gas-Cooled Reactors," KTA3102.1, Carl Heymanns Verlag KG, Köln, 1983.

[29] Petersen, H., "Tables of Thermo-physical Properties of Helium", Dragon Project Report No. 734, England, 1971.

[30] Sage, M., "Material Datasheet for Helium", PBMR Doc. No. PP380-022152-4026, Rev. 2, 2004.

[31] Röllig, K., "Release of Metallic Fission products from the PBMR core", Westinghouse Reaktor GmbH, Doc. No. GBRA 052 341, 1999.