

Mathematical and computational models for simulating transient nuclear criticality excursions within plutonium nitrate systems

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ABSTRACT

This paper presents a novel methodology for the analysis of transient nuclear criticality in aqueous solutions of plutonium nitrate. The transient methodology includes one-dimensional thermal hydraulics and a detailed description of radiolytic gas formation (including aqueous concentrations of radiolysis species and bubble population, nucleation radius and advection velocity). The positive temperature feedback effect in dilute plutonium solutions, due to a low lying resonance (at ≈ 0.3 eV) in the microscopic fission cross section, is investigated. The solutions' nuclear properties, such as intrinsic neutron source and mean neutron generation time; thermophysical properties and heat transfer coefficients; linear energy transfer and dynamics of radiolytic gas nucleation; and subcritical power, are also investigated. The effect of step and ramp reactivity insertions on transient nuclear criticality behaviour is examined, alongside the effect of fuel solution ingress and egress from the system. For a solution containing 16.0 g L^{-1} plutonium with an acidity of 0.2 mol L^{-1} , increasing the width of the prescribed step reactivity insertion from 2.25 to 2.50 s increased the magnitude of the initial power peak, and decreased the time to boil, by an order of magnitude. It was observed that the characteristics of the radiolytic gas were dependent on the magnitude of the initial power peak. For example, the transients with the highest initial power peak produced an initially large quantity of radiolytic gas, with defined oscillations in their quantity (and other properties) as the transient progressed. For transients with lower power peaks, the oscillations became less defined, with a reduced period and magnitude, due to the lower quantity of radiolytic gas produced due to the initial power peak. Many of the presented simulations of nuclear criticality transients were terminated when the solution started to boil, a phenomenon which is not included in the presented methodology. Boiling occurred when the initial reactivity input induced a power spike that raised the solution temperature enough for the positive reactivity feedback effect to sustain the transient even when the reactivity input was removed.

1. Introduction

As part of the nuclear fuel cycle, fissile material (such as uranium- or plutonium-bearing compounds) is dissolved into an aqueous solution to enable its chemical processing into nuclear fuel, or to reprocess spent reactor fuel and nuclear waste products (Crossland, 2012; Irish and Reas, 1957; Wilson, 1996; Zohuri, 2019). Fissile solutions are also used in experimental and research facilities (Crossland, 2012; McLaughlin et al., 2000; Wilson, 1996; Zohuri, 2019).

Solutions of dilute plutonium nitrate are known to have a positive reactivity feedback when their temperature increases (Haeck et al., 2008; Kornreich, 1993), which can lead to autocatalytic nuclear criticality excursions (Hetrick, 1999), which is a concern particularly when storing spent fuel in geological repositories (Bowman and Venneri,

1996; Haeck et al., 2008; Hetrick, 1999; Kastenberget al., 1996; Kornreich, 1993; Leclaire and Grivot, 2006; Parks et al., 1995). This positive temperature effect is due to the low lying (at ≈ 0.3 eV) resonance in the microscopic neutron fission cross section of ^{239}Pu , and the thermal neutron energy spectrum (caused by effective neutron moderation due to the high quantity of hydrogen in the system) (Dyson, 1980; Haeck and Leclaire, 2008; Stratton, 1983; Yamamoto and Miyoshi, 2002). When the solution temperature increases, the low lying resonance peak broadens due to the Doppler effect, and the neutron energy spectrum shifts slightly higher, thus increasing the fission rate and overall reactivity.

A criticality accident is defined as any unplanned and/or uncontrolled nuclear criticality excursion in a fissile system or material (Paxton, 1989). They can expose facility workers, the general public and

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Nomenclature**Latin Symbols**

$\dot{E}$	Linear energy transfer [MeV μm^{-1}]
A	Area [m^2]
C	Concentration [mol m^{-3}]
c_{Pu}	Solution plutonium concentration [g L^{-1}]
C_D	Coefficient of drag [–]
C_p	Specific heat capacity [$\text{J kg}^{-1} \text{K}^{-1}$]
c_{HNO_3}	Solution excess acidity [mol L^{-1}]
D_{mix}	Mixing coefficient [$\text{m}^2 \text{s}^{-1}$]
D_{H_2}	Diffusivity of aqueous hydrogen [$\text{m}^2 \text{s}^{-1}$]
E	Energy [J]
g	Acceleration due to gravity [m s^{-2}]
G_{H_2}	Radiolytic gas generation coefficient [mol J^{-1}]
H	Height [m]
h	Heat transfer coefficient [$\text{J m}^2 \text{K}^{-1} \text{s}^{-1}$]
$H_{i,\text{sol}}$	Henry's law constant for species i [$\text{mol m}^{-3} \text{Pa}^{-1}$]
k_{bub}	Bubble collapse proportionality constant [$\text{W}^{-3/2} \text{m}^{3/2}$]
k_{coll}	Bubble collapse time constant [$\text{m}^2 \text{s}^{-1}$]
k_{eff}	Effective neutron multiplication factor [–]
k_s	Subcritical neutron multiplication factor [–]
k_d	H_2O_2 decomposition rate [s^{-1}]
M	Mass [kg]
m	Mass fraction [–]
M_{H_2}	Molar mass of hydrogen [kg mol^{-1}]
N	Number of moles [mol]
N_b	Bubble population [–]
P	Power [J s^{-1}]
p	Pressure [Pa]
P_C	Delayed neutron precursor population [–]
r_{nuc}	Bubble nucleation radius [m]
r_b	Bubble radius [m]
S	Intrinsic neutron source [neutrons s^{-1}]
T	Temperature [K]
t	Time [s]
V	Volume [m^3]
v_b	Average bubble velocity [m s^{-1}]
y_i	Yield fraction of species i [–]
z	Axial location [m]

Greek Symbols

α_c	Phase transfer rate constant [s^{-1}]
β	Fraction of fission neutrons that are delayed [–]
ΔH_r	Enthalpy of the radiolysis reaction [J mol^{-1}]
ΔH_{vap}	Enthalpy of vapourisation of water [J kg^{-1}]
ϵ	Energy released per fission [J fission^{-1}]
$\hat{\phi}$	Scalar neutron flux shape profile [m^{-1}]
κ	Thermal conductivity [$\text{J m}^{-1} \text{K}^{-1} \text{s}^{-1}$]
Λ	Mean neutron generation time [s]

λ	Delayed neutron precursor decay constant [s^{-1}]
μ	Dynamic viscosity [$\text{kg m}^{-1} \text{s}^{-1}$]
$\bar{\nu}$	Average number of neutrons produced per fission [neutrons]
ρ	Density [kg m^{-3}]
σ	Surface tension [J m^{-2}]
θ	Void fraction [–]
ξ	Reactivity [–]

Subscripts

crit	Critical
eff	Effective
eq	Equilibrium
ext	External
int	Internal
rg	Radiolytic gas
sat	Saturation
th	Thermal
vess	Vessel

and on-site repair, in addition to and increased need for healthcare and mitigation (Bizet and L  v  que, 2017).

As it is more likely for process criticality accidents to occur in fissile solutions or liquid media than in dry systems (McLaughlin, 2003), the understanding of such systems is paramount for the prevention of nuclear criticality excursions (International Atomic Energy Agency, 2014).

Further, well-developed phenomenological codes can aid emergency planning and preparedness, assisting in the minimisation of the risks and costs associated with nuclear criticality accidents (Kimpland, 1993; McLaughlin, 2003; Srinivasan et al., 1992; Whitesides et al., 2010).

This paper presents a computational model for simulating criticality transients in solutions of plutonium nitrate. Section 2 describes the potential for plutonium nitrate solutions to have a positive thermal reactivity feedback, and introduces the conceptual reactor used in the presented research.

Section 3 details the phenomenological models used in the presented research. Sections 4 and 5 present the calculation of material properties needed by the phenomenological models, Section 6 presents analysis of parameters relating to radiolytic gas generation in plutonium nitrate solutions, and Section 7 details the calculation of required nuclear parameters, such as reactivity feedbacks and neutron kinetics data.

Sections 8, 9 and 10 present results from the transient model, investigating the effects of step reactivity, ramp reactivity, and mass insertion on the resulting transient behaviour of solutions with a selection of plutonium and nitric acid concentrations.

The motivation for the presented research includes a more thorough understanding of criticality transients involving plutonium nitrate solutions, in particular the affect solution temperature has on transient behaviour, for risk assessment and safety analysis.

2. Thermal reactivity feedback in plutonium nitrate solutions

The temperature feedback effect is the change in reactivity due to a change in temperature of a fissile system. Changes in temperature cause properties like density to (usually) decrease, which reduces the probability of neutron collisions and results in a higher rate of neutron leakage, resulting in a decrease in reactivity (Knief, 1985).

In addition, changes in temperature induce Doppler broadening of absorption resonances (Kerlin and Upadhyaya, 2019). For systems containing uranium, Doppler broadening increases the neutron absorption

the wider environment to harmful ionising radiation (Crossland, 2012; Kimpland, 1993; Knief, 1985; Srinivasan et al., 1992). Significant economic costs may be associated with the following radiation cleanup

cross section of ^{238}U nuclei, reducing reactivity (Kerlin and Upadhyaya, 2019). However, for systems containing plutonium, the effect of Doppler broadening can increase reactivity (due to a reduction in absorption cross section and increase in fission cross section), inducing a positive feedback loop (Yamamoto and Miyoshi, 1999, 2002).

As noted by Bowman and Venneri (1996), the sign and magnitude of thermal reactivity feedback in plutonium nitrate solutions is dependent on many factors, including fissile material composition, quantities of water and other moderating materials, and system configuration.

2.1. Previous research

Many studies have theoretically shown the positive temperature effect that can occur in dilute plutonium systems (e.g., plutonium nitrate within nuclear fuel and reprocessing facilities and plutonium contaminated porous media in deep geological disposal facilities). The majority of scenarios investigated have focussed on the safe disposal of fissile material underground.

Previous work (for example by Atz et al. (2019), Bowman and Venneri (1996), Hetrick (1999), Kastenberget al. (1996), Kornreich (1993), Leclaire and Grivot (2006) and Parks et al. (1995)) concluded that, as long as canisters containing fissile material remain intact, criticality is not a concern. However, breached canisters (enabling water ingress into a geological repository or the dispersion of fissile material into the underground surroundings) may give rise to autocatalytic criticality, which could have significant nuclear yield.

In addition to an increase in fuel temperature, Ehud Greenspan and Burch (1997) discuss how events such as water removal (e.g. via an increase in temperature of the surrounding rock), heterogeneity in the wider system (e.g. layered fissile material with rock) and pressure changes can impact the positive temperature effect. Mathematical discussions have also been made by Kornreich (1997). Building on previous work by Eberle et al. (1996) and Sanchez et al. (1998) discuss the potential for the positive temperature effect to occur in various mixtures of ^{239}Pu , SiO_2 , Nevada Tuff and H_2O .

Pain et al. (2001b) coupled the time and spatially dependent neutronics kinetics code EVENT (EVEN parity Neutral particle Transport) with the computational multiphase and multicomponent fluid dynamics (CMMFD) code FLUIDITY to produce a multiphysics modelling and simulation (M&S) framework FETCH (Finite Element Transient Criticality). EVENT solves the second order even-parity form of the neutron transport equation and utilises adaptive, implicit time-stepping and a finite element based spatial discretisation along with a spherical harmonic (P_N) angular discretisation and a multigroup approximation to discretise the energy variable (de Oliveira, 1986). FLUIDITY solves the multiphase Navier–Stokes equations using a two-fluid Eulerian–Eulerian model and utilises a mixed finite element spatial discretisation along with an adaptive implicit time-stepping approach (Pain et al., 2001c). Due to the different time-step requirements for the neutron kinetics and the multiphase fluid dynamics a sub-cycling time-stepping approach was utilised in the FETCH M&S framework. The FETCH multiphysics M&S framework was applied to analysing transient nuclear criticality excursion scenarios of plutonium nitrate solutions within cylindrical vessels using two-dimensional (2D) $r-z$ geometry models. The results of applying FETCH to plutonium nitrate transient nuclear criticality excursion scenarios demonstrate that radiolytic gas evolution should eventually terminate these transients. However, if escape of the liquid from the vessel is prevented during continuous filling, or if the radiolytic gas is suppressed due to pressure, then this results in more energetic transient nuclear criticality excursions and consequent greater fission yields (Pain et al., 2001a).

Yamamoto and Miyoshi (1999) discuss the reactivity effects of an increase in temperature in dilute plutonium solutions, and plutonium solutions also containing gadolinium. Their subsequent research investigated the positive temperature effect using perturbation theory and the four-factor formula (Yamamoto and Miyoshi, 2002).

2.1.1. The physics of autocatalytic criticality

The positive temperature effect observed in dilute plutonium nitrate systems can be attributed to the low lying resonance (at ≈ 0.3 eV) in the microscopic fission cross section, which was first postulated by Dyson (1980).

Fig. 1 presents the microscopic fission cross sections of ^{235}U and ^{239}Pu . As shown in Fig. 1, there is a large peak at ≈ 0.3 eV (the low lying resonance) in the ^{239}Pu microscopic fission cross section spectrum. At this energy, the ^{239}Pu cross section spectrum is over 10 times that of ^{235}U , as demonstrated by the right-hand graph of Fig. 1.

Increasing the temperature of a fissile system causes Doppler broadening in the effective cross sections at the resonance energy (Stratton, 1983; Yamamoto and Miyoshi, 2002). In addition, the microscopic neutron upscattering cross sections in the thermal energy range increase, which shifts the neutron spectrum in the thermal energy range slightly higher in energy (Stratton, 1983; Yamamoto and Miyoshi, 2002).

Thus, an increase in temperature causes an increase in reactivity because of the doppler broadening of the low-lying resonance at 0.3 eV, and a slight increase in neutrons' energy spectrum, meaning a larger proportion of neutrons have an energy around the resonance region, increasing the fission rate, and thus reactivity, of such a system (Stratton, 1983; Yamamoto and Miyoshi, 1999).

When analysing any fissile system, the thermal scattering ($S(\alpha, \beta)$) data also needs to be correctly used (i.e. at the appropriate temperature) to ensure accurate results. This is particularly relevant for dilute solutions of plutonium nitrate: as the moderator (hydrogen) atoms far outnumber the fissile atoms, the neutron spectrum is notably thermalised; and the high proportion of water molecules also elicit the need for accurate $S(\alpha, \beta)$ data (Haack and Leclaire, 2008).

2.1.2. Apparatus B

Apparatus B was a criticality research facility at the Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA) nuclear research centre in Valduc, France, where, between 1963 and 1976, experiments were performed during the 'French Plutonium Temperature Effect Programme', to experimentally show the positive temperature reactivity feedback of dilute plutonium solutions; previously, only theoretical analysis had been performed (Barbry et al., 2003; Haack et al., 2008; Leclaire and Grivot, 2006).

In one set of experiments (Barbry et al., 2003; Haack et al., 2008), plutonium nitrate solutions (with plutonium concentrations of 20, 15 and 14.3 g L^{-1}) were held in a cylindrical steel vessel, with a cylindrical water jacket to act as a reflector. Though the first phase of the experiments had no definitive conclusion, results from the second phase indicated the 14.3 g L^{-1} solution had a positive temperature feedback of approximately 2 pcm K^{-1} (Barbry et al., 2003; Haack et al., 2008; Leclaire and Jaiswal, 2023).

In another set of experiments (Leclaire and Grivot, 2006), the critical heights of plutonium solutions in cylindrical vessels were determined, such that the results could be used in benchmarking problems (International Criticality Safety Benchmark Evaluation Project, 2020). The key components of the experimental set-up are demonstrated in Fig. 2 (additional structural and instrumental components were also present). Two vessels were used, with r_{in} and r_{out} being either 10 and 25 cm, or 15 and 25 cm, and the cylindrical water jacket was replaced with a parallelepiped-shaped water tank.

Many other experiments were performed using Apparatus B, which was modified several times. For example, several geometrical configurations for both the fuel and reflector (e.g. cylinders, annular cylinders, parallelepipeds and various arrays) have been used. A review of the general facility and experimental procedures have been presented by Barbry et al. (2003).

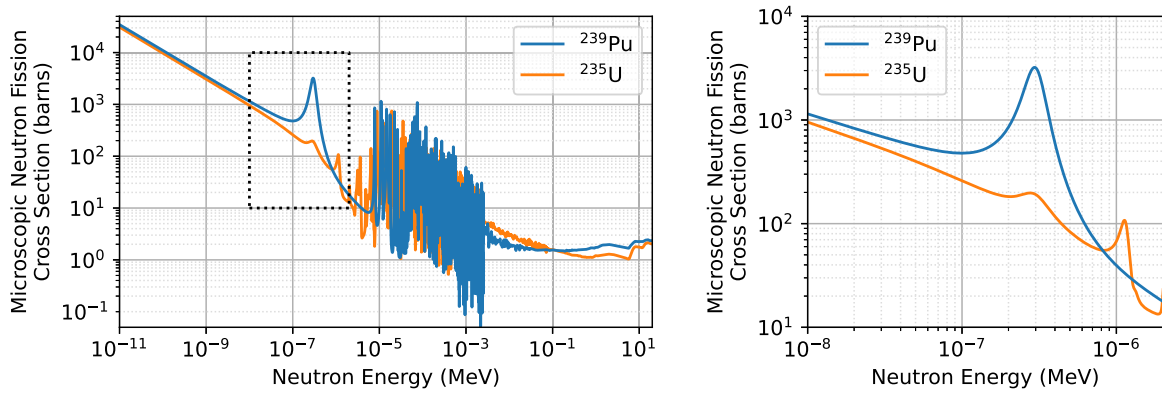


Fig. 1. The microscopic fission cross sections of ^{235}U and ^{239}Pu across all energies (left) and around the low-lying resonance region (right), obtained using data from the ENDF/B-VIII.0 nuclear data library (Brown et al., 2018; Conlin et al., 2018).

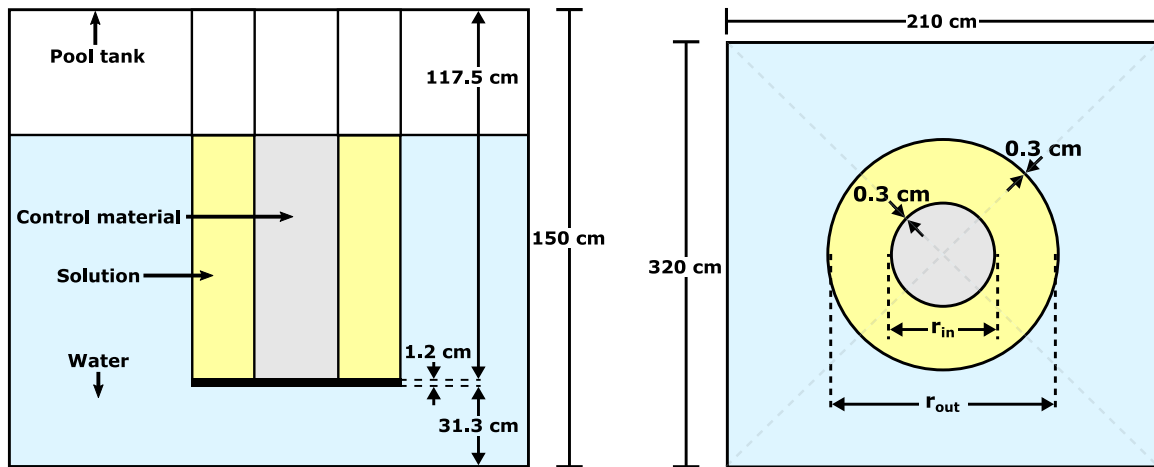


Fig. 2. Side elevation (left) and plan view (right) schematics demonstrating the geometry of the conceptual reactor modelled in the presented research.

2.2. Conceptual reactor

Fig. 2 demonstrates the system geometry used in the presented research. The solution vessel is placed in a parallelepiped-shaped reflector pool with a footprint measuring 320 cm $\times$ 210 cm and a height of 150 cm. The base of the vessel is 32.5 cm above the bottom of the reflector pool, and the vessel walls are 0.3 cm thick. In these regards, this is the same set-up employed in the experiments by Leclaire and Grivot (2006). However, the system utilised in this section does not include the walls of the reflector pool, or details of inlet and outlet pipes and other structural details. In addition, the base of the vessel is taken to be a constant thickness of 1.2 cm.

2.3. Demonstration of temperature feedback in plutonium nitrate solutions

In the remainder of the presented research, the change in reactivity due to an increase in temperature above 293.6 K is defined as $\Delta\xi_{\text{th}}(\bar{T}, t) = \xi(\bar{T}, t) - \xi(293.6, t)$, where ξ , $\bar{T}$ and t represent reactivity, average solution temperature, and time. In addition, the plutonium and excess acid concentrations will be represented by c_{Pu} and c_{HNO_3} respectively. In all examples presented in this section, the system geometry of Fig. 2 has been used, with air as the control material, and the height of the solution is 80.0 cm at 293.6 K. MCNP (Werner et al., 2018) and the ENDF/B-VIII.0 nuclear data library (Brown et al., 2018) were used in all calculations.

2.3.1. The effect of vessel radii

The left-hand graph of Fig. 3 shows that increasing the inner radius of the vessel decreases the magnitude of a positive temperature feedback. In the right-hand graph of Fig. 3, it can be seen that increasing the vessel's outer radius increases the magnitude of a positive temperature feedback.

In general, increasing the ratio of the outer radius to the inner radius increases the degree of the positive temperature feedback. For cases when this ratio is low, the temperature feedback becomes negative.

Increasing the inner radius of the vessel decreases the positive temperature effect because the vessel is occupied by less fissile solution. This means that the system is moderated less effectively due to the lower water content of the system, in turn meaning that the neutron energy spectrum becomes less thermal; when the neutron spectrum shifts past the ≈ 0.3 eV resonance in the microscopic fission cross section, the positive temperature effect will be reduced. Conversely, the opposite is true when the vessel's outer radius is increased: the increased quantity of solution (and thus water) will aid neutron moderation, making the neutron energy spectrum more thermal, in addition to there being a reduced rate of radial neutron leakage from the fissile region of the system.

2.3.2. The effect of plutonium and acid concentrations

Figs. 4 and 5 show that increasing the solution's acidity either decreases the magnitude of a positive temperature feedback, or increases the magnitude of a negative temperature feedback.

From Figs. 4 and 5, it can be seen that increasing the solution's plutonium concentration will decrease the positive temperature coefficient of reactivity of the solution. For example, when $c_{\text{HNO}_3} = 0.0$

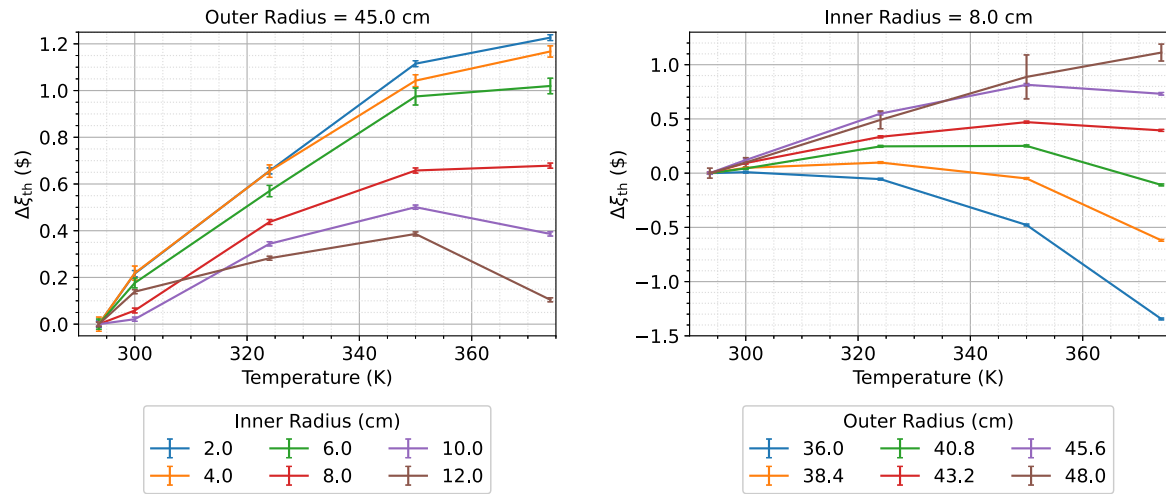


Fig. 3. Thermal reactivity feedbacks for a range of vessel inner and outer radii. The plutonium and excess acid concentrations are 15.0 g L^{-1} and 1.0 mol L^{-1} respectively, and the isotopic composition of plutonium is detailed in Table A.17.

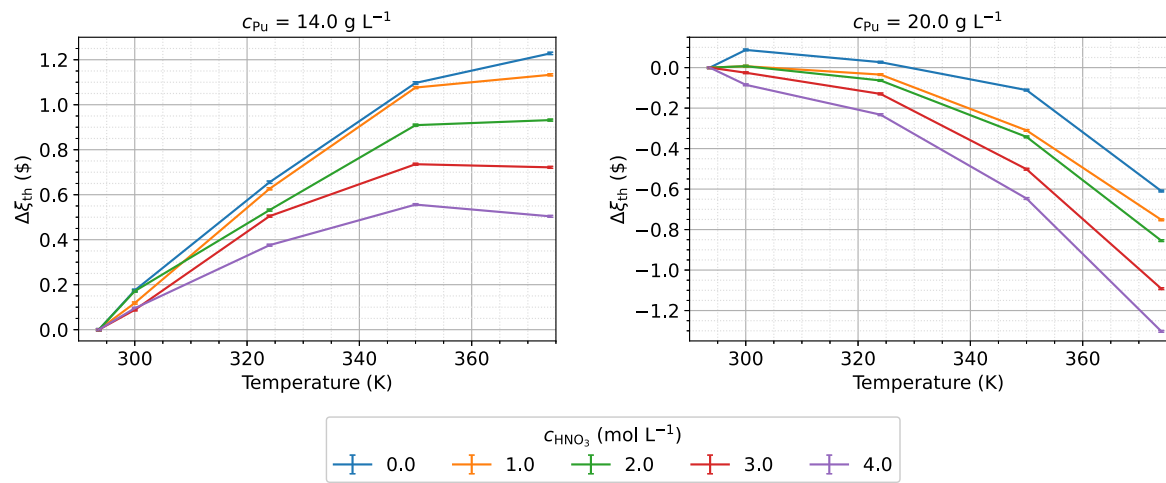


Fig. 4. Thermal reactivity feedbacks for a range of excess acid concentrations. The inner and outer radii are 8.0 and 45.0 cm respectively, and the isotopic composition of plutonium is detailed in Table A.17.

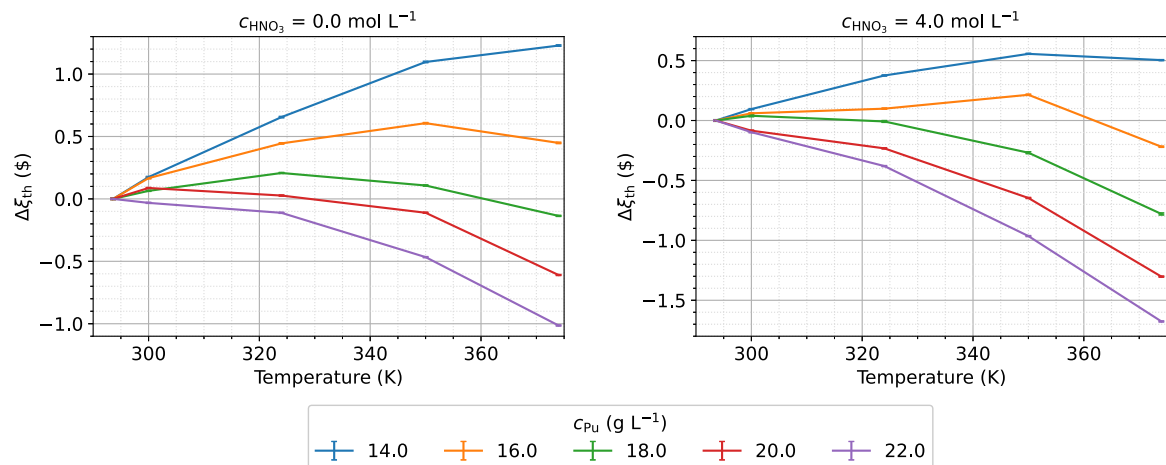


Fig. 5. Thermal reactivity feedbacks for a range of plutonium concentrations. The inner and outer radii are 8.0 and 45.0 cm respectively, and the isotopic composition of plutonium is detailed in Table A.17.

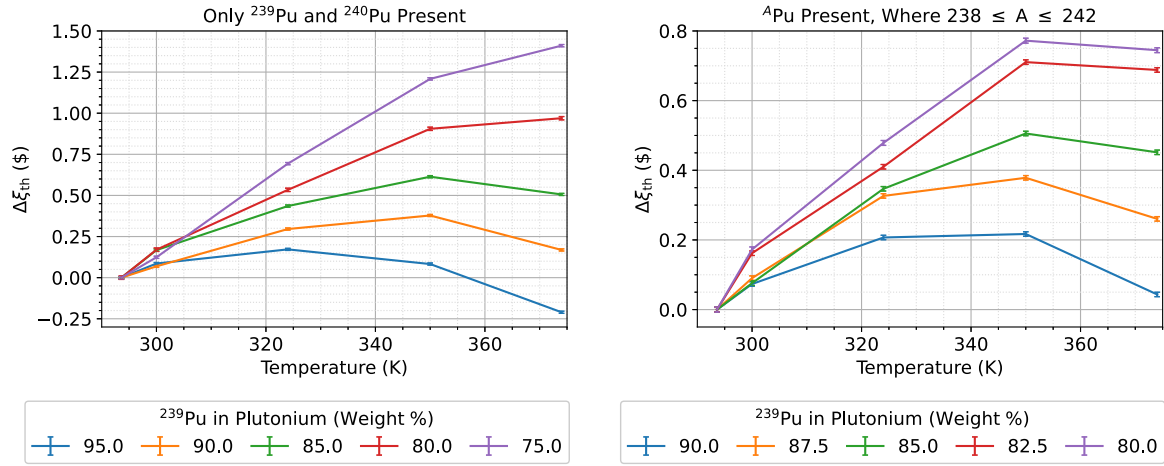


Fig. 6. Thermal reactivity feedbacks for a range of plutonium isotopic compositions. The inner and outer radii are 8.0 and 48.0 cm respectively. The plutonium and excess acid concentrations are 15.0 g L⁻¹ and 1.0 mol L⁻¹ respectively. In the right-hand graphs, the isotopic compositions of Table A.18 are used.

mol L⁻¹ and $c_{\text{Pu}} = 14.0$ g L⁻¹, increasing the temperature from 293.6 K to 374.0 K will result in a reactivity increase of 1.25 \$. When the plutonium concentration is increased to 20.0 g L⁻¹, the same increase in temperature will result in a reactivity decrease of ~ 0.6 \$.

Increasing both plutonium and nitric acid concentrations reduces the relative concentration of water molecules in the system, thus reducing the amount of neutron moderation. As above, the shift in the neutron energy spectrum past the ≈ 0.3 eV resonance reduces the positive temperature effect.

2.3.3. The effect of plutonium isotopic composition

In Fig. 6, it can be seen that decreasing the isotopic abundance of ²³⁹Pu will increase the thermal reactivity feedback of a plutonium nitrate solution.

For solutions with plutonium comprising a relatively large amount of ²³⁹Pu, Fig. 6 shows that a positive thermal reactivity feedback can be observed up to a temperature limit. This temperature limit decreases with increasing ²³⁹Pu isotopic abundance. Once this limit has been exceeded, the positive thermal reactivity feedback starts decreases, and in some cases turns negative.

Decreasing the isotopic abundance of ²³⁹Pu will decrease the reactivity of the plutonium-containing system. As the probability of fission decreases, whilst the probability of other interactions remain the same, there is a relative increase in neutron moderation. As a higher proportion of neutrons become thermalised, the neutron energy spectrum shifts into the range of the ≈ 0.3 eV resonance, thus increasing the positive temperature effect.

3. Transient model phenomenology

3.1. Point kinetics

The overall transient behaviour of a fissile system can be determined using the point kinetics equations (Lewins, 1978), the derivations of which are well-documented (Duderstadt and Hamilton, 1976; Stacey, 2007). Eqs. (1) and (2) describe the change in power, P , and the change in power associated with delayed neutron precursor population, $P_{C,i}$, in a three-layered fissile liquid system over time, t :

$$\frac{dP(t)}{dt} = \frac{\beta_{\text{eff}} P(t)(\xi(t) - 1)}{\Lambda(t)} + \sum_{i=1}^6 \lambda_i P_{C,i}(t) + \frac{S(t)\epsilon}{\Lambda(t)\bar{v}}, \quad (1)$$

$$\frac{dP_{C,i}(t)}{dt} = -\lambda_i P_{C,i}(t) + \frac{\beta_i}{\Lambda(t)} P(t). \quad (2)$$

Here, i represents the precursor group, such that β_i and λ_i refer to the delayed neutron fraction and decay constant for neutrons in precursor

group i ; β_{eff} is the total delayed neutron fraction. S , ϵ and $\bar{v}$ are the total intrinsic neutron source in the system, the average energy released per fission event (3.318×10^{-11} J fission⁻¹ for ²³⁹Pu (Sher and Beck, 1981)), and the average number of neutrons produced per fission.

The mean neutron generation time, Λ , and reactivity, ξ , will vary depending on solution properties such as plutonium and excess acid concentration, mass, temperature and void fraction. In the presented research, they will be calculated using

$$\begin{aligned} \Lambda(t) &= \Lambda_{\text{init}}(c_{\text{Pu}}, c_{\text{HNO}_3}, M) + \Delta\Lambda_{\text{th}}(c_{\text{Pu}}, c_{\text{HNO}_3}, M, \bar{T}) \\ &\quad + \Delta\Lambda_{\text{rg}}(c_{\text{Pu}}, c_{\text{HNO}_3}, M, \bar{\theta}) \end{aligned} \quad (3)$$

and

$$\begin{aligned} \xi(T) &= \xi_{\text{init}}(c_{\text{Pu}}, c_{\text{HNO}_3}, M) + \Delta\xi_{\text{ext}}(t) + \Delta\xi_{\text{th}}(c_{\text{Pu}}, c_{\text{HNO}_3}, M, \bar{T}) \\ &\quad + \Delta\xi_{\text{rg}}(c_{\text{Pu}}, c_{\text{HNO}_3}, M, \bar{\theta}) \end{aligned} \quad (4)$$

where c_{Pu} (in g L⁻¹) and c_{HNO_3} (in mol L⁻¹) are the concentrations of plutonium and excess acid in the system, respectively, $\bar{T}(t)$ and $\bar{\theta}(t)$ are the average temperature and void fraction in the system, and $M(t)$ is the mass of the solution. As such, Λ_{init} and ξ_{init} are the generation time and reactivity for a system at 293.6 K with no voids; $\Delta\Lambda_{\text{th}}$ and $\Delta\xi_{\text{th}}$ are the changes in generation time and reactivity due to a change in temperature; and $\Delta\Lambda_{\text{rg}}$ and $\Delta\xi_{\text{rg}}$ are the changes in generation time and reactivity due to a change in void fraction. $\Delta\xi_{\text{ext}}(t)$ is the user-prescribed external reactivity insertion, due to the removal or insertion of control material into the centre of the system.

The energy produced during the transient can be calculated using

$$\frac{dE(t)}{dt} = P(t) \quad (5)$$

3.1.1. Intrinsic neutron source

Intrinsic neutron sources include spontaneous fissions (SFs), (α, n) reactions, (γ, n) reactions and cosmic ray spallation (Rossi, 1933). In a fissile system, distributed intrinsic source(s) are often present (Radkowsky, 1964), with SF and (α, n) reactions often dominating in nuclear criticality excursion problems such that the (γ, n) reactions and cosmic ray spallation can be neglected.

For systems containing plutonium, the relative neutron source density generated from SF and (α, n) reactions will depend upon the relative concentration of the system's plutonium isotopes (Dolan et al., 2014) (e.g. ²⁴⁰Pu has a high SF rate compared to other isotopes of plutonium Marcat et al., 2016). For fissile liquid systems, the intrinsic neutron source strength will depend on the concentration and acidity of the solution (Kudryavtsev et al., 2020; Swinhoe, 2011).

When determining the neutron source in a system domain then the spatial, energy, angular and temporal variations of the neutron

source must be adequately accounted for using an appropriate adjoint weighting (Spriggs et al., 1999).

Deterministic code SOURCES-4C is currently the standard when calculating SF and (α, n) neutron source rates and spectra in homogeneous media (Griesheimer et al., 2017; Wilson et al., 2002), and will be used in the presented research.

The calculation of the intrinsic neutron sources in aqueous solutions of plutonium nitrate using SOURCES-4C is detailed in Section 7.5.

3.1.2. Initial conditions

Prescribed initial conditions are often derived by assuming the (initially subcritical) system is in a steady state prior to the nuclear criticality excursion (Kerlin and Upadhyaya, 2019; Lewis, 1977):

$$P(0) = -\frac{S(0)\epsilon}{\xi(0)\beta_{\text{eff}}\bar{v}}, \quad (6)$$

$$P_{C,i}(0) = \frac{\beta_i P(0)}{\lambda_i \Lambda(0)}. \quad (7)$$

3.1.3. Axial power distribution

The effect of a non-uniform axial power distribution on the solution's thermal energy, E_{th} , can be modelled using

$$\left[\frac{\partial E'_{\text{th}}(t, z)}{\partial t} \right]_{\text{fiss}} = P(t) \hat{\phi}(t, z), \quad (8)$$

where E'_{th} is the thermal energy of the solution per unit height, and $\hat{\phi}(t, z)$ is a shape function describing the axial variation in scalar neutron flux:

$$\hat{\phi}(t, z) = \frac{\phi(t, z)}{\int_0^H dz \phi(t, z)} (1.0 - \theta(t, z)) \quad (9)$$

where $\phi(t, z)$ is calculated using Eq. (132), θ is the local void fraction and H is the solution height.

3.2. Addition of fuel to the solution

In the presented research, it will be assumed that any solution added to, or removed from, the system will be distributed across the domain such that

$$\frac{\partial M_{\text{in}}(t, z)}{\partial t} = \dot{M}_{\text{in}}(t) \frac{M(t, z)}{\frac{1}{H} \int_0^H dz M(t, z)}, \quad (10)$$

$$\frac{\partial M_{\text{out}}(t, z)}{\partial t} = \dot{M}_{\text{out}}(t) \frac{M(t, z)}{\frac{1}{H} \int_0^H dz M(t, z)}, \quad (11)$$

and

$$\frac{\partial M(t, z)}{\partial t} = \frac{\partial M_{\text{in}}(t, z)}{\partial t} - \frac{\partial M_{\text{out}}(t, z)}{\partial t} \quad (12)$$

where $M(t, z)$ is the mass of fuel solution at location z and time t , $\dot{M}(t)$ represents the total mass flow rate in a given direction, subscripts 'in' and 'out' refer to the direction (either into or out of the vessel), and H is the height of the fuel solution.

Mass flow rates will effect the thermal energy of the solution, such that

$$\left[\frac{\partial E'_{\text{th}}(t, z)}{\partial t} \right]_{\text{mass}} = \frac{\partial}{\partial z} \left[C_p(t, z) T_{\text{ext}} \frac{\partial M_{\text{in}}(t, z)}{\partial t} - C_p(t, z) T(t, z) \frac{\partial M_{\text{out}}(t, z)}{\partial t} \right] \quad (13)$$

where C_p is the solution's specific heat capacity, T_{ext} is the temperature of any solution being added to the vessel and T is the temperature of the solution already existing in the vessel.

Any fuel solution draining from the vessel will contain entrained dissolved and gaseous radiolysis products. This phenomenon will be accounted for by using

$$\left[\frac{\partial N'_x(t, z)}{\partial t} \right]_{\text{mass}} = -\frac{\partial}{\partial z} \left[\frac{C_x(t, z)}{\rho(t, z)} \frac{\partial M_{\text{out}}(t, z)}{\partial t} \right] \quad (14)$$

where N'_x represents the number of moles of any of the dissolved or gaseous radiolysis products, or the bubble population, per unit height (described further in Section 3.4); C_x represents the corresponding concentration of that variable; ρ is the fuel solution density.

3.3. Convective heat transfer

The variation in thermal energy of the solution due to heat transfer between the solution and the vessel wall can be described by

$$\left[\frac{\partial E'_{\text{th}}(t, z)}{\partial t} \right]_{\text{conv}} = -\frac{\partial}{\partial z} \left[(T(t, z) - T_{\text{vess}}(t, z)) h_{\text{int}}(t, z) A_{\text{int}}(t, z) \right], \quad (15)$$

with the change in thermal energy of the vessel wall given by

$$\frac{\partial E'_{\text{vess}}(t, z)}{\partial t} = \frac{\partial}{\partial z} \left[(T(t, z) - T_{\text{vess}}(t, z)) h_{\text{int}}(t, z) A_{\text{int}}(t, z) - (T_{\text{vess}}(t, z) - T_{\text{ext}}) h_{\text{ext}} A_{\text{ext}}(t, z) \right]. \quad (16)$$

In these equations, E'_{vess} is the thermal energy of the vessel per unit height and T_{vess} is the temperature of the vessel. h_{int} and h_{ext} are the heat transfer coefficients between the vessel and solution, and between the vessel and reflector pool, respectively, and A_{int} and A_{ext} are the corresponding surface areas available for heat transfer.

3.4. Radiolysis and gas formation

3.4.1. Radiolysis

Radiolysis is the dissociation of molecules induced by ionising radiation. In aqueous fissile systems, radiolysis of water molecules is caused by charged fission fragments (a type of ionising radiation).

The passage of heavy fission fragments through aqueous solutions is conducive to high yields of molecular radiolysis products (Lane et al., 1958), such that the radiolysis reaction for water can be described by:



i.e. the production of free radicals is negligible (Allen, 1961; Lane et al., 1958; Winter et al., 2022).

When considering solutions of nitric acid, experiments and reviews by Sheppard (1968) show that the generation of N_2 from the radiolysis of nitric acid contributes, at most, 10% to the total amount of radiolytic gas produced, and thus will not be considered in the presented research. Though the mechanism of nitric acid radiolysis is not agreed upon, details of theorised reactions, and more general discussions of the radiation chemistry of plutonium nitrate solutions are discussed by Kubic and Jackson (2012) and Miner and Seed (1967).

The number of molecules of radiolytic gas formed per 100 eV of energy absorbed is known as the G value (Baird et al., 1990). The amount of hydrogen produced per 100 eV of deposited fission energy, $\tilde{G}_{\text{H}_2}$, can be converted to SI units using Eq. (18):

$$G_{\text{H}_2} = \frac{1}{1.602 \times 10^{-17}} \frac{\tilde{G}_{\text{H}_2}}{N_A} \quad (18)$$

where G_{H_2} is the hydrogen gas generation coefficient in mol J^{-1} and N_A is the Avogadro constant.

As per Eq. (17), radiolysis produces hydrogen and hydrogen peroxide in equal quantities, such that $G_{\text{H}_2} = G_{\text{H}_2\text{O}_2}$.

Hydrogen peroxide decomposes into water and oxygen, per the equation



which occurs at a rate k_d (in units s^{-1}). For aqueous solutions of uranyl nitrate, Cooling (2014) fitted experimental data from Lane et al. (1958) to the following equation:

$$k_d(t, z) = 1.578 \times 10^{-20} e^{(0.1066T(t, z))}. \quad (20)$$

As similar experimental data for solutions of plutonium nitrate are not available in the literature, this equation will be used in the presented research to determine the decomposition rate of hydrogen peroxide. As such, there is some uncertainty in the results of the model. However, for dilute uranium concentrations ($\leq 0.65 \text{ mol L}^{-1}$), Lane et al. (1958) notes that k_d is independent of uranium concentration. Thus, as the presented research primarily concerns dilute plutonium solutions, the effect on the overall (or more general) behaviour of simulated transients is expected to be minimal.

Accounting for the decomposition of hydrogen peroxide, the rate of production of dissolved gas species can be described by:

$$\left[\frac{\partial N'_{\text{H}_2(\text{aq})}}{\partial t} \right]_{\text{prod}} = \left[\frac{\partial N'_{\text{H}_2\text{O}_2(\text{aq})}}{\partial t} \right]_{\text{prod}} = P(t)\hat{\phi}(t, z)G_{\text{H}_2}, \quad (21)$$

$$2 \left[\frac{\partial N'_{\text{O}_2(\text{aq})}}{\partial t} \right]_{\text{prod}} = - \left[\frac{\partial N'_{\text{H}_2\text{O}_2(\text{aq})}}{\partial t} \right]_{\text{decomp}} = k_d(z, t)N'_{\text{H}_2\text{O}_2(\text{aq})}(z, t), \quad (22)$$

where $N'_{x(\text{aq})}$ denotes the number of moles of species x dissolved in the solution per unit height.

3.4.2. Mass transfer

In aqueous solutions, the equilibrium concentration of a species i , $C_{i,\text{eq}}$, is the concentration of that species in the aqueous phase which is in equilibrium with the partial pressure of that species in the gaseous phase (Barbry et al.; Winter et al., 2022):

$$C_{i,\text{eq}}(t, z) = \left(p + \frac{2\sigma(t, z)}{r_b(t, z)} \right) H_{i,\text{sol}}(t, z)y_i(t, z), \quad (23)$$

where p is the hydrostatic pressure, σ is the solution surface tension, $H_{i,\text{sol}}$ is the Henry's law constant for species i (calculated using the methodology of Winter et al. (2022)), and y_i is the yield fraction of species i . The term $(p + \frac{2\sigma(t, z)}{r_b(t, z)})$ represents the pressure inside a bubble with radius r_b (Spiegler et al., 1962).

When this equilibrium concentration is exceeded, molecules will be transferred from the aqueous phase to the gaseous phase. As bubbles grow in size, their pressure tends towards ambient pressure and the concentration of dissolved gas tends towards the concentration in equilibrium with the bubble pressure (Winter et al., 2022).

As such, the rate of mass transfer between the dissolved and gaseous phases can be expressed as

$$\left[\frac{\partial N'_{\text{H}_2(\text{g})}(t, z)}{\partial t} \right]_{\text{trans}} = - \left[\frac{\partial N'_{\text{H}_2(\text{aq})}(t, z)}{\partial t} \right]_{\text{trans}} = \alpha_c(t, z)(N'_{\text{H}_2(\text{aq})}(t, z) - C_{\text{H}_2,\text{eq}}(t, z)A(t, z)) \quad (24)$$

$$\left[\frac{\partial N'_{\text{O}_2(\text{g})}(t, z)}{\partial t} \right]_{\text{trans}} = - \left[\frac{\partial N'_{\text{O}_2(\text{aq})}(t, z)}{\partial t} \right]_{\text{trans}} = \alpha_c(t, z)(N'_{\text{O}_2(\text{aq})}(t, z) - C_{\text{O}_2,\text{eq}}(t, z)A(t, z)) \quad (25)$$

where A is the cross sectional area of the vessel and α_c is the rate constant, which will be calculated using (Winter et al., 2022)

$$\alpha_c(t, z) = 1.9436 \times 10^{-10} C_b(t, z)^{0.78926} \left(\frac{D_{\text{mix}}(t)}{D_{\text{H}_2}(t, z)} \right)^{1/2} \quad (26)$$

where $C_b(t, z) = N_b(t, z)/V(t, z)$ is the number of bubbles per unit volume of fuel solution, D_{mix} is the solution mixing coefficient, described in Section 3.6, and D_{H_2} is the diffusivity of aqueous hydrogen, which can be calculated using (Winter et al., 2022; Yaws, 2009):

$$-\log_{10}(D_{\text{H}_2}(t, z)) = 5.46551 + \frac{842.59}{T(t, z)}. \quad (27)$$

3.4.3. Bubble population: Stable bubble formation

The critical concentration, defined with respect to the properties of newly formed bubbles (with radius r_{nuc}), occurs when the net flow of all species of gas between the dissolved and gaseous phases is zero (Winter

et al., 2022). As fission track bubbles consist of mostly hydrogen gas, and assuming that the presence of aqueous H_2O_2 can be neglected, Eq. (28) can be used to determine the critical concentration in aqueous fissile solutions (Winter et al., 2022):

$$C_{\text{crit}}(t, z) = \left(p + \frac{2\sigma(t, z)}{r_{\text{nuc}}(t, z)} \right) H_{\text{H}_2,\text{sol}}(t, z) - C_{\text{O}_2(\text{aq})}(t, z). \quad (28)$$

As shown in Eq. (28), the capacity of a solution to contain dissolved gas, up to a critical concentration, is dictated by Henry's law. If the concentration of dissolved gas is lower than the critical concentration, gas bubbles will tend to shrink and dissolve into the solution. However, if the critical concentration is met, gas bubbles will form.

Previous work by Winter et al. (2022) demonstrated that the rate of stable bubble formation in solutions of uranyl nitrate can be calculated using

$$\left[\frac{\partial N'_b(t, z)}{\partial t} \right]_{\text{stab}} = \alpha k_f \left[V(t, z)^{(1-\alpha)} E_{\text{sat}}(t, z)^{(\alpha-1)} P(t)\hat{\phi}(t, z) \right], \quad (29)$$

where E_{sat} is the amount of energy deposited in excess of the energy required to saturate the solution. As such, Eq. (29) will only be applicable when $C_{\text{H}_2(\text{aq})} \geq C_{\text{crit}}(t, z)$, and

$$\frac{\partial E'_{\text{sat}}(t, z)}{\partial t} = P(t)\hat{\phi}(t, z) \quad \text{when } C_{\text{H}_2(\text{aq})} \geq C_{\text{crit}}(t, z), \quad (30)$$

$$\frac{\partial E'_{\text{sat}}(t, z)}{\partial t} = 0 \quad \text{otherwise.} \quad (31)$$

In the above, α and k_f are empirically determined constants, which Winter et al. (2022) determined to be equal to 2.5 and $0.05 \text{ m}^{4.5} \text{ J}^{-2.5}$ respectively.

Once again, as there is limited data available for plutonium nitrate systems, the approach detailed here is assumed to be applicable for solutions of plutonium nitrate. Whilst this assumption introduces additional uncertainty in the results of the model, it is unlikely to have a noticeable effect on the overall behaviour of simulated transients.

3.4.4. Bubble population: Bubble collapse due to diffusion

As described by Winter (2019), the equilibrium concentration of stable bubbles can be calculated using

$$C_{b,\text{eq}}(t, z) = k_{\text{bub}} \left(\frac{P(t)\hat{\phi}(t, z)}{A(t, z)} \right)^{3/2}, \quad (32)$$

where k_{bub} is a constant of proportionality, which will be taken to be equal to $1.58 \times 10^{15} \text{ W}^{-3/2} \text{ m}^{3/2}$, based on the work of Winter (2019).

Due to the diffusion of dissolved gas towards larger expanding bubbles, if the stable bubble number density exceeds the equilibrium number density then smaller bubbles will start to collapse.

By defining the average bubble separation, s , as

$$s(t, z) = \left(\frac{A(t, z)}{N'_b(t, z)} \right)^{1/3}, \quad (33)$$

the rate of bubble collapse can be expressed as

$$\left[\frac{\partial N'_b(t, z)}{\partial t} \right]_{\text{coll}} = \frac{k_{\text{coll}}}{s(t, z)^2} \left[N'_b(t, z) - C_{b,\text{eq}}(t, z)A(t, z) \right] \quad (34)$$

where k_{coll} is the bubble collapse time constant, equal to $5.27 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Winter, 2019). Eq. (34) will only be applicable when $N'_b > C_{b,\text{eq}}(t, z)A(t, z)$.

3.5. Gas bubble advection

Due to their low density, buoyancy will advect bubbles in the fuel solution upwards. The shape of small bubbles ($r_b(t, z) < 10^{-5} \text{ m}$) can be assumed to be spherical (Celata et al., 2007; Cooling, 2014). As such, Stoke's law can be used to calculate the terminal velocity of the bubble:

$$v_b(t, z) = \frac{2(\rho(t, z) - \rho_b(t, z))g}{9\mu(t, z)} \quad (35)$$

where g is the acceleration due to gravity, μ is the solution's dynamic viscosity, and ρ_b is the density of the bubble, which can be calculated using

$$\rho_b(t, z) = \frac{M_{H_2}}{RT(t, z)} \left(p + \frac{2\sigma(t, z)}{r_b(t, z)} \right). \quad (36)$$

where M_{H_2} is the molar mass of hydrogen and R is the universal gas constant (equal to $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

As bubbles increase in size, they begin to deform, which effects the drag force experienced by the bubble. Celata et al. (2007) notes that the coefficient of drag, C_D , acting on a bubble can be described by the following correlation:

$$C_D(t, z) = \max \left(\frac{24(1 + 0.15 Re_b^{0.687}(t, z))}{Re_b(t, z)}, \frac{8}{3} \frac{E_0(t, z)}{E_0(t, z) + 4} \right), \quad (37)$$

where Re and E_0 are the Reynolds number and Eötvös number, defined as

$$Re_b(t, z) = \frac{2\rho(t, z)v_b(t, z)r_b(t, z)}{\mu(t, z)} \quad (38)$$

and

$$E_0(t, z) = \frac{4gr_b^2(t, z)(\rho(t, z) - \rho_b(t, z))}{\sigma(t, z)}. \quad (39)$$

The terminal velocity of larger bubbles ($r_b(t, z) \geq 10^{-5} \text{ m}$) can then be obtained by equating the drag and buoyancy forces and rearranging to give

$$v_b(t, z) = \left(\frac{8r_b(t, z)g}{3C_D(t, z)} \right)^{0.5}, \quad (40)$$

which can be solved iteratively (Celata et al., 2007; Winter et al., 2022).

The effect of bubble advection on bubble distribution within the solution can be described using

$$\left[\frac{\partial X'(t, z)}{\partial t} \right]_{\text{adv}} = -v_b(t, z) \frac{\partial X'(t, z)}{\partial z} \quad (41)$$

where X' can be either $N'_{H_2(g)}$, $N'_{O_2(g)}$, or N'_b .

3.6. Fuel solution mixing

In aqueous solutions of plutonium nitrate, turbulent mixing will occur if solution is added or removed from the system. Due to the r, z distribution of the power profile, non-uniform heating of the solution will induce buoyancy-driven flow, which will contribute to turbulence alongside the production and advection of radiolytic gas bubbles. As such, the rate of turbulent mixing will be a function of r, z , and t .

Cooling (2014) developed a simplified method to account for turbulent mixing in aqueous homogeneous reactors by describing turbulence as a Fickian diffusive process. The rate of mixing in a fuel solution is characterised by a mixing coefficient, D_{mix} :

$$D_{\text{mix}}(t) = \frac{U_{\text{eddy}}(t)r_{\text{eddy}}(t)}{\pi}, \quad (42)$$

where U_{eddy} and r_{eddy} are the velocity and radius, respectively, of the largest eddies predicted to be in the system (Cooling, 2014).

As such, turbulent mixing is accounted for by using

$$\left[\frac{\partial X'(t, z)}{\partial t} \right]_{\text{mix}} = \nabla \cdot [D_{\text{mix}}(t, z) \nabla X'(t, z)]. \quad (43)$$

Mixing of the solution will affect its thermal energy and the local concentrations of radiolysis products. As such, X' can be either E'_{th} , $N'_{H_2(g)}$, $N'_{O_2(g)}$, $N'_{H_2(aq)}$, $N'_{O_2(aq)}$, $N'_{H_2O_2(aq)}$ or N'_b .

3.7. Complete principal governing differential equations

In this section, a summary of the ODEs and PDEs solved by the proposed model are presented. The solution uses a Lagrangian finite volume method to axially discretise the system, and the time discretisation algorithm described by Shampine and Gordon (1975).

3.7.1. Point kinetics equations

$$\frac{dP(t)}{dt} = \frac{\beta_{\text{eff}} P(t)(\xi(t) - 1)}{\Lambda(t)} + \sum_{i=1}^6 \lambda_i P_{C,i}(t) + \frac{S(t)\epsilon}{\Lambda(t)\bar{v}}, \quad (44)$$

$$\frac{dP_{C,i}(t)}{dt} = -\lambda_i P_{C,i}(t) + \frac{\beta_i}{\Lambda(t)} P(t). \quad (45)$$

$$\frac{dE(t)}{dt} = P(t) \quad (46)$$

3.7.2. Mass flow rate

$$\frac{\partial M_{\text{in}}(t, z)}{\partial t} = \dot{M}_{\text{in}}(t) \frac{M(t, z)}{\frac{1}{H} \int_0^H dz M(t, z)}, \quad (47)$$

$$\frac{\partial M_{\text{out}}(t, z)}{\partial t} = \dot{M}_{\text{out}}(t) \frac{M(t, z)}{\frac{1}{H} \int_0^H dz M(t, z)}, \quad (48)$$

$$\frac{\partial M(t, z)}{\partial t} = \frac{\partial M_{\text{in}}(t, z)}{\partial t} - \frac{\partial M_{\text{out}}(t, z)}{\partial t} \quad (49)$$

3.7.3. Thermal hydraulics

$$\begin{aligned} \frac{\partial E'_{\text{th}}(t, z)}{\partial t} &= P(t)\hat{\phi}(t, z) + \frac{\partial}{\partial z} \left[C_p(t, z) T_{\text{ext}} \frac{\partial M_{\text{in}}(t, z)}{\partial t} \right. \\ &\quad \left. - C_p(t, z) T(t, z) \frac{\partial M_{\text{out}}(t, z)}{\partial t} - \right. \\ &\quad \left. (T(t, z) - T_{\text{vess}}(t, z)) h_{\text{int}}(t, z) A_{\text{int}}(t, z) + D_{\text{mix}}(t, z) \frac{\partial E'_{\text{th}}(t, z)}{\partial z} \right] \end{aligned} \quad (50)$$

$$\begin{aligned} \frac{\partial E_{\text{vess}}(t, z)}{\partial t} &= (T(t, z) - T_{\text{vess}}(t, z)) h_{\text{int}}(t, z) A_{\text{int}}(t, z) \\ &\quad - (T_{\text{vess}}(t, z) - T_{\text{ext}}) h_{\text{ext}} A_{\text{ext}}(t, z) \end{aligned} \quad (51)$$

3.7.4. Radiolytic gas

For $j = H_2, O_2$:

$$\begin{aligned} \frac{\partial N'_{j(g)}(t, z)}{\partial t} &= \alpha_c(t, z) (N'_{j(aq)}(t, z) - C_{j,eq}(t, z) A(t, z)) - v_b(t, z) \frac{\partial N'_{j(g)}(t, z)}{\partial z} \\ &\quad + \frac{\partial}{\partial z} \left[D_{\text{mix}}(t, z) \frac{\partial N'_{j(g)}(t, z)}{\partial z} - \frac{C_{j(g)}(t, z)}{\rho(t, z)} \frac{\partial M_{\text{out}}(t, z)}{\partial t} \right] \end{aligned} \quad (52)$$

$$\begin{aligned} \frac{\partial N'_{H_2(aq)}(t, z)}{\partial t} &= G_{H_2} P(t) \hat{\phi}(t, z) - \alpha_c(t, z) \\ &\quad \times (N'_{H_2(aq)}(t, z) - C_{H_2,eq}(t, z) A(t, z)) \\ &\quad + \frac{\partial}{\partial z} \left[D_{\text{mix}}(t, z) \frac{\partial N'_{H_2(aq)}(t, z)}{\partial z} - \frac{C_{H_2(aq)}(t, z)}{\rho(t, z)} \frac{\partial M_{\text{out}}(t, z)}{\partial t} \right] \end{aligned} \quad (53)$$

$$\begin{aligned} \frac{\partial N'_{H_2O_2(aq)}(t, z)}{\partial t} &= G_{H_2} P(t) \hat{\phi}(t, z) - k_d(t, z) N'_{H_2O_2(aq)} \\ &\quad + \frac{\partial}{\partial z} \left[D_{\text{mix}}(t, z) \frac{\partial N'_{H_2O_2(aq)}(t, z)}{\partial z} - \frac{C_{H_2O_2(aq)}(t, z)}{\rho(t, z)} \frac{\partial M_{\text{out}}(t, z)}{\partial t} \right] \end{aligned} \quad (54)$$

$$\begin{aligned} \frac{\partial N'_{O_2(aq)}(t, z)}{\partial t} &= \frac{1}{2} k_d(t, z) \\ &\quad \times N'_{H_2O_2(aq)}(t, z) - \alpha_c(t, z) (N'_{O_2(aq)}(t, z) - C_{O_2,eq}(t, z) A(t, z)) \\ &\quad + \frac{\partial}{\partial z} \left[D_{\text{mix}}(t, z) \frac{\partial N'_{O_2(aq)}(t, z)}{\partial z} - \frac{C_{O_2(aq)}(t, z)}{\rho(t, z)} \frac{\partial M_{\text{out}}(t, z)}{\partial t} \right] \end{aligned} \quad (55)$$

$$\begin{aligned} \frac{\partial N'_b(t, z)}{\partial t} &= \delta_a \alpha k_f [V^{(1-\alpha)}(t, z) E_{\text{sat}}^{(\alpha-1)}(t, z) P(t) \hat{\phi}(t, z)] \\ &\quad - \delta_b \frac{k_{\text{coll}}}{s(t, z)^2} [N'_b(t, z) - N'_{b,eq}(t, z)] \end{aligned}$$

$$-v_b(t, z) \frac{\partial N'_b(t, z)}{\partial z} + \frac{\partial}{\partial z} \left[D_{\text{mix}}(t, z) \frac{\partial N'_b(t, z)}{\partial z} - \frac{C_b(t, z)}{\rho(t, z)} \frac{\partial M_{\text{out}}(t, z)}{\partial t} \right] \quad (56)$$

where $\alpha = 2.5$, $k_f = 0.05 \text{ m}^{4.5} \text{ J}^{-2.5}$, $k_{\text{coll}} = 5.27 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$,

$$\delta_a = \begin{cases} 1 & \text{when } C_{\text{H}_2(\text{aq})}(t, z) \geq C_{\text{crit}}(t, z), \\ 0 & \text{otherwise.} \end{cases} \quad (57)$$

and

$$\delta_b = \begin{cases} 1 & \text{when } N'_b(t, z) > k_{\text{bub}} A(t, z)^{-1/2} (P(t) \hat{\phi}(t, z))^{3/2} \\ 0 & \text{otherwise.} \end{cases} \quad (58)$$

$$\frac{\partial E_{\text{sat}}(t, z)}{\partial t} = \begin{cases} P(t) \hat{\phi}(t, z) & \text{when } C_{\text{H}_2(\text{aq})}(t, z) \geq C_{\text{crit}}(t, z) \\ 0 & \text{otherwise.} \end{cases} \quad (59)$$

3.8. Boundary conditions

As no radiolysis products can be transferred between the solution and the vessel, the following boundary conditions can be applied at the base of the vessel:

$$U_b(t, 0) N'_b(t, 0) = D_{\text{mix}}(t, 0) \frac{\partial N'_b(t, 0)}{\partial z}, \quad (60)$$

$$U_b(t, 0) N'_{j(\text{g})}(t, 0) = D_{\text{mix}}(t, 0) \frac{\partial N'_{j(\text{g})}(t, 0)}{\partial z}, \quad (61)$$

$$\frac{\partial N'_{k(\text{aq})}(t, 0)}{\partial z} = 0. \quad (62)$$

where $j = \text{O}_2$ or H_2 , and $k = \text{O}_2$, H_2 or H_2O_2 . At the top of the vessel,

$$\frac{\partial N'_j(t, H)}{\partial z} = 0 \quad (63)$$

where N'_j refers to any of the molar quantities of aqueous or gaseous radiolysis product species, or the number of bubbles, per unit height.

The following equations account for heat transfer between the solution and vessel base ($z = 0$) and between the solution and plenum gas ($z = H$):

$$D_{\text{mix}}(t, 0) \frac{\partial E'_{\text{therm}}(t, 0)}{\partial z} = (T_{\text{vess}}(t, 0) - T(t, 0)) h_{\text{int}}(t, 0) A_{\text{int}}(t, 0) \quad (64)$$

$$D_{\text{mix}}(t, H) \frac{\partial E'_{\text{therm}}(t, H)}{\partial z} = (T_{\text{ext}} - T(t, H)) h_{\text{sur}} A_{\text{sur}} \quad (65)$$

Here, $A_{\text{ext}}(t, 0) \approx A_{\text{int}}(t, 0) = \pi r_{\text{eq}}^2(t, 0)$ is the surface area of the base of the vessel. Thus:

$$\begin{aligned} \frac{\partial E_{\text{vess}}(t, 0)}{\partial t} &= (T(t, 0) - T_{\text{vess}}(t, 0)) h_{\text{int}}(t, 0) A_{\text{int}}(t, 0) \\ &\quad - (T_{\text{vess}}(t, 0) - T_{\text{ext}}) h_{\text{ext}} A_{\text{ext}}(t, 0) \end{aligned} \quad (66)$$

3.9. Initial conditions

The following equations describe the initial conditions of the fissile liquid system. It has been assumed that the system begins in thermodynamic equilibrium: a constant temperature of $T_{\text{ext}} = 293.6 \text{ K}$ is applied throughout the system. The initial mass of solution is prescribed and it is assumed that no radiolytic gas is present at the start of the transient.

$$P(0) = \frac{S(0)\epsilon}{\xi(0)\beta_{\text{eff}}V} \quad (67)$$

$$P_{C,i}(0) = \frac{\beta_i P(0)}{\lambda_{i,A}(0)} \quad (68)$$

$$E(0) = F(0) = 0 \quad (69)$$

$$E'_{\text{th}}(0, z) = \rho(0, z) C_p(0, z) T_{\text{ext}} A(0, z) \quad (70)$$

$$E'_{\text{vess}}(0, z) = \rho_{\text{vess}} C_{p,\text{vess}}(0, z) T_{\text{ext}} A_{\text{vess}}(0, z) \quad (71)$$

$$N'_l(0, z) = 0. \quad (72)$$

Again, N'_l refers to any of the molar quantities of aqueous or gaseous radiolysis product species, or the number of bubbles, per unit height.

3.10. Spatial and temporal discretisation and software workflow

Fig. 7 describes the proposed workflow of the numerical algorithm and model. Inputs to the algorithm include solution intrinsic and thermophysical properties (such as plutonium concentration and various HTCs); system properties such as reactivity and mass insertions; and t_{end} , the simulation end time, and a user-specified time step, from which the array of times ($t_1, \dots, t_i, \dots, t_I$) are calculated.

4. Thermophysical properties of aqueous plutonium nitrate

4.1. Density

To determine the density, of aqueous plutonium nitrate, the correlation proposed by Sakurai and Tachimori (1996) will be used, which describes density as a function of solution temperature and concentrations of tetravalent plutonium, hexavalent uranium, and nitric acid. To ensure closest agreement with the density of water between 20 and 100 °C, a factor of 1.009 will be applied. Accounting for this factor, and omitting terms containing uranyl nitrate, Eq. (73) is obtained:

$$\begin{aligned} \rho &= 1.0017 \times 10^3 + 1.7286 c_{\text{Pu}} + 3.9390 \times 10^1 c_{\text{HNO}_3} - 9.8317 \times 10^{-5} c_{\text{Pu}}^2 \\ &\quad - 7.4272 \times 10^{-1} c_{\text{HNO}_3}^2 \\ &\quad - 5.5979 \times 10^{-3} T^2 - 4.9199 \times 10^{-2} c_{\text{Pu}} c_{\text{HNO}_3} - 1.4398 \times 10^{-3} c_{\text{Pu}} T \\ &\quad - 8.5704 \times 10^{-2} c_{\text{HNO}_3} T, \end{aligned} \quad (73)$$

which will be used to describe the solution density, ρ , in kg m^{-3} , where T is the temperature in °C, c_{Pu} is the plutonium concentration in g L^{-1} and c_{HNO_3} is the concentration of nitric acid in mol L^{-1} .

Research by Kumar and Koganti (1997) built upon the work of Sakurai and Tachimori (1996) by increasing the inter-dependencies between solution temperature and the concentrations of uranium, plutonium and nitric acids. However, for the aqueous solutions presented in this paper, the residual error from the Equations of both Kumar and Koganti (1997) and Sakurai and Tachimori (1996) are similar in value. Thus the employment of the simpler equation of Sakurai and Tachimori (1996).

4.2. Dynamic viscosity

Eq. (74) can be used to calculate the viscosity, μ_{aq} , of aqueous solutions:

$$\mu_{\text{aq}} = \mu_{\text{w}}^{m_{\text{w}}} \prod_{n=1}^N \mu_n^{m_n}, \quad (74)$$

where subscript 'w' represents water, m_n is the mass fraction of solute n , and N is the number of solutes in the solution (Laliberté, 2009). In addition, Eqs. (75) and (76) can be used to calculate the temperature-dependent viscosities of water and nitric acid ($\mu_{\text{H}_2\text{O}}$ and μ_{HNO_3} respectively):

$$\begin{aligned} \log_{10}(\mu_{\text{H}_2\text{O}}) &= -1.16225 \times 10^1 + 1.94896 \times 10^3 T^{-1} + 2.16414 \times 10^{-2} T \\ &\quad - 1.59901 \times 10^{-5} T^2, \end{aligned} \quad (75)$$

$$\begin{aligned} \log_{10}(\mu_{\text{HNO}_3}) &= -3.42600 + 7.19635 \times 10^2 T^{-1} + 3.65191 \times 10^{-3} T \\ &\quad - 1.90240 \times 10^{-6} T^2, \end{aligned} \quad (76)$$

where viscosity is given in mPa s, and temperature, T , in Yaws (2014).

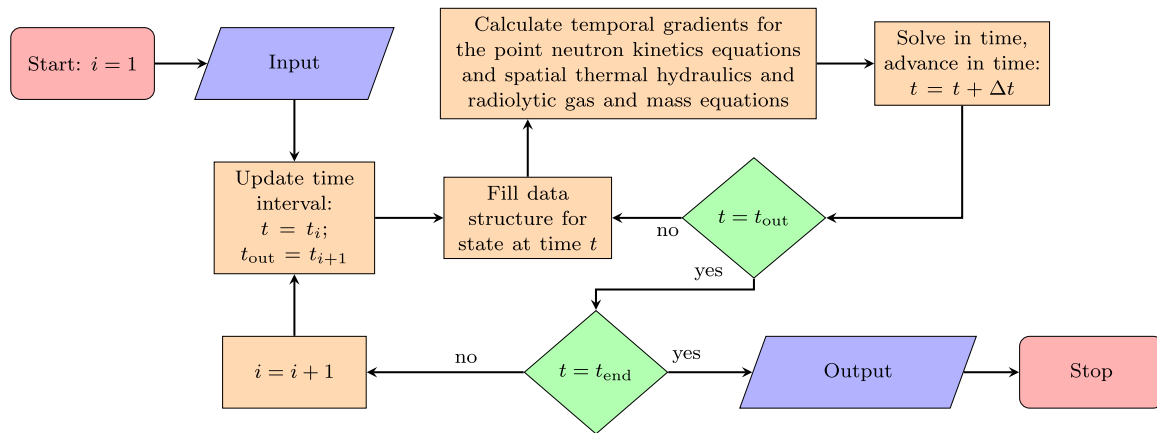


Fig. 7. Flowchart demonstrating the workflow of the proposed numerical algorithm and model.

Assuming that the concentration of plutonium nitrate in a solution has a negligible effect on the solution's dynamic viscosity, Eqs. (75) and (76) can be substituted into Eq. (74), and rearranged to give

$$\log_{10}(\mu) = \left(8.196472 - 1.229328 \times 10^3 T^{-1} - 1.798952 \times 10^{-2} T + 1.408772 \times 10^{-5} T^2 \right) m + \left(-14.622477 + 1.948963 \times 10^3 T^{-1} + 2.164143 \times 10^{-2} T - 1.599012 \times 10^{-5} T^2 \right) \quad (77)$$

which describes the dynamic viscosity, μ , of the solution in Pa s, where the temperature is measured in Kelvin, and m is defined as

$$m = \frac{m_{\text{HNO}_3}}{m_{\text{H}_2\text{O}} + m_{\text{HNO}_3}}. \quad (78)$$

Here, $m_{\text{H}_2\text{O}}$, m_{HNO_3} and $m_{\text{Pu}(\text{NO}_3)_4}$ refer to the mass fractions of H_2O , HNO_3 , and $\text{Pu}(\text{NO}_3)_4$ in the solution respectively, and their sum is equal to unity.

4.3. Specific heat capacity

As previously determined, an increase in water temperature from 290.0 K to 335.0 K corresponds to a 0.05% increase in $C_{p,\text{H}_2\text{O}}$ (Daniels et al., 2024; Incropera et al., 2013). Thus, due to limited data regarding the temperature-dependent specific heat capacities of aqueous solutions containing heavy ions (such as plutonium), it will be assumed that the specific heat capacity of aqueous plutonium nitrate is independent with respect to solution temperature.

Eq. (79) can be used to describe the specific heat capacity, $C_{p,\text{aq}}$, of aqueous nitric acid at 293.15 K:

$$C_{p,\text{aq}} = 4.1860 - 6.0121m + 9.1307m^2 - 5.4941m^3 \quad \text{for } 0.0 < m < 0.8 \quad (79)$$

where m is the mass fraction of HNO_3 in the solution (Yaws, 2014).

In the presented research, the effect of $\text{Pu}(\text{NO}_3)_4$ on solution specific heat capacity will be accounted for by using the apparent molar heat capacities of Pu^{4+} and NO_3^- ions, which are available in the literature. Hepler and Hovey (1996) gives $C_{p,\text{NO}_3^-} = -71 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298.15 K, and Lemire and Tremaine (1980) gives an average value of $C_{p,\text{Pu}^{4+}} = -63 \text{ J K}^{-1} \text{ mol}^{-1}$ over the temperature range $298.15 < T \text{ (K)} < 473.15$. Using these two values, it will be assumed that the presence of $\text{Pu}(\text{NO}_3)_4$ will modify the specific heat capacity of the solution by $C_{p,\text{Pu}(\text{NO}_3)_4}^\phi = -347 \text{ J mol}^{-1} \text{ K}^{-1}$, and that the effect of temperature can be neglected.

To account for the effect of the three molecular constituents in aqueous plutonium nitrate, H_2O , HNO_3 and $\text{Pu}(\text{NO}_3)_4$, on the solutions specific heat capacity, the following method will be used.

First, the specific heat capacity of aqueous nitric acid, $C_{p,\text{aq}}$, will be calculated using Eq. (79), where the definition of m from Eq. (78) is used. Then, the 'effective' specific heat capacity of $\text{Pu}(\text{NO}_3)_4$ will be calculated using

$$C_{p,\text{Pu}(\text{NO}_3)_4} = \frac{C_{p,\text{Pu}(\text{NO}_3)_4}^\phi}{0.001 M_{\text{Pu}(\text{NO}_3)_4}^0}, \quad (80)$$

where $M_{\text{Pu}(\text{NO}_3)_4}^0$ is the molar mass of $\text{Pu}(\text{NO}_3)_4$, in g mol^{-1} . Finally, the overall specific heat capacity of the solution will be calculated using

$$C_p = (m_{\text{H}_2\text{O}} + m_{\text{HNO}_3})C_{p,\text{aq}} + m_{\text{Pu}(\text{NO}_3)_4}C_{p,\text{Pu}(\text{NO}_3)_4}. \quad (81)$$

4.4. Surface tension

Using the proposed equation for the surface tension of water by Jones (1984) and Hosoma et al. (2000) used Eq. (82) to estimate surface tension of a solution of aqueous plutonium nitrate, σ :

$$\sigma = 7.5675 \times 10^{-2} - 1.3762 \times 10^{-4}T - 3.938 \times 10^{-7}T^2 + 1.076 \times 10^{-9}T^3 + 1.2 \times 10^{-5}c_{\text{Pu}} - 5.6 \times 10^{-4}c_{\text{HNO}_3} \quad (82)$$

where c_{Pu} is the plutonium concentration (in g L^{-1}) of the solution, c_{HNO_3} is the free nitric acid concentration (in mol L^{-1}) in the solution and the temperature T is measured in $^\circ\text{C}$.

4.5. Thermal conductivity

Eq. (83) can be used to determine the thermal conductivity, κ , of a liquid at temperature T :

$$\kappa = A + B T + C T^2 \quad \text{for } T_{\min} < T < T_{\max} \quad (83)$$

where A , B and C are liquid-dependent constants, and T is measured in Kelvin.

A number of correlations have been postulated to determine the heat capacity of liquid mixtures. Due to the lack of experimental data, the usability of other correlations is limited (Gaitonde et al., 1978). Thus, the correlation of Filippov and Novoselova (1955) will be used:

$$\kappa_m = \kappa_1 m_1 + \kappa_2 m_2 - 0.72|\kappa_1 - \kappa_2|m_1 m_2, \quad (84)$$

where subscript 'm' denotes 'mixture' and m refers to the mass fraction of component 1 or 2.

Due to a lack of available data, it will be assumed that the effect of $\text{Pu}(\text{NO}_3)_4$ on the thermal conductivity of the solution can be neglected (i.e. only the effects of H_2O and HNO_3 need to be considered). Thus, combining Eqs. (83) and (84), the following expression can be formed:

$$\kappa = (0.72m^2 - 1.72m)\kappa_{\text{comp}} + \kappa_{\text{H}_2\text{O}} \quad (85)$$

Table 1
Parameters in Eq. (83) for H₂O and HNO₃ (Yaws, 2014), and the composite.

Liquid	A (W m ⁻¹ K ⁻¹)	B (W m ⁻¹ K ⁻²)	C (W m ⁻¹ K ⁻³)	T _{min} (K)	T _{max} (K)
H ₂ O	-2.98749 × 10 ⁻¹	4.70537 × 10 ⁻³	-5.62090 × 10 ⁻⁶	273.16	633.15
HNO ₃	1.21070 × 10 ⁻¹	5.38300 × 10 ⁻⁴	0.0	233.15	433.15
comp	-4.19819 × 10 ⁻¹	4.16707 × 10 ⁻³	-5.62090 × 10 ⁻⁶	273.16	433.15

where κ is the thermal conductivity of the plutonium nitrate solution and m is defined in Eq. (78). Table 1 gives the values of A , B , C , $T_{\min}$ and $T_{\max}$ for the liquid components H₂O and HNO₃, and the composite liquid, 'comp'.

In the proposed model, it will be assumed that U_{eddy} is constant throughout the vessel, taking a value of 15 cm s⁻¹ if solution is entering and/or draining from the vessel, and 5 cm s⁻¹ otherwise. The parameter r_{eddy} is assumed to be spatially independent and is defined as

$$r_{\text{eddy}}(t) = 0.25(H(t) + r_{\text{vess}}), \quad (86)$$

where H is the height of the solution, and r_{vess} is the vessel's effective radius. Calculated values of r_{eddy} and U_{eddy} can be substituted into Eq. (42) to calculate D_{mix} .

5. Heat transfer in aqueous plutonium nitrate systems

The rate of convective heat transfer between a fluid and a solid depends on the fluid's temperature profile, which will effect the speed of circulating currents; the properties of rising bubbles within the fluid; and any forced convection, e.g. due to mechanical agitation or fluid being poured into the system.

5.1. Convective heat transfer between the solution and the vessel

The speeds of circulating currents within aqueous homogeneous reactor ARGUS were investigated by Milian Pérez et al. (2015): average fluid velocities of 0.104 m s⁻¹ and 0.016 m s⁻¹ for systems with and without gas voids, respectively, were determined.

Winter (2019) and Daniels et al. (2024) have previously used the correlation proposed by Chilton et al. (1944) to determine heat transfer coefficients (HTCs) between agitated fissile solutions and vessel walls. The correlation is given as

$$Nu \left(\frac{\mu_s}{\mu} \right)^{0.14} = 0.36 Ro^{2/3} Pr^{1/3}, \quad (87)$$

where Nu , Ro and Pr are the Nusselt, Roshko and Prandtl numbers, respectively:

$$Nu = \frac{h_{\text{int}} L_c}{\kappa}, \quad (88)$$

$$Ro = \frac{d_{\text{imp}}^2 f_{\text{shed}} \rho_s}{\mu}, \quad (89)$$

$$Pr = \frac{C_p \mu}{\kappa}. \quad (90)$$

In these dimensionless numbers, $L_c = 2r_{\text{vess}}$ is the characteristic length, h_{int} is the convective HTC and d_{imp} is the diameter of the impeller blade used by Chilton et al. (1944) to agitate the vessel. Subscript s means the solution property is to be taken at the wall, though in the presented research it will be assumed that properties are constant throughout the domain, at a temperature of 293.6 K and atmospheric pressure. Additionally, f_{shed} is the vortex shedding rate, such that $f_{\text{shed}} = 2N$, where N is the impeller shaft speed (in revolutions per second), as the impeller of Chilton et al. (1944) has two blades. As such, the impeller blade velocity is equal to $0.5\pi d_{\text{imp}} f_{\text{shed}}$. Other variables are as previously defined.

Using an equivalent vessel radius, r_{vess} , of 0.473 m, Fig. 8 shows the convective HTC for aqueous solutions of plutonium nitrate. Four solutions have been presented, to cover a range of concentrations of plutonium and nitric acid in the solution.

From Fig. 8, it can be seen that the impeller diameter (and thus the degree of agitation in the vessel) has a much larger effect on the convective HTC than the composition of the aqueous solution. The convective HTC between the solution and vessel wall, h_{int} , was chosen to be 600 W m⁻² K⁻¹, as shown in Fig. 8.

For water, this HTC corresponds to either a large impeller ($d_{\text{imp}} = 1.75r_{\text{vess}}$) moving slowly (~ 0.16 m s⁻¹), or a small impeller ($d_{\text{imp}} = 0.75r_{\text{vess}}$) moving relatively quickly (~ 0.37 m s⁻¹).

When increasing the solution's plutonium and nitric acid concentrations to 20.0 g L⁻¹ and 4.0 mol L⁻¹ respectively, a HTC of 600 W m⁻² K⁻¹ corresponds to either a large impeller moving at ~ 0.14 m s⁻¹, or a small impeller moving at ~ 0.32 m s⁻¹.

As shown in Fig. 8, for a convective HTC of 600 W m⁻² K⁻¹, all configurations presented correspond to fluid velocities in the range 0.14 to 0.37 m s⁻¹, which is of the same order of magnitude as the 0.016 to 0.104 m s⁻¹ calculated by Milian Pérez et al. (2015).

5.2. Heat transfer between the vessel and reflector pool

Heat can be transferred from a solid to a fluid by either radiation or convection. In this Section, the degree of heat transfer due to both methods will be investigated.

5.2.1. Radiative heat transfer

Eq. (91) (Incropera et al., 2013) describes the rate of radiation, E , released from a surface:

$$E = \epsilon \sigma_{\text{SB}} (T_{\text{vess}}^4 - T_{\infty}^4), \quad (91)$$

where $\sigma_{\text{SB}} = 5.67 \times 10^{-8}$ W m⁻² K⁻⁴ is the Stephan Boltzmann constant, T_{∞} is the temperature of the surroundings, and T_{vess} is the temperature of the vessel (the emitter of radiative energy).

The emissivity, ϵ , of a surface describes how efficiently it emits energy, with $\epsilon = 1$ indicating blackbody radiation and with real surfaces having an emissivity in the range $0 < \epsilon < 1$. A value of 0.657 will be used to describe the emissivity of the vessel, which corresponds to that of sheet steel (Coulson et al., 1996).

Using an assumed constant ambient temperature of 293.6 K and maximum vessel temperature of 348.6 K, Eq. (91) gives the radiative heat flux from the vessel's outer surface to be 273 W m⁻².

5.2.2. Heat transfer due to natural convection

By assuming the vessel's walls can be modelled as a flat plate, an Equation of the form

$$Nu = f(Gr, Pr) \quad (92)$$

can be used to estimate the rate of heat loss due to natural convection from the reactor surface to its surroundings, where Nu , Gr and Pr are the Nusselt, Grashof and Prandtl numbers, respectively, defined as:

$$Nu = \frac{h_{\text{ext}} L_c}{\kappa_{\text{H}_2\text{O}}}, \quad (93)$$

$$Gr = \frac{g \beta_{\text{H}_2\text{O}} (T_{\text{vess}} - T_{\infty}) L_c^3 \rho_{\text{air}}^2}{\mu_{\text{H}_2\text{O}}^2}, \quad (94)$$

$$Pr = \frac{C_{p,\text{H}_2\text{O}} \mu_{\text{H}_2\text{O}}}{\kappa_{\text{H}_2\text{O}}}. \quad (95)$$

In the above, $L_c = H_{\text{vess}}$ is the characteristic length, equal to the height of the vessel (1.175 m), g is the acceleration due to gravity and

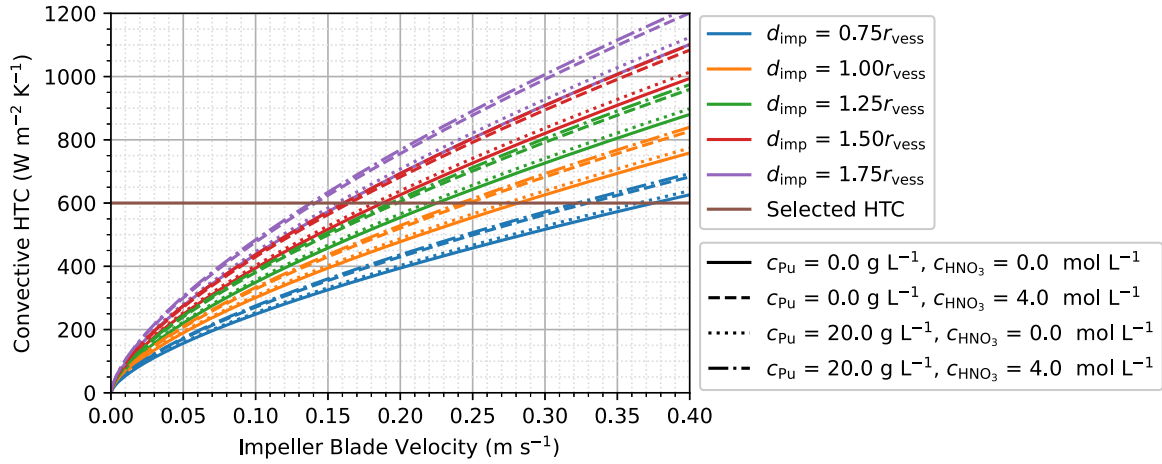


Fig. 8. Predicted HTCs for various solutions of plutonium nitrate, as a function of impeller blade speed, for a variety of impeller blade lengths.

Table 2

Properties of air at 293.6 K.

Property	Symbol	Value	Unit	Reference
Density	$\rho_{\text{H}_2\text{O}}$	998.283	kg m ⁻³	[D]
Viscosity	$\mu_{\text{H}_2\text{O}}$	9.929×10^{-4}	Pa s	[D]
Thermal conductivity	$\kappa_{\text{H}_2\text{O}}$	0.604	W m ⁻¹ K ⁻¹	[D]
Specific heat capacity	$C_{p,\text{H}_2\text{O}}$	4.182×10^3	J kg ⁻¹ K ⁻¹	[D]
Coefficient of thermal expansion	$\beta_{\text{H}_2\text{O}}$	2.111×10^{-4}	K ⁻¹	[A]
Prandtl number	Pr	6.877	–	–

[A] Yaws (2014), [D] Incropera et al. (2013).

T_{vess} and T_{∞} are as previously defined. Subscripts ‘H₂O’ indicate the property is that of water, as defined in Table 2.

For $T_{\text{vess}} = 348.6$ K and $T_{\infty} = 293.6$ K, the Grashof and Nusselt numbers are calculated to be 1.9×10^{11} and 1.3×10^3 respectively. For $Gr > 10^9$, Eq. (96) (Coulson et al., 1996; Hiroharu et al., 1968) can be used to describe the heat transfer from vertical cylinders:

$$Nu = 0.138Gr^{0.36}(Pr^{0.175} - 0.55). \quad (96)$$

Thus, h_{ext} is calculated to be 689 W m⁻² K⁻¹, which corresponds to a heat transfer rate of 38 kW m⁻².

As shown, the rate of heat loss due to radiation is two orders of magnitude smaller than the rate of heat loss due to natural convection.

5.3. Convective heat transfer from the solution surface to the plenum gas

Heat transfer from the solution's surface to the plenum gas could occur via forced or natural convection. Any addition of solution to the vessel could induce forced convection by disrupting the plenum gas at the top of the vessel. Correlations for natural convection and forced convection for laminar flow are presented in Eqs. (97) and (98) respectively (Incropera et al., 2013):

$$Nu = 0.15(GrPr)^{1/3} \quad \text{for } 10^7 < GrPr < 10^{11}, \quad (97)$$

$$Nu = 0.66Re^{1/2}Pr^{1/3} \quad \text{for } 0.6 \leq Pr \leq 60 \quad (98)$$

where Re is the Reynolds number:

$$Re = \frac{\rho_{\text{air}} u_{\text{air}} L_c}{\mu_{\text{air}}}. \quad (99)$$

In these equations, u_{air} is the speed of the plenum gas. The surface of the solution is treated as a solid flat plate, and the characteristic length L_c is equal to the solution's hydraulic diameter ($2(r_o - r_i)$ for an annular vessel).

In this application, $GrPr = 2.9 \times 10^8$, resulting in a HTC due to natural convection, $h_{\text{nat,sur}}$ of 6.875 W m⁻² K⁻¹.

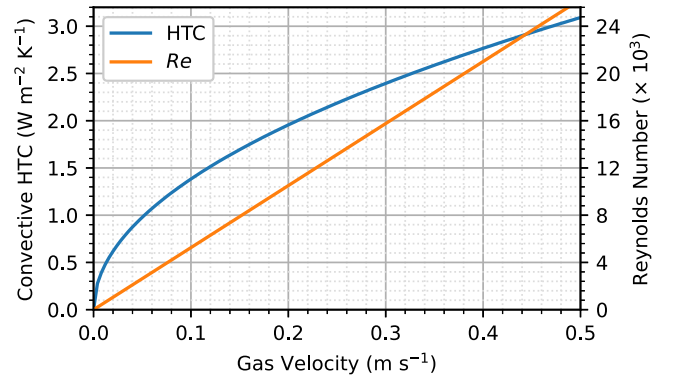


Fig. 9. HTCs describing heat transfer from the solution's surface to the plenum gas due to forced convection, and the corresponding Reynolds numbers.

The HTCs due to forced convection are presented in Fig. 9 as a function of the velocity of the plenum gas. Fig. 9 shows that, even at gas velocities of 0.48 m s⁻¹ (and a corresponding $Re = 2.5 \times 10^4$), the HTC due to forced convection, $h_{\text{conv,sur}}$ is only 3.030 W m⁻² K⁻¹.

The overall HTC between the solution and the plenum gas, h_{sur} , will depend on the resistance to heat transfer from the solution bulk and solution surface to the plenum gas. Taking this into account, the overall HTC between the solution and the plenum gas can be calculated using Eq. (100):

$$\frac{1}{h_{\text{sur}}} = \frac{1}{h_{\text{int}}} + \frac{1}{h_{\text{nat,sur}}}. \quad (100)$$

The first term on the right-hand side represents the resistance to heat transfer between the bulk and surface of the solution, and has been approximated as h_{int} , calculated in Section 5.1 to be 600 W m⁻² K⁻¹.

The second term represents the resistance to heat transfer between the surface of the solution and the plenum gas, where $h_{\text{nat,sur}}$ has been chosen (6.875 W m⁻² K⁻¹), as it is greater than the possible HTCs for forced convection.

As such, h_{sur} is calculated to be 6.797 W m⁻² K⁻¹.

6. Linear energy transfer, radiolysis and bubble nucleation

In fissile solutions, the daughter products (fission fragments) from a fission event are emitted fully ionised and at a high velocity. As these fragments travel through the solution, energy is transferred to the solution, inducing radiolysis and thus leaving tracks of radiolysis products in their wake. The linear energy transfer (LET) of a fission fragment is the amount of energy deposited by the fragment per unit distance travelled.

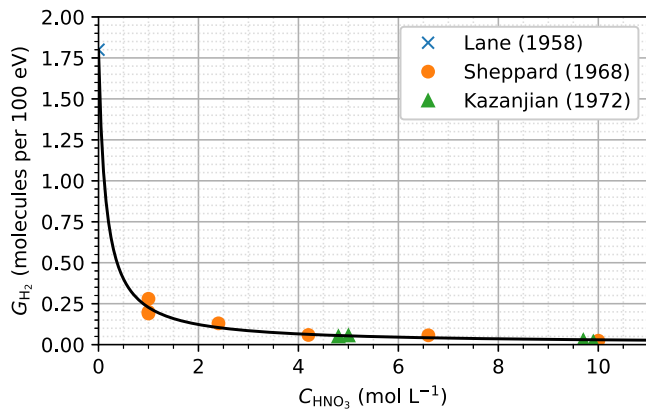


Fig. 10. Variation in $\tilde{G}_{H_2}$ with c_{HNO_3} , using data from Kazanjian and Horrell (1972), Sheppard (1968) and Lane et al. (1958), and the fitted Eq. (101).

6.1. Radiolytic gas generation coefficient

In aqueous solutions, high LET radiations produce high yields of H_2 , O_2 and H_2O_2 , whereas low LET radiations produce high yields of free radicals $H^\bullet$ and $HO^\bullet$. These free radicals very quickly recombine in dense fission tracks, and therefore are not considered in the proposed model (Lane et al., 1958).

Experiments to determine the production of radiolytic gas due to the fission of ^{239}Pu have been performed by Kazanjian and Horrell (1972) and Sheppard (1968). Lane et al. (1958) determined the radiolytic gas generation coefficient in pure water to be 1.8 molecules per 100 eV of fission energy. The experimental data from these sources can be fitted to Eq. (101):

$$\tilde{G}_{H_2} = [5.555843 \times 10^{-1} + 3.905721 c_{HNO_3} - 5.605583 \times 10^{-2} c_{HNO_3}^2]^{-1}, \quad (101)$$

where $\tilde{G}_{H_2}$ is the radiolytic gas generation coefficient of aqueous plutonium nitrate, and c_{HNO_3} is the concentration of nitric acid in the solution. When compared to the experimental data, Eq. (101) has $\bar{R}^2 = 0.99779$. Eq. (101) differs from that of Daniels et al. (2024), and historical fits by Maimoni (1979), due to the need to adequately determine $\tilde{G}_{H_2}$ for systems with low c_{HNO_3} . The experimental data and the results from Eq. (101) are presented in Fig. 10.

Kazanjian and Horrell (1972) notes that varying plutonium concentration has a minimal effect on $\tilde{G}_{H_2}$ for aqueous plutonium nitrate, which was later discussed and verified by Kuno et al. (1993). More recent work by Silver and Anderson-Cook (2005) presents Equations to determine $\tilde{G}_{H_2}$ as a function of both nitric acid and plutonium concentration, also based on the work of Kazanjian and Horrell (1972); their equations are valid for $1 \leq c_{HNO_3} \leq 10 \text{ mol L}^{-1}$ and $50 \leq c_{Pu} \leq 100 \text{ g L}^{-1}$, making them unsuitable for use in the presented research.

Finally, there is insufficient data in the available literature to determine the effect of temperature on $\tilde{G}_{H_2}$.

6.2. Linear energy transfer

Previous research by Ghormley (1958), Lane et al. (1958), Norman and Spiegler (1963) and Deitrich and Connolly (1973) concluded that the quantities and proportions of radiolysis products, alongside the size of bubbles generated along fission tracks, depend on the LET of the fission fragments.

The LET of a fission fragment is a complex function of the fragment's velocity and charge, and the surrounding medium's stopping power with respect to that fragment (Tavernier, 2010). In addition, fission fragments have a very large initial charge, and continuously de-ionise along their track (Chadderton, 1988). This differs to the LET of smaller particles (such as electrons, protons and alpha particles), which retain

their charge until, and experience a peak in LET towards, the end of their track.

When an atom of ^{239}Pu undergoes fission, an average of 2.88 prompt neutrons (ν_p) are produced, alongside (predominantly) two charged fragments (a very small number of ternary and quaternary fissions can occur) (Gönnenwein, 2004). Assuming momentum is conserved, the initial energy, E_0 , of a fission fragment can be calculated using

$$E_0 = \frac{E_{k,\text{fiss}}}{1 + \frac{M}{239 - \nu_p - M}}, \quad (102)$$

where M is the mass of the fragment and $E_{k,\text{fiss}}$ is the total kinetic energy of the two fission fragments, which is around 207 MeV for the fission of ^{239}Pu (Sher and Beck, 1981).

6.2.1. Predicting LET profiles for fission fragments in plutonium nitrate

A list of ^{239}Pu fission products by yield was obtained from National Nuclear Data Center (2011). From this, the 300 highest yielding fission products were obtained. Some of these fission products of ^{239}Pu were listed as different isomers of the same isotope, which can be treated identically when calculating LET profiles, reducing the list of fission products to 240 distinct isotopes. These fragments account for 97.33% of the total fission yield.

From this list, the LET profiles for the 300 highest yielding fission products of ^{239}Pu were calculated (for various solution temperatures and plutonium and acid concentrations) using PHITS 3.320 (Sato et al., 2013), alongside Eq. (102) for the initial conditions.

Example LET profiles are presented in Fig. 11. As shown, the shape of the LET profile is heavily dependent on the ionised nucleus. As the weight of the ionised nucleus increases from 81 to 134 amu, so does initial LET, but as nucleus weight increases from 134 to 156 amu, initial LET decreases.

Fig. 11 also shows the initial gradient of the LET profile tends to increase with increased nucleus weight. The gradient then increases, until 10–20 μm before the end of the profile, where the LET plateaus, before dropping sharply to 0 across the last 2–3 μm of the track.

Larger bubbles form at locations with higher LET, and they are of greater significance as nucleation sites for gas voids when compared to smaller bubbles formed along the same fission track but at lower LETs (Winter, 2019).

As shown in Fig. 11, the highest LET occurs at the start of the track. Fig. 12 depicts the variation in initial LET with temperature T , excess acid molarity c_{HNO_3} , and plutonium concentration c_{Pu} .

As shown in Fig. 12, the initial LET increases (apparently linearly) with increasing c_{HNO_3} and c_{Pu} , but decreases (apparently quadratically) with increasing temperature.

As such, the following equation can be used to determine $\dot{E}$, the initial LET of ^{239}Pu fission fragments in aqueous solutions of plutonium nitrate:

$$\begin{aligned} \dot{E} = & (c_1 + c_2 T + c_2 T^2) + (c_4 + c_5 T + c_6 T^2) c_{HNO_3} + (c_7 + c_8 T + c_9 T^2) c_{Pu} \\ & + (c_{10} + c_{11} T + c_{12} T^2) c_{Pu} c_{HNO_3} \end{aligned} \quad (103)$$

where c_{HNO_3} , c_{Pu} and T are measured in mol L^{-1} , g L^{-1} and K, respectively, and coefficients c_i are given in Table 3. Eq. (103) is valid for the ranges $0.0 \leq c_{HNO_3} \leq 4.0 \text{ mol L}^{-1}$, $0.0 \leq c_{Pu} \leq 20.0 \text{ g L}^{-1}$ and $293.6 \leq T \leq 372.4 \text{ K}$.

6.3. Bubble nucleation radius

As a fission fragment travels through an aqueous solution, it imparts energy to the surrounding water, causing a jet of water vapour to form along the fission fragment track. This jet then breaks up into vapour bubbles, which also contain hydrogen gas (a direct product of radiolysis) (Spiegler et al., 1962; Winter et al., 2020).

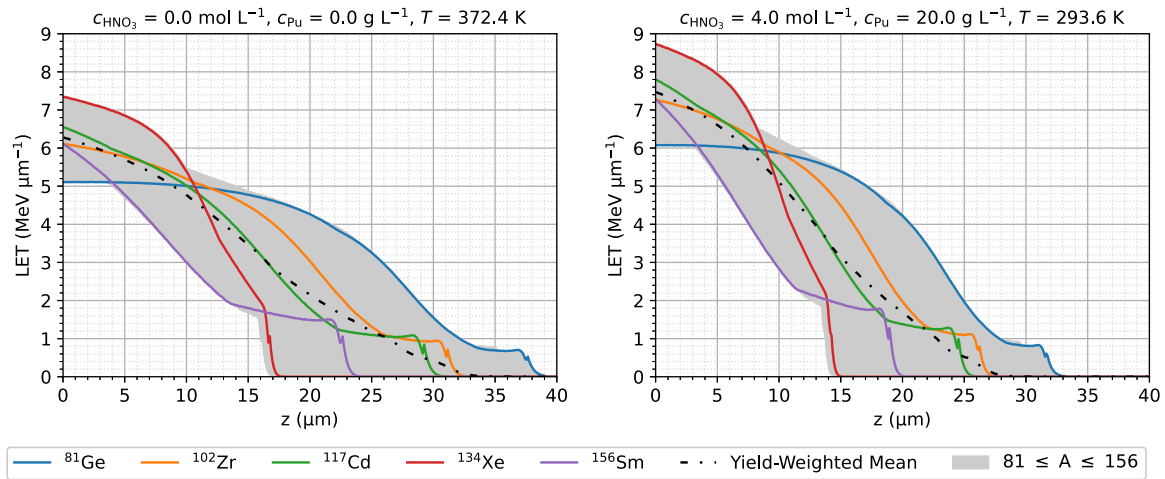


Fig. 11. The LET profiles for ^{239}Pu fission fragments in water at 372.4 K and a solution of plutonium nitrate at 293.6 K.

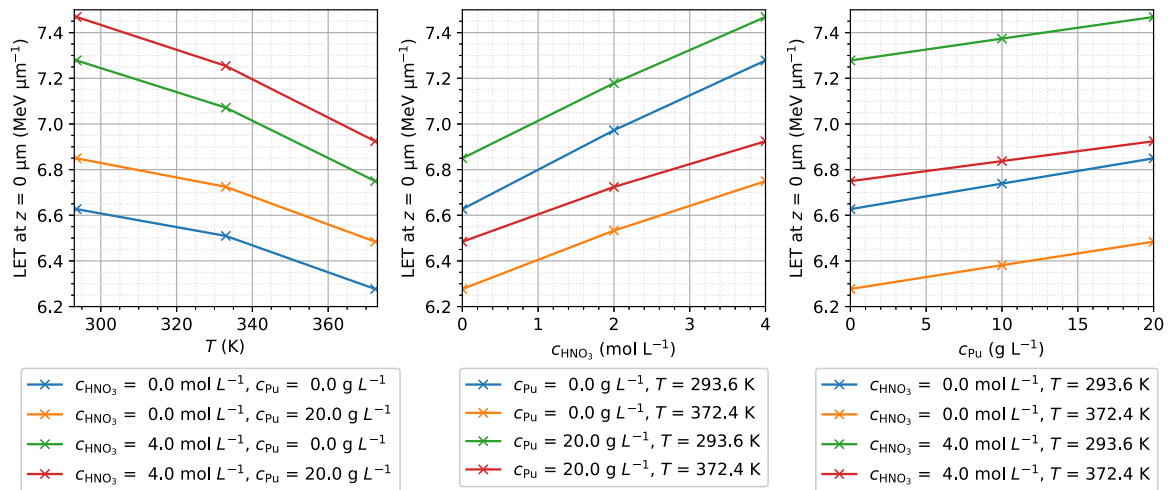


Fig. 12. The variation in the initial, yield-weighted average LET of ^{239}Pu fission fragments with solution temperature, plutonium concentration and excess acid concentration.

Table 3

The coefficients c_i used in Eq. (103).

i	c_i	i	c_i	i	c_i	i	c_i
1	3.881708×10^0	4	3.298124×10^{-1}	7	1.394032×10^{-2}	10	-4.635386×10^{-4}
2	2.026078×10^{-2}	5	-5.693235×10^{-4}	8	-9.468433×10^{-6}	11	4.223729×10^{-7}
3	-3.708475×10^{-5}	6	2.147266×10^{-9}	9	$-3.757724 \times 10^{-10}$	12	$-7.247028 \times 10^{-10}$

The water vapour will condense on a timescale of the order 10^{-8} s if the solution is subcooled. The remaining hydrogen bubble will collapse on a timescale of the order 10^{-6} s if the concentration of dissolved gas is low (Spiegler et al., 1962; Winter et al., 2020).

The total energy deposited by an average fission fragment, E_b , can be expressed simply as

$$E_b = \dot{E}L \quad (104)$$

where $\dot{E}$ is the initial LET, and L is the track length over which the water vapour and hydrogen form a single bubble.

Previous studies (Deitrich and Connolly, 1973; Norman and Spiegler, 1963; Rayleigh, 1945; Winter et al., 2020) have determined that $2\pi r_{\text{nuc}} \leq L \leq 4\pi r_{\text{nuc}}$, where r_{nuc} is the radius of a bubble containing both water vapour and hydrogen gas. The limits have significance as $2\pi r_{\text{nuc}}$ is the circumference of the bubble and $4\pi r_{\text{nuc}}$ is the track length that corresponds to the most rapid break up of the vapour jet. To account for this range of values, $L = 3\pi r_{\text{nuc}}$ has been used in the presented research.

Before the condensation of water vapour, the energy, E_b , imparted to the solution by the average fission fragment acts to vapourise the water within the bubble, create the gas-liquid interface around the bubble, work against the liquid pressure to create the bubble, and induce the radiolysis reaction.

These terms can be used to form an energy balance equation:

$$E_b = \frac{4}{3}\pi r_v^3 \rho_v \Delta H_{\text{vap}} + 4\pi \left(\sigma - T \frac{d\sigma}{dT} \right) r_{\text{nuc}}^2 + \frac{4}{3}\pi p r_{\text{nuc}}^3 + N_{\text{H}_2} \Delta H_r, \quad (105)$$

where r_{nuc} is the radius of the bubble before steam condensation (i.e. containing both water vapour and hydrogen gas) and r_v is the radius of the bubble if it contained just water vapour (Winter et al., 2020). p , σ and T are the pressure, surface tension and temperature of the solution, ρ_v is the density of water vapour within the bubble, and N_{H_2} is the number of moles of hydrogen gas produced. Finally, ΔH_{vap} and ΔH_r are the enthalpy of vapourisation of water and enthalpy of the radiolysis reaction, respectively.

Table 4

Calculation conditions used throughout Section 6.4, except where otherwise stated.

Variable	Symbol	Value	Unit
Initial LET	$\dot{E}$	8.0	MeV μm^{-1}
Solution temperature	T	293.6	K
Hydrostatic pressure	p	1.0	atm
Radiolytic gas generation coefficient	$\tilde{G}_{\text{H}_2}$	1.8	molecules per 100 eV
Excess acid molarity	c_{HNO_3}	0.0	mol L ⁻¹
Plutonium concentration	c_{Pu}	0.0	g L ⁻¹

Using the relation

$$N_{\text{H}_2} = G_{\text{H}_2} \dot{E} L, \quad (106)$$

and the ideal gas equation:

$$pV = NRT, \quad (107)$$

the volume of hydrogen gas produced can be expressed using

$$V_{\text{H}_2} = N_{\text{H}_2} \frac{RT}{p} = 3\pi G_{\text{H}_2} \dot{E} r_{\text{nuc}} \frac{RT}{p}. \quad (108)$$

As $V_b = V_v + V_{\text{H}_2}$, r_v can be expressed as

$$r_v = \left(r_{\text{nuc}}^3 - \frac{9}{4} \frac{RT}{p} \dot{E} G_{\text{H}_2} r_{\text{nuc}} \right)^{1/3}. \quad (109)$$

Substituting Eqs. (104), (106) and (109) into Eq. (105) and rearranging yields

$$\begin{aligned} \frac{4}{3} r_{\text{nuc}}^2 (\rho_v \Delta H_{\text{vap}} + p) + 4r_{\text{nuc}} \left(\sigma - T \frac{d\sigma}{dT} \right) \\ + 3\dot{E} \left(G_{\text{H}_2} \Delta H_r - \frac{3}{4} \frac{RT}{p} G_{\text{H}_2} \rho_v \Delta H_{\text{vap}} - 1 \right) = 0, \end{aligned} \quad (110)$$

which can be solved iteratively to determine r_{nuc} . To do this, ρ_v was determined from steam tables, given the solution temperature and bubble pressure (which is calculated using Eq. (111)).

$$P_b = p + \frac{2\sigma_s}{r_{\text{nuc}}}. \quad (111)$$

 ΔH_r was estimated by Winter et al. (2020) to be 2.958×10^5 J per mole of hydrogen gas produced, and ΔH_{vap} , in kJ kg⁻¹, was calculated using (Winter et al., 2020)

$$\Delta H_{\text{vap}} = 3168 - 2.4367T. \quad (112)$$

6.4. Sensitivity of bubble nucleation radius to solution properties

By inspecting Eq. (110), the bubble nucleation radius is shown to be dependent on the solution's temperature and hydrostatic pressure, as well as the energy deposited by fission fragments as they travel through the solution. It will also be dependent on the excess acid concentration, via the solution's surface tension and radiolytic gas generation coefficient, as demonstrated by Eqs. (82) and (101). Finally, the bubble nucleation radius will depend on the solution's plutonium concentration, again via the solution's surface tension.

Except where otherwise stated, the results presented in this section were calculated using the conditions presented in Table 4.

Fig. 13 shows that the bubble nucleation radius increases with both LET and solution temperature, with LET having a more significant impact on bubble radius.

Whilst increasing the LET increases the energy available to create the bubble, increasing the temperature increases the bubble radius as values such as surface tension, enthalpy of vaporisation and steam density (at a given pressure) decrease.

From Fig. 14, it can be seen that the bubble nucleation radius decays exponentially with increasing hydrostatic pressure, as more energy is required to balance the higher pressures experienced by a bubble.

Table 5The coefficients a_i used in Eq. (113).

i	a_i	i	a_i	i	a_i
1	1.56370×10^{-8}	5	-1.24602×10^{-1}	9	1.81231×10^{-1}
2	-5.81205×10^{-1}	6	2.48375×10^{-1}	10	1.62900×10^{-11}
3	3.79363×10^0	7	6.34040×10^{-9}	11	3.50302×10^{-2}
4	-4.05653×10^{-12}	8	1.04294×10^{-0}	12	-7.15411×10^{-2}

Table 6

The data ranges used to fit Eq. (113), which therefore also serve as ranges of validity.

Variable	Symbol	Min.	Max.	Unit
LET	$\dot{E}$	0.5	10.0	MeV μm^{-1}
Solution temperature	T	273.15	373.15	K
Excess acid molarity	c_{HNO_3}	0.0	10.0	mol L ⁻¹

Fig. 14 also shows that bubble nucleation radius increases with radiolytic gas generation coefficient, as more hydrogen gas is produced per unit energy when G_{H_2} increases.

Fig. 15 shows that the dependence of bubble nucleation radius on the solution's plutonium concentration is negligible. However, bubble nucleation radius decreases significantly with increased nitric acid concentration. This is due to the radiolytic gas generation coefficient being dependent on the inverse of a second order polynomial with respect to nitric acid concentration, as demonstrated by Eq. (101).

From Figs. 13–15, it can be seen that the bubble nucleation radius is most highly dependent on the fission fragment's LET, the solution temperature and pressure, and the concentration of excess acid in the solution. Limiting analysis to systems at atmospheric pressure, and neglecting the effect of plutonium concentration, the following Equation can be used to calculate the bubble nucleation radius:

$$\begin{aligned} r_{\text{nuc}} = & \left(a_1 e^{(a_2 - a_3 c_{\text{HNO}_3})} + a_4 e^{(a_5 - a_6 c_{\text{HNO}_3}) T} \right) \dot{E} + \left(a_7 e^{(a_8 - a_9 c_{\text{HNO}_3})} \right. \\ & \left. + a_{10} e^{(a_{11} - a_{12} c_{\text{HNO}_3}) T} \right) \dot{E}^{0.5} \end{aligned} \quad (113)$$

where the values of a_i are presented in Table 5, the temperature, T , is measured in K, $\dot{E}$ is measured in MeV μm^{-1} , and c_{HNO_3} is measured in mol L⁻¹. Eq. (113) was fitted to 51³ data points using variable ranges detailed in Table 6, and the coefficients in Table 5 result in an R^2 value of 0.98471.

6.5. Bubble radius after steam condensation

As described in Section 3.4, bubbles of gas produced by radiolysis will collapse unless the concentration of dissolved gas in the solution is at a 'critical concentration' (Spiegler et al., 1962; Winter et al., 2020).

If the critical concentration is exceeded, the bubbles will grow and appear as voids in the solution. The number of moles of hydrogen gas, N_{H_2} produced during radiolysis can be calculated using Eq. (106), and the pressure of the gas bubble can be calculated using $p + \frac{2\sigma}{r_b}$. Substituting these into the ideal gas law ($pV = NRT$), and rearranging yields

$$4pr_b^3 + 8\sigma r_b^2 - 9RTG_{\text{H}_2} \dot{E} r_b = 0, \quad (114)$$

which can be used to iteratively determine r_b , the bubble radius after steam condensation (Winter et al., 2020).

7. Nuclear properties of aqueous plutonium nitrate

In the remainder of the presented research, the conceptual reactor detailed in Section 2.2, with r_{in} and r_{out} equal to 8.0 and 48.0 cm respectively, is examined, and the plutonium isotopic composition detailed in Table A.17 has been utilised in all solutions.

In this section, MCNP (Werner et al., 2018) and the ENDF/B-VIII.0 nuclear data library (Brown et al., 2018) was used to determine kinetics parameters and reactivity feedbacks. For a range of temperatures

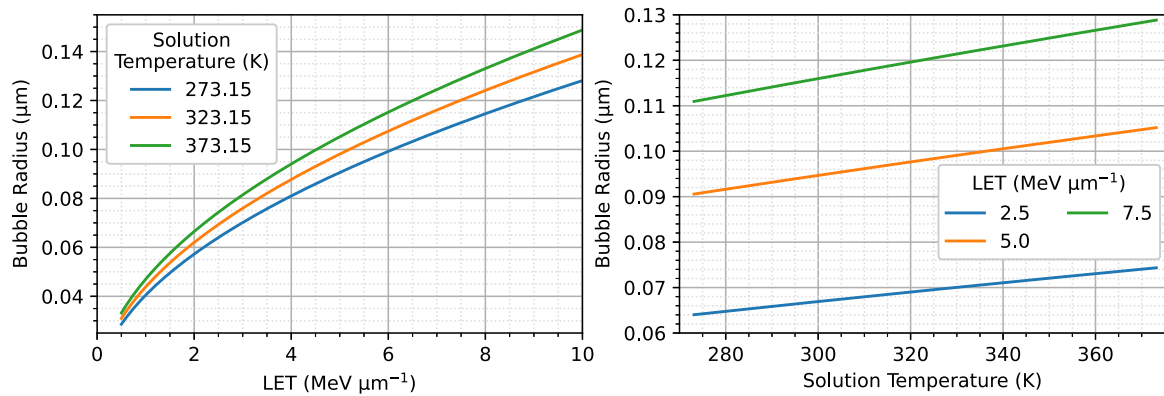


Fig. 13. The variation in bubble nucleation radius with LET (left), and solution temperature (right), calculated using Eq. (110).

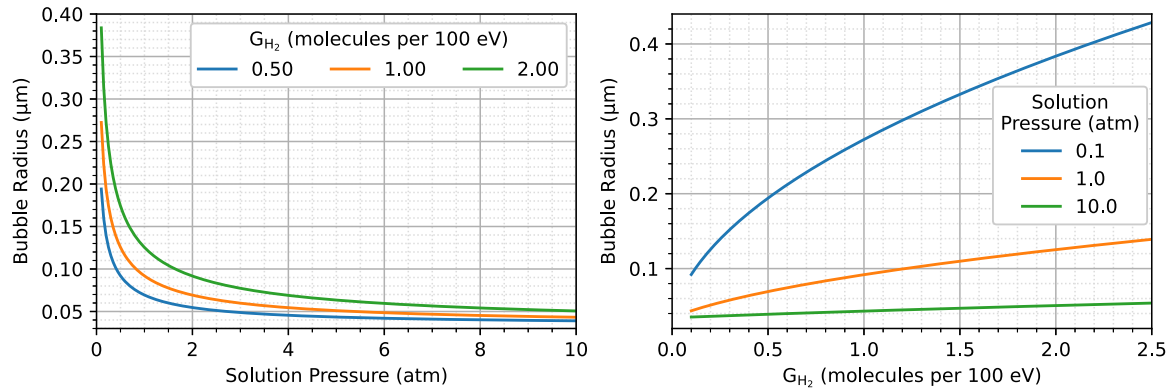


Fig. 14. The variation in bubble nucleation radius with hydrostatic pressure (left), and radiolytic gas generation coefficient (right), calculated using Eq. (110).

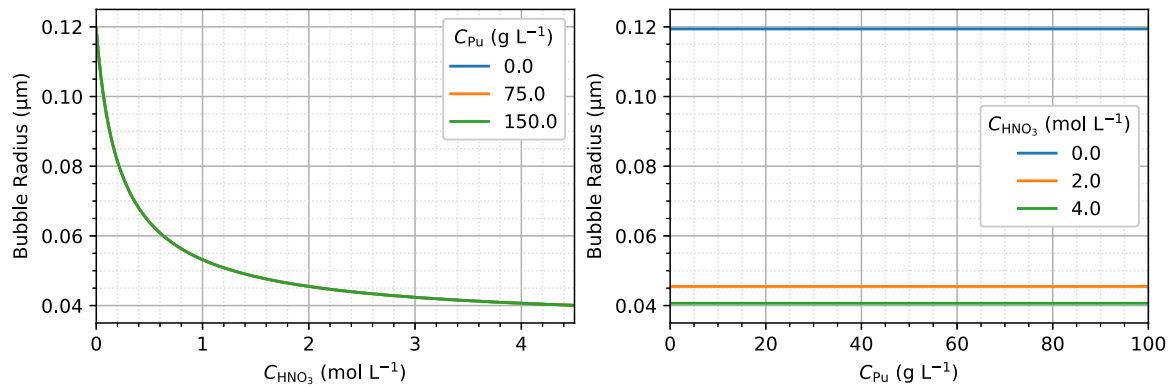


Fig. 15. The variation in bubble nucleation radius with excess acid molarity (left), and plutonium concentration (right), calculated using Eq. (110). G_{H_2} was varied in accordance with Eq. (101).

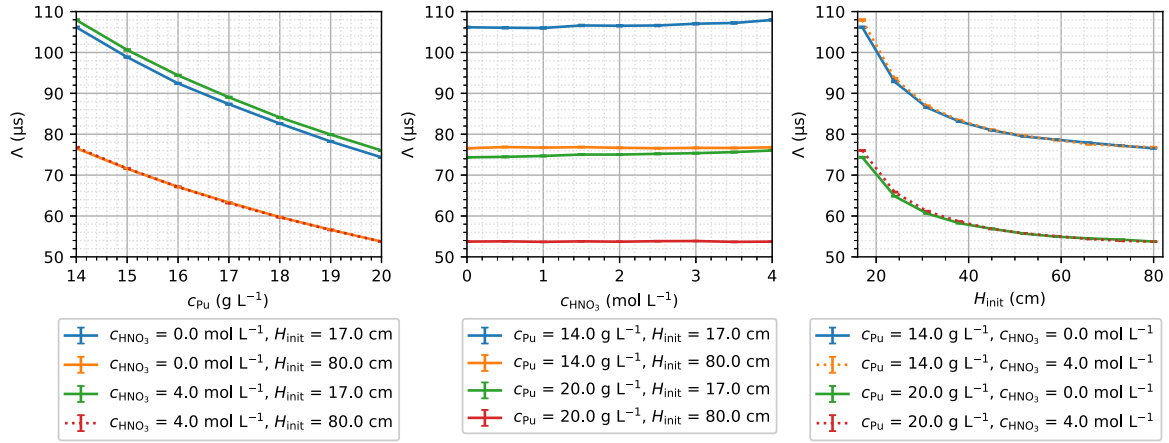


Fig. 16. Variation in mean neutron generation time with system properties, for solutions at 293.6 K and no voids.

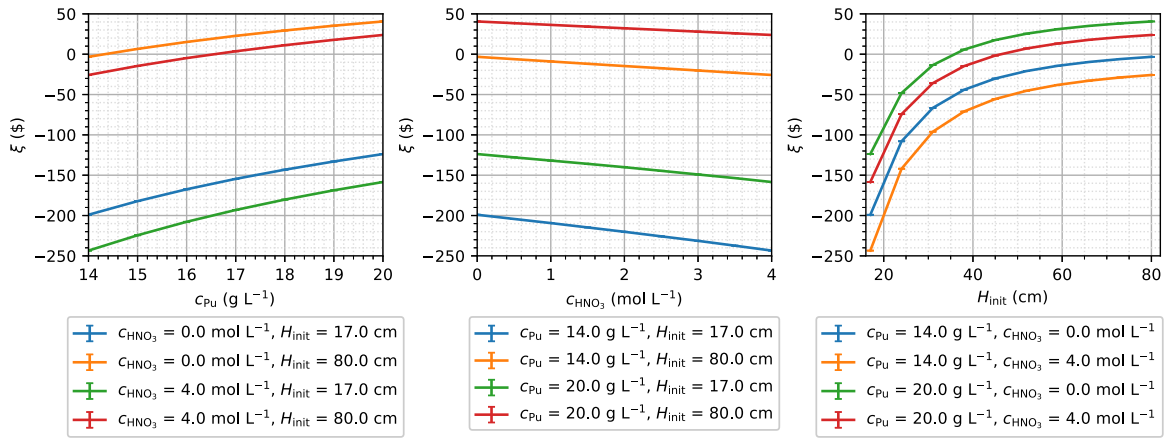


Fig. 17. Variation in reactivity with system properties, for solutions at 293.6 K and no voids.

($293.6 \leq \bar{T} \leq 374.0 \text{ K}$) or void fractions ($0.00 \leq \bar{\theta} \leq 0.25$), the solution composition and mass were modified in the ranges detailed in Table 7.

In addition, deterministic code SOURCES-4C (Wilson et al., 2002, 2005) was used to determine the intrinsic neutron sources (due to spontaneous fission and (α, n) reactions) of solutions with the range of plutonium and excess acid concentrations detailed in Table 7, and at temperatures between 293.6 and 374 K.

7.1. Kinetics data

From the MCNP results, ν , β_{eff} , β_i and λ_i were observed to independent of solution height, temperature and void fraction. The averaged results give $\beta_{\text{eff}} = 0.00257$, $\nu = 2.871$, and β_i and λ_i detailed in Table 8. The standard deviations of all results are a maximum of 5×10^{-6} .

7.2. Mean neutron generation time and reactivity

Figs. 16 and 17 depict variations in mean neutron generation time and reactivity with plutonium and excess acid concentrations and solution height, calculated using MCNP.

As shown in Fig. 16, the mean neutron generation time is weakly dependent on excess acid concentration, with this dependence diminishing with increased solution height. For solution heights of 17.0 cm, Λ is seen to increase by just 1 μs when c_{HNO_3} increases from 0.0 to 4.0 mol L⁻¹.

Conversely, increasing either c_{Pu} or H_{init} will result in a decrease in Λ , with the gradient also decreasing with increasing c_{Pu} or H_{init} .

Similarly, Fig. 17 shows that reactivity is more heavily dependent on c_{HNO_3} and H_{init} . In these cases, ξ increased with increasing c_{HNO_3}

Table 7

Parameter ranges used to determine kinetics and reactivity feedback data.

Variable	Symbol	Min.	Max.	Unit
Plutonium concentration	c_{Pu}	14.0	20.0	g L ⁻¹
Excess acid molarity	c_{HNO_3}	0.0	4.0	mol L ⁻¹
Solution height at 293.6 K with no voids	H_{init}	17.0	80.0	cm

Table 8

Delayed neutron fractions and yields.

i	β_i	$\lambda_i \text{ (s}^{-1}\text{)}$
1	0.00009	0.01328
2	0.00060	0.03084
3	0.00047	0.11349
4	0.00083	0.29319
5	0.00044	0.85812
6	0.00014	2.74493

or H_{init} , with the gradients again decreasing with increasing c_{HNO_3} or H_{init} .

As shown in Fig. 17, ξ decreases linearly with c_{HNO_3} , with the gradient being slightly shallower for larger values of H_{init} .

The reactivity and mean neutron generation time data from MCNP can be fitted to the following equation:

$$Z_{\text{init}} = \sum_{i=1}^5 A_i \quad (115)$$

where

$$A_1 = a_1 + \frac{a_2}{M} + a_3 c_{\text{Pu}} + a_4 c_{\text{HNO}_3} \quad (116)$$

$$A_2 = \frac{a_5}{M^2} + a_6 c_{\text{Pu}}^2 + a_7 c_{\text{HNO}_3}^2 + a_8 \frac{c_{\text{Pu}}}{M} + a_9 \frac{c_{\text{HNO}_3}}{M} + a_{10} c_{\text{Pu}} c_{\text{HNO}_3} \quad (117)$$

$$A_3 = a_{11} \frac{c_{\text{Pu}}}{M^2} + a_{12} \frac{c_{\text{HNO}_3}}{M^2} + a_{13} \frac{c_{\text{Pu}}^2}{M} + a_{14} c_{\text{Pu}}^2 c_{\text{HNO}_3} + a_{15} \frac{c_{\text{HNO}_3}^2}{M} + a_{16} c_{\text{HNO}_3}^2 c_{\text{Pu}} + a_{17} \frac{c_{\text{Pu}} c_{\text{HNO}_3}}{M} \quad (118)$$

$$A_4 = a_{18} \left(\frac{c_{\text{Pu}}}{M} \right)^2 + a_{19} \left(\frac{c_{\text{HNO}_3}}{M} \right)^2 + a_{20} (c_{\text{Pu}} c_{\text{HNO}_3})^2 + a_{21} \frac{c_{\text{Pu}} c_{\text{HNO}_3}}{M^2} + a_{22} \frac{c_{\text{Pu}}^2 c_{\text{HNO}_3}}{M} + a_{23} \frac{c_{\text{Pu}} c_{\text{HNO}_3}^2}{M} \quad (119)$$

$$A_5 = a_{24} \left(\frac{c_{\text{Pu}}}{M} \right)^2 c_{\text{HNO}_3} + a_{25} \left(\frac{c_{\text{HNO}_3}}{M} \right)^2 c_{\text{Pu}} + a_{26} \frac{(c_{\text{Pu}} c_{\text{HNO}_3})^2}{M} + a_{27} \left(\frac{c_{\text{Pu}} c_{\text{HNO}_3}}{M} \right)^2 \quad (120)$$

Here, Z corresponds to either Λ or ξ , and coefficients a_1 to a_{27} are presented in Table B.19 for Λ and B.20 for ξ . When fitted to the data from MCNP, this equation yields an $\bar{R}^2$ of 0.99983 when calculating Λ and 0.99997 when calculating ξ .

7.3. Variations due to temperature and voidage

As with data for Λ_{init} and ξ_{init} , the changes mean neutron generation time and reactivity due to the effects of temperature and void fraction can be determined by creating best-fit equations from the MCNP results.

These equations take the form:

$$\Delta Z_{xx} = \bar{X}(B_1 + B_2 + B_3 + B_4 + B_5) + \bar{X}^2(B_6 + B_7 + B_8 + B_9 + B_{10}) \quad (121)$$

where

$$B_1 = b_1 + \frac{b_2}{M} + b_3 c_{\text{Pu}} + b_4 c_{\text{HNO}_3} \quad (122)$$

$$B_2 = \frac{b_5}{M^2} + b_6 c_{\text{Pu}}^2 + b_7 c_{\text{HNO}_3}^2 + b_8 \frac{c_{\text{Pu}}}{M} + b_9 \frac{c_{\text{HNO}_3}}{M} + b_{10} c_{\text{Pu}} c_{\text{HNO}_3} \quad (123)$$

$$B_3 = b_{11} \frac{c_{\text{Pu}}}{M^2} + b_{12} \frac{c_{\text{HNO}_3}}{M^2} + b_{13} \frac{c_{\text{Pu}}^2}{M} + b_{14} c_{\text{Pu}}^2 c_{\text{HNO}_3} + b_{15} \frac{c_{\text{HNO}_3}^2}{M} + b_{16} c_{\text{HNO}_3}^2 c_{\text{Pu}} + b_{17} \frac{c_{\text{Pu}} c_{\text{HNO}_3}}{M} \quad (124)$$

$$B_4 = b_{18} \left(\frac{c_{\text{Pu}}}{M} \right)^2 + b_{19} \left(\frac{c_{\text{HNO}_3}}{M} \right)^2 + b_{20} (c_{\text{Pu}} c_{\text{HNO}_3})^2 + b_{21} \frac{c_{\text{Pu}} c_{\text{HNO}_3}}{M} + b_{22} \frac{c_{\text{Pu}}^2 c_{\text{HNO}_3}}{M} + b_{23} \frac{c_{\text{Pu}} c_{\text{HNO}_3}^2}{M} \quad (125)$$

$$B_5 = b_{24} \left(\frac{c_{\text{Pu}}}{M} \right)^2 c_{\text{HNO}_3} + b_{25} \left(\frac{c_{\text{HNO}_3}}{M} \right)^2 c_{\text{Pu}} + b_{26} \frac{(c_{\text{Pu}} c_{\text{HNO}_3})^2}{M} + b_{27} \left(\frac{c_{\text{Pu}} c_{\text{HNO}_3}}{M} \right)^2 \quad (126)$$

$$B_6 = b_{28} + \frac{b_{29}}{M} + b_{30} c_{\text{Pu}} + b_{31} c_{\text{HNO}_3} \quad (127)$$

$$B_7 = \frac{b_{32}}{M^2} + b_{33} c_{\text{Pu}}^2 + b_{34} c_{\text{HNO}_3}^2 + b_{35} \frac{c_{\text{Pu}}}{M} + b_{36} \frac{c_{\text{HNO}_3}}{M} + b_{37} c_{\text{Pu}} c_{\text{HNO}_3} \quad (128)$$

$$B_8 = b_{38} \frac{c_{\text{Pu}}}{M^2} + b_{39} \frac{c_{\text{HNO}_3}}{M^2} + b_{40} \frac{c_{\text{Pu}}^2}{M} + b_{41} c_{\text{Pu}}^2 c_{\text{HNO}_3} + b_{42} \frac{c_{\text{HNO}_3}^2}{M} + b_{43} c_{\text{HNO}_3}^2 c_{\text{Pu}} + b_{44} \frac{c_{\text{Pu}} c_{\text{HNO}_3}}{M} \quad (129)$$

$$B_9 = b_{45} \left(\frac{c_{\text{Pu}}}{M} \right)^2 + b_{46} \left(\frac{c_{\text{HNO}_3}}{M} \right)^2 + b_{47} (c_{\text{Pu}} c_{\text{HNO}_3})^2 + b_{48} \frac{c_{\text{Pu}} c_{\text{HNO}_3}}{M} + b_{49} \frac{c_{\text{Pu}}^2 c_{\text{HNO}_3}}{M} + b_{50} \frac{c_{\text{Pu}} c_{\text{HNO}_3}^2}{M} \quad (130)$$

$$B_{10} = b_{51} \left(\frac{c_{\text{Pu}}}{M} \right)^2 c_{\text{HNO}_3} + b_{52} \left(\frac{c_{\text{HNO}_3}}{M} \right)^2 c_{\text{Pu}} + b_{53} \frac{(c_{\text{Pu}} c_{\text{HNO}_3})^2}{M} + b_{54} \left(\frac{c_{\text{Pu}} c_{\text{HNO}_3}}{M} \right)^2 \quad (131)$$

Table 9

$\bar{R}^2$ values describing the suitability of the fitted equations.

Property	$\bar{R}^2$
$\Delta \Lambda_{\text{th}}$	0.95145
$\Delta \Lambda_{\text{rg}}$	0.99961
$\Delta \xi_{\text{th}}$	0.99678
$\Delta \xi_{\text{rg}}$	0.99985

Subscript ‘xx’ in Eq. (121) can refer to either thermal ‘th’ or voidage ‘rg’. If ‘xx’ = ‘rg’, $\bar{X} = \bar{\theta}$, i.e. the average void fraction in the solution. If ‘xx’ = ‘th’, $\bar{X} = \bar{T} - 293.6$, i.e. the change in temperature from ambient conditions.

For $\Delta \Lambda_{\text{th}}$, $\Delta \Lambda_{\text{rg}}$, $\Delta \xi_{\text{th}}$ and $\Delta \xi_{\text{rg}}$, the values of the coefficients in Eq. (121) are been detailed in Tables C.21, C.22, C.23 and C.24.

Table 9 presents the $\bar{R}^2$ values, describing the goodness of fit, for each use of Eq. (121). As shown, the goodness of fit for the ΔZ_{th} equations is slightly less than those for the ΔZ_{rg} equations. However, with a minimum $\bar{R}^2$ of 0.95, the equations describe the variation in any ΔZ_{xx} suitably well.

The top graphs of Fig. 18 depict examples of the variation in $\Delta \Lambda_{\text{th}}$ with solution temperature. The MCNP data presented in the top-left graph shows that there is $\Delta \Lambda_{\text{th}}$ generally increases slightly with increasing temperature, though the exact relationship is hard to determine and dependent on solution properties.

As shown in Fig. 18, $\Delta \Lambda_{\text{th}}$ values calculated using Eq. (121) differ slightly from the MCNP data. However, the trends are comparable to those displayed in the data, with the equation results effectively ‘smoothing’ any fluctuations and uncertainty in the data. As $\Delta \Lambda_{\text{th}}$ is weakly dependent on temperature, the differences between the data and equation results are small enough for the equation results to be considered sufficient

Conversely, 18 shows that $\Delta \xi_{\text{th}}$ values calculated using Eq. (121) match the MCNP data extremely closely, due to the smoothness of the original data.

As shown in the bottom-left graph of Fig. 18, the variation in $\Delta \xi_{\text{th}}$ with temperature is heavily dependent on system properties. Vessels containing a relatively large amount of a solution with lower plutonium and acid concentrations have a $\Delta \xi_{\text{th}}$ that increases with solution temperature. As plutonium and acid concentrations, and solution H_{init} decreases, the extent of the positive temperature feedback effect decreases, until $\Delta \xi_{\text{th}}$ decreases with increasing temperature.

Fig. 19 shows that $\Delta \Lambda_{\text{rg}}$ increases, and $\Delta \xi_{\text{rg}}$ decreases, apparently quadratically, with increasing void fraction. The differences between the data and equation results are minimal, due to the smoothness of the MCNP data. This in turn could be an artefact of the fact that $\Delta \Lambda_{\text{rg}}$ and $\Delta \xi_{\text{rg}}$ are much more strongly dependent on void fraction than $\Delta \Lambda_{\text{th}}$ and $\Delta \xi_{\text{th}}$ are dependent on temperature.

7.4. Scalar neutron flux profile

From the previous MCNP simulations, height-dependent scalar neutron flux profiles were obtained and fitted to the following equation (based on that derived by Cooling (2014)):

$$\phi(z) = \frac{\frac{1}{H_F} \sin\left(\pi \frac{(z-\delta_b)}{H_F}\right)}{\cos\left(\pi \frac{\delta_b}{H_F}\right) - \cos\left(\pi \frac{(H+\delta_b)}{H_F}\right)} \quad (132)$$

where $\phi(z)$ is the scalar neutron flux at height z , H is the height of the fuel solution, δ_b and δ_p are the flux extrapolation distance at the base and height of the fuel solution, respectively, and H_F is the height of the flux profile ($H_F = \delta_b + H + \delta_p$). To apply this equation to all systems simulated using MCNP, δ_b and δ_p were set equal to 0.05718 and 0.02651 m, respectively.

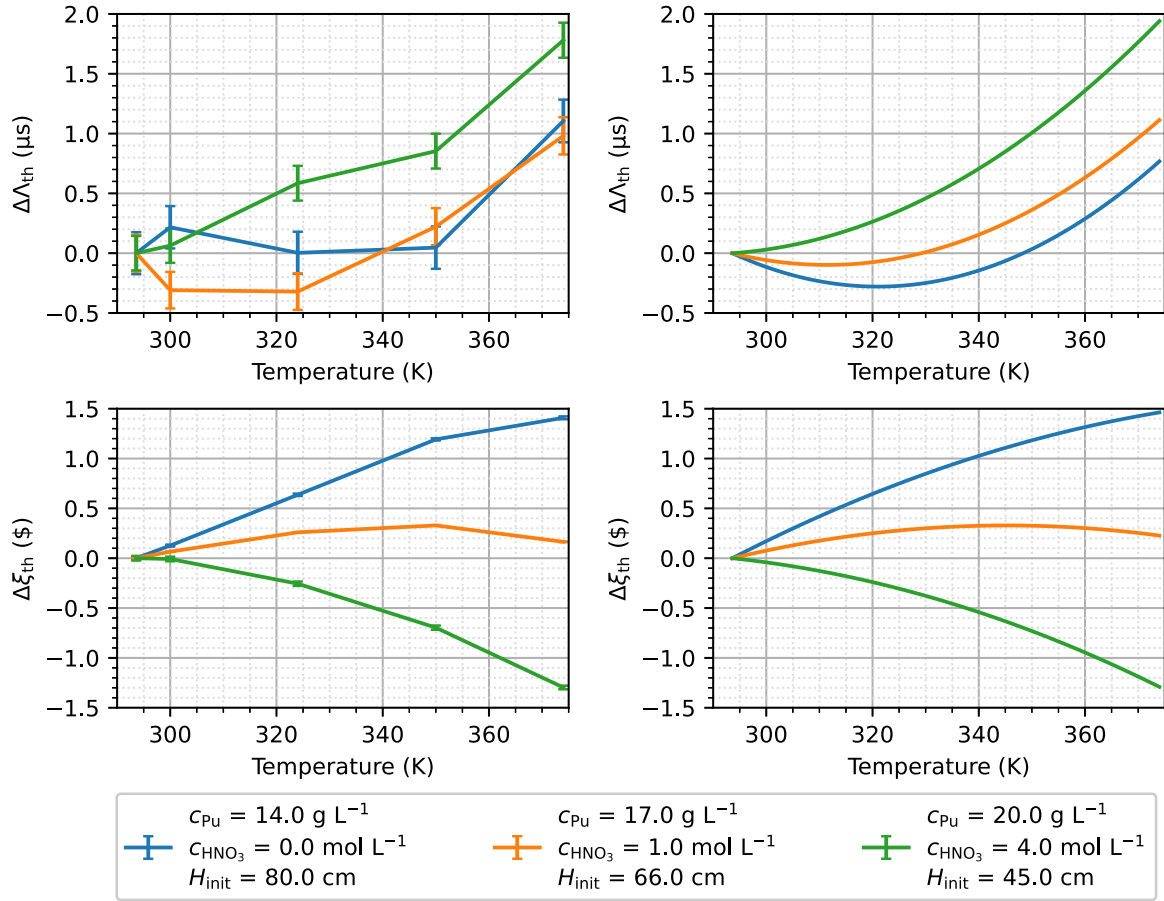


Fig. 18. Variation in $\Delta\Lambda_{th}$ and $\Delta\xi_{th}$ with solution temperature. Left-hand graphs depict data from MCNP, right-hand graphs depict the results of Eq. (121).

Table 10
The system properties for the graphs of 20.

Property	Left-hand graph	Right-hand graph
Plutonium concentration (g L^{-1})	16.0	20.0
Excess acid concentration (mol L^{-1})	3.5	0.5
Height when at 293.6 K with no voids (cm)	59.0	17.0
Temperature (K)	300.0	293.6
Void fraction	0.0	0.0

Fig. 20 depicts, for two examples, the scalar neutron flux calculated using MCNP and Eq. (132). The system properties giving rise to these graphs are detailed in Table 10.

As shown in Fig. 20, Eq. (132) fits the data reasonably well.

For the system depicted in the left-hand graph of Fig. 20, Eq. (132) slightly over-estimates the magnitude of the flux peak relative to the rest of the profile, though the shape of the equation matches very well.

For the system depicted in the right-hand graph of Fig. 20, Eq. (132) slightly under-estimates the magnitude of the flux peak relative to the rest of the profile, and calculates a wider flux profile when compared to the MCNP data.

In fact, in general, the equation is a poorer fit to the data for systems with lower solution heights (at 293.6 K), with agreement improving with increased solution height. As systems containing less fuel are likely to be heavily subcritical, the poorly-fitting equation is expected to have a negligible impact on transient behaviour.

7.5. Intrinsic neutron source

Using results from SOURCES-4C, the total intrinsic neutron source for a variety of plutonium nitrate systems are presented in Fig. 21.

Fig. 21 shows that the intrinsic neutron source (per unit volume of solution) increases linearly with increasing plutonium concentration. The intrinsic source decreases slightly with C_{HNO_3} , with the dependency becoming stronger with increasing temperature. Finally, the intrinsic neutron source decreases, apparently quadratically, with increasing temperature.

The results from SOURCES-4C can be fitted to the following equation:

$$s = (c_1 + c_2T + c_3T^2) + (c_4 + c_5T + c_6T^2)c_{HNO_3} + (c_7 + c_8T + c_9T^2)c_{Pu} + (c_{10} + c_{11}T + c_{12}T^2)c_{Pu}c_{HNO_3} \quad (133)$$

where C_{HNO_3} , C_{Pu} and T are measured in mol L^{-1} , g L^{-1} and K, respectively, and coefficients c_i are given in Table 11. This equation fits the data extremely well, with an $\overline{R}^2 > 0.9999$.

SOURCES-4C can also calculate the energy spectrum of such an intrinsic neutron source (Wilson et al., 2002, 2005). Fig. 22 depicts examples of the (α, n) and SF neutron source spectra in plutonium nitrate systems. As SOURCES-4C cannot calculate these spectra when ^{14}N isotopes are present (Wilson et al., 2002, 2005), the presented spectra have been obtained by assuming the effect of ^{14}N is negligible, and normalised to the intrinsic source magnitude calculated using Eq. (133).

It is unknown if such an assumption is valid, however for the purposes of the presented research (determining the subcritical power of plutonium nitrate solutions), these results are not expected to make a noticeable difference on subsequent results, as they are only to be used as inputs to Monte Carlo neutron transport code Serpent (Leppänen et al., 2015).

As shown in Fig. 22, the (α, n) neutron source spectrum in energy peaks at around 0.8 MeV, whilst that of the SF neutron source peaks

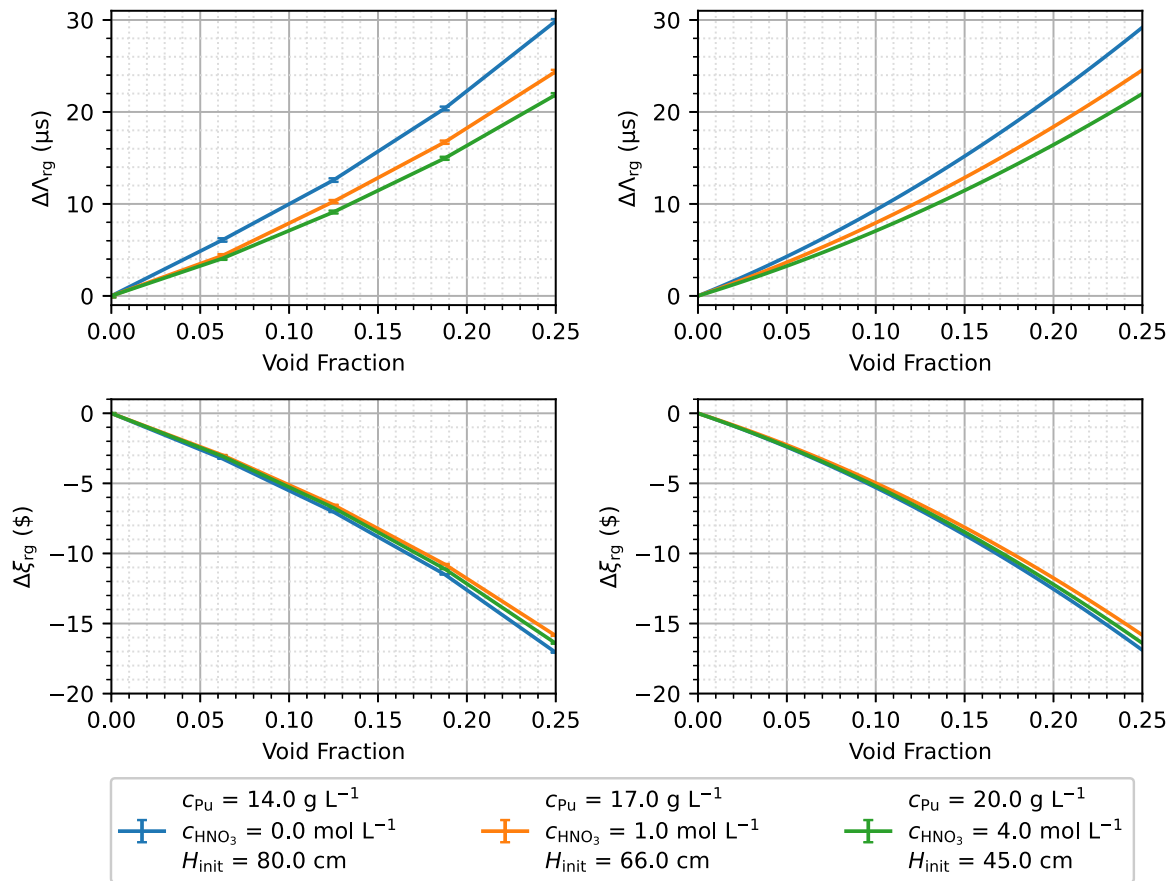


Fig. 19. Variation in $\Delta\Lambda_{rg}$ and $\Delta\xi_{rg}$ with solution void fraction. Left-hand graphs depict data from MCNP, right-hand graphs depict the results of Eq. (121).

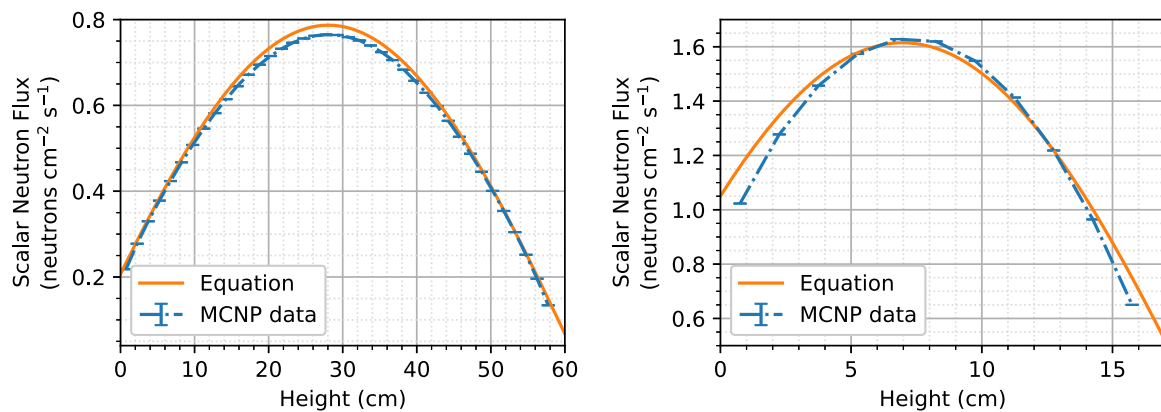


Fig. 20. Scalar neutron flux profiles for the cases where Equation performs best (left) and worst (right).

Table 11
The coefficients c_i used in Eq. (133).

i	c_i	i	c_i	i	c_i	i	c_i
1	-1.704321×10^{-2}	4	2.856465×10^{-2}	7	4.735869×10^{-4}	10	1.482273×10^{-3}
2	1.117376×10^{-4}	5	1.267685×10^{-4}	8	-3.652458×10^{-6}	11	-7.069635×10^{-6}
3	-1.673626×10^{-7}	6	-2.366420×10^{-7}	9	6.166722×10^{-9}	12	6.898400×10^{-3}

at around 2.5 MeV, with a second, much smaller peak, at around 0.45 MeV. Fig. 22 shows that the vast majority (around 99.97%) of intrinsic source neutrons are born with energies less than 10 MeV. The relative, energy-dependent contributions from (α ,n) and SF neutrons are independent of plutonium concentration, such that when the source profiles are normalised (e.g. to unity), the spectra are identical.

7.6. Subcritical multiplication and power in plutonium nitrate solutions

Regarding neutron transport, the physical behaviour of a system is only dominated by the fundamental mode of the system when it is at or near criticality (Kobayashi and Nishihara, 2000). Thus, the fundamental mode eigenvalue (k_{eff}) is only valid at or near criticality,

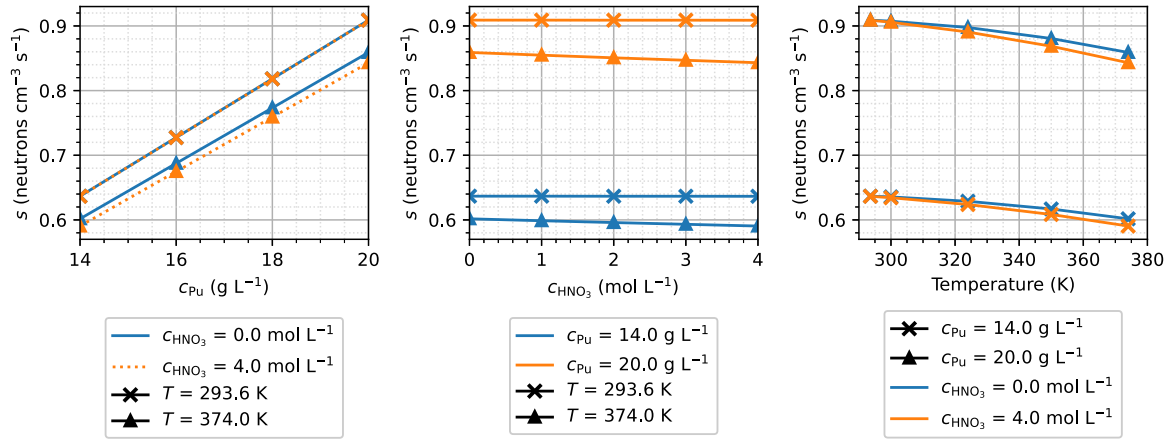


Fig. 21. Variation in intrinsic neutron source with plutonium concentration, excess acid concentration, and solution temperature.

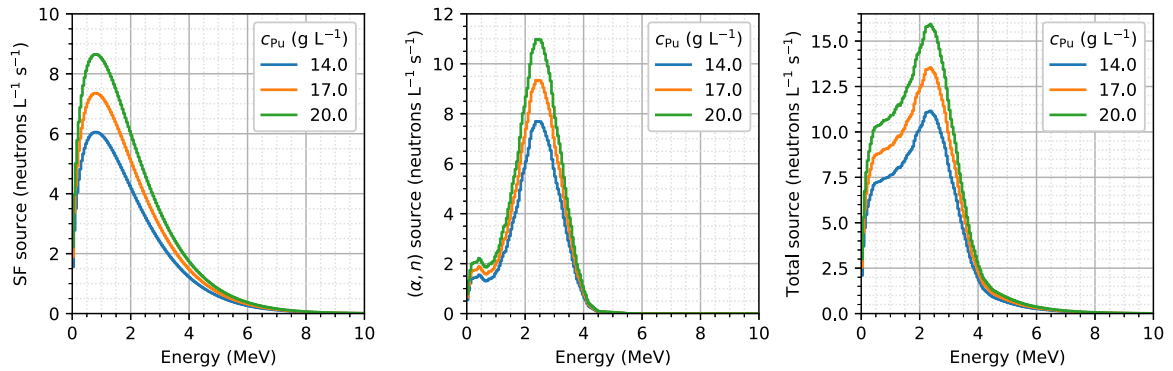


Fig. 22. Intrinsic neutron sources for solutions of plutonium nitrate.

and subcritical fissile systems (with an intrinsic distributed and/or extraneous neutron source) may have a neutron multiplication factor that differs significantly from the calculated k_{eff} .

For these subcritical systems, the subcritical multiplication factor, k_s , can be used to accurately calculate the neutron multiplication factor, as per the following:

$$k_s = \frac{F}{F + S}, \quad (134)$$

$$F = \int_0^\infty dE_n \int_0^{4\pi} d\Omega \int_V d^3r \nu \Sigma_f(\mathbf{r}, \Omega, E_n) \psi(\mathbf{r}, \Omega, E_n), \quad (135)$$

$$S = \frac{1}{4\pi} \int_0^\infty dE_n \int_V d^3r S_{\text{ext}}(\mathbf{r}, E_n). \quad (136)$$

In these equations, E_n , Ω and r are the energy, angular direction and position vector, respectively, and ψ is the angular neutron flux. ν , Σ_f and S_{ext} are the average number of neutrons per fission, the macroscopic neutron fission cross section, and intrinsic/extraneous neutron source.

As demonstrated in Eq. (134), k_s is the ratio of the steady-state fission neutron production rate to the total neutron generation rate (i.e. from both fission and external and/or intrinsic neutron sources) (Gandini and Salvatores, 2002; Greenspan, 1975; Shang et al., 2018). The subcritical power of the system, P_s , can be calculated using

$$P_s = \epsilon \int_0^\infty dE_n \int_0^{4\pi} d\Omega \int_V d^3r \Sigma_f(\mathbf{r}, \Omega, E_n) \psi(\mathbf{r}, \Omega, E_n), \quad (137)$$

where ϵ is the energy released per fission (3.318×10^{-11} J fission⁻¹ for ²³⁹Pu Sher and Beck, 1981).

Using Serpent (Leppänen et al., 2015), simulations using both fixed-source (k_s) and fundamental eigenvalue (k_{eff}) modes have been performed, for five different plutonium nitrate solutions (detailed in Table 12) in the conceptual reactor (as described in Section 2.2).

Table 12

Plutonium and nitric acid concentrations for the five solutions investigated in this Section.

	c_{Pu} (g L ⁻¹)	c_{HNO_3} (mol L ⁻¹)
Case 1	14.0	0.0
Case 2	14.0	1.0
Case 3	17.0	1.0
Case 4	20.0	0.0
Case 5	20.0	2.0

The relative difference between k_{eff} and k_s , Δk_s has been calculated using

$$\Delta k_s(\%) = \frac{k_s - k_{\text{eff}}}{k_{\text{eff}}} \times 100. \quad (138)$$

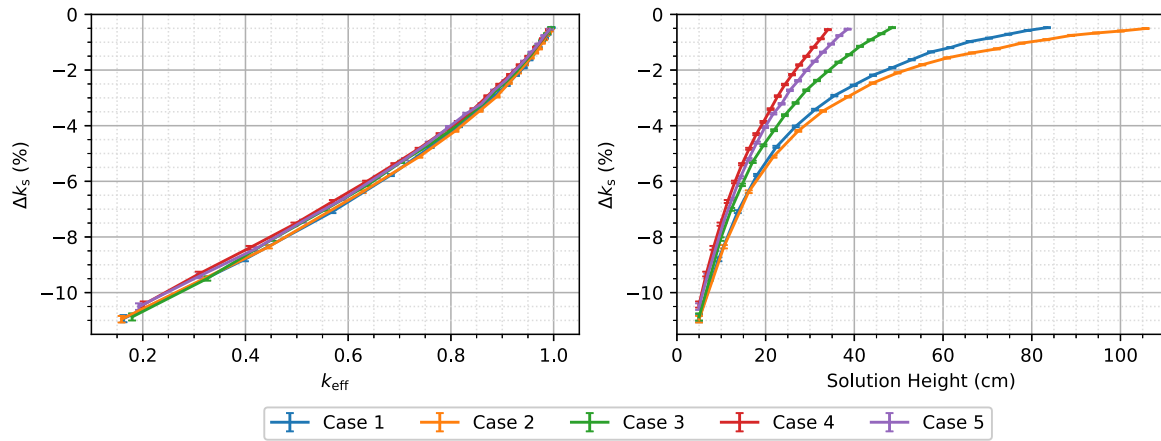
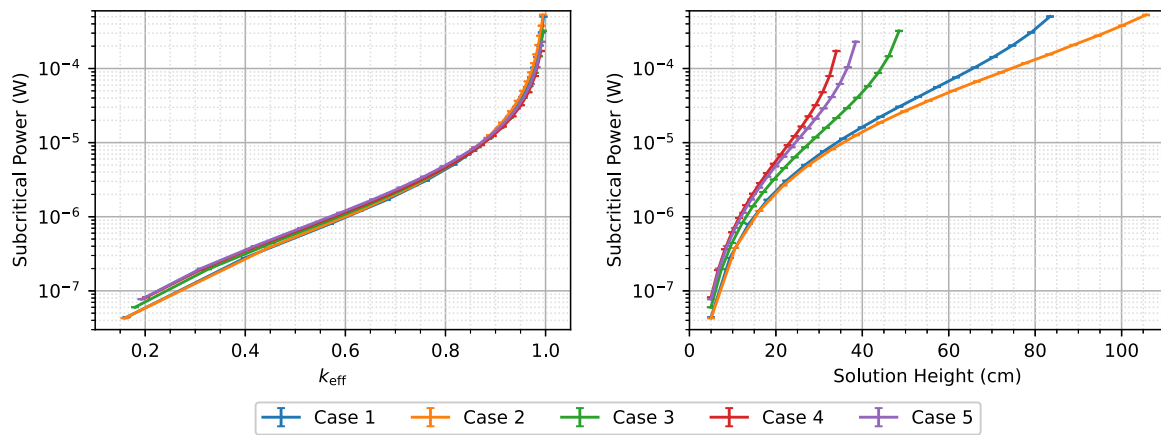
In addition, the maximum solution heights give rise to k_{eff} values in the range $0.991 \leq k_{\text{eff}} \leq 1.000$.

As demonstrated in Fig. 23, k_s is underpredicted by up to 11.5% when compared to k_{eff} . As the solution height increases (and criticality is approached), the agreement between k_s and k_{eff} improves, meaning $|\Delta k_s|$ decreases to around 0.5% when criticality is reached.

As shown in Fig. 23, the Δk_s is very similar for solutions with the same k_{eff} , though different solutions may be at noticeably different heights to have the same k_{eff} .

The left-hand graph of Fig. 23 shows that $|\Delta k_s|$ decreases with increasing k_{eff} , with the gradient also increasing with increasing k_{eff} .

The right-hand graph of Fig. 23 shows that $|\Delta k_s|$ also decreases with increasing solution height, but with the gradient decreasing with increasing solution height.

Fig. 23. The variation in Δk_s with k_{eff} and solution height.Fig. 24. The variation in steady-state, subcritical power, with k_{eff} and solution height.

As demonstrated in Fig. 24, the subcritical power of a solution increases with solution height, and thus also with k_{eff} . As with Δk_s , solutions with the same k_{eff} will have very similar subcritical powers.

The left-hand graph of Fig. 24 shows that the subcritical power increases from $\sim 4 \times 10^{-8}$ to 5×10^{-4} W when k_{eff} increases from 0.15 to 0.99. The graph takes on an apparent S-shape, indicating the gradient tends to infinity as $k_{\text{eff}} \rightarrow 1.0$ and as $k_{\text{eff}} \rightarrow 0.0$.

A similar trend can be seen in the right-hand graph of Fig. 24, though for the cases with lower plutonium concentrations the graph is stretched such that the gradient does not increase significantly at the solutions reach their maximum height.

7.7. Determination of the subcritical regime

If the intrinsic (or extrinsic) neutron source in a subcritical system is weak, stochastic fluctuations in the neutron population could be significant (Hansen, 1960; Hurwitz et al., 1963), requiring the use of either Monte Carlo methods (Cooling et al., 2016) or the Pál-Bell equations (Bell, 1963; Pál, 1958) to model these fluctuations.

Moreover, a weak intrinsic and/or extrinsic neutron source can lead to wait time probability distribution functions (PDFs) which have a significant statistical variance, inducing significant uncertainties in the eventual fission yield from a fast burst system, with consequent uncertainties in the radiation dose to nuclear workers. Therefore, for fissile systems with weak intrinsic and/or extrinsic neutron sources, it is important to account for the wait time PDF when computing the eventual fission yield from the fast burst system (Winter et al., 2018).

In addition to an accurate determination of intrinsic/extrinsic neutron source magnitudes and distributions, an understanding of the

system regime is required to accurately model nuclear criticality excursions (including the prescription of initial conditions). A simple method to determine whether systems have a weak neutron source, such that they are in the stochastic regime, is to use Hansen's criterion (Hansen, 1960), which states that a source should be considered weak if

$$\frac{2S\tau_s}{\nu\Gamma_2} \ll 1. \quad (139)$$

Here, S , τ_s and ν represent the total distributed neutron source [neutrons s^{-1}], prompt neutron removal lifetime [s] and average number of neutrons produced per fission [–], respectively (Hansen, 1960), with the Diven factor, Γ_2 defined as

$$\Gamma_2 = \frac{\nu(\nu - 1)}{\nu^2}. \quad (140)$$

In Fig. 21 of Section 7.5, it can be seen that the lowest intrinsic neutron source, s , for the systems under investigation occurs when $c_{\text{Pu}} = 14 \text{ g L}^{-1}$ and $c_{\text{HNO}_3} = 4 \text{ mol L}^{-1}$. In Section 7.1, it was determined that ν was 2.871, and MCNP results also gave calculations of τ_s . Using this data, when the solution fills the conceptual reactor to a height of 17 cm at 293.6 K, the Hansen criteria for the solution at 293.6 and 373 K are given in Table 13.

As shown in Table 13, the Hansen criterion for the solution is above unity for either of the two temperatures. As such, the system does not have a weak neutron source and is in the deterministic regime. This is true for solutions with $c_{\text{Pu}} \geq 14 \text{ g L}^{-1}$ and $c_{\text{HNO}_3} \leq 4 \text{ mol L}^{-1}$, filling the conceptual reactor to a height of at least 17.0 cm.

Table 13

The intrinsic neutron source, prompt removal lifetime, and Hansen criteria for a solution with $c_{\text{Pu}} = 14 \text{ g L}^{-1}$ and $c_{\text{HNO}_3} = 4 \text{ mol L}^{-1}$, filling the conceptual reactor to a height of 17 cm.

Temperature (K)	S ($\times 10^4$ neutrons s^{-1})	τ_s ($\times 10^{-4}$ s)	Hansen criterion
293.6	7.61	9.9031 ± 0.0010	8.0607 ± 0.0009
374.0	7.06	9.3129 ± 0.0011	7.0325 ± 0.0008

Table 14

Basic system properties for the presented case study.

Property	Symbol	Value	Unit
Pu concentration	c_{Pu}	16.0	g L^{-1}
Nitric acid concentration	c_{HNO_3}	0.2	mol L^{-1}
Plutonium nitrate concentration	$c_{\text{Pu}(\text{NO}_3)_4}$	0.06686	mol L^{-1}
Mass fraction of HNO_3	m_{HNO_3}	0.01259	–
Mass fraction of H_2O	$m_{\text{H}_2\text{O}}$	0.98741	–
Hydrogen gas generation coefficient	G_{H_2}	7.766472×10^{-8}	mol J^{-1}
External temperature	T_{ext}	293.6	K
System pressure	p	0.101325	MPa
Initial solution volume	$V(0)$	0.385	m^3

8. Effect of step reactivity insertion on transient behaviour

8.1. System characteristics

Table 14 details the basic system properties used in the case study simulation. Two criticality transients are presented, with the following step reactivity insertion:

$$\Delta \epsilon_{\text{ext}}(t) = \begin{cases} 1.5 & \text{when } 0.5 \leq t \leq t_{\text{react}} \\ 0 & \text{otherwise.} \end{cases} \quad (141)$$

For the first transient (Case 1), $t_{\text{react}} = 3.0$ s, and for the second transient (Case 2), $t_{\text{react}} = 2.75$ s.

Both transients used a 50-cell discretisation for the 1D thermal hydraulics and radiolytic gas models, such that z_{25} indicates the location of the 25th cell in z .

8.2. Results

In both cases, the simulation terminates when the solution reaches 273.15 K and thus starts to boil. As shown in the right-hand graph of Fig. 25, this happens at 84.06 s and 769.25 s for Cases 1 and 2 respectively.

The left-hand graph of Fig. 25 depicts the variation in fission power and energy for both cases. As shown, the energy released from both transients is similar; around 131 and 145 MJ for Cases 1 and 2 respectively. However, due to the differences in reactivity insertion, the Case 1 transient experiences a much larger power peak of 650 MW compared to 41 MW in the Case 2 transient.

As demonstrated in Fig. 26, the positive reactivity feedback due to increased temperature is initially more prevalent in the Case 1 transient due to the longer period of reactivity insertion. As shown in Fig. 25, the average solution temperature increases to 331 K before the reactivity insertion is removed. This acts to increase the reactivity of the system which reaches a peak of 1.5 β at 3.0 s, whereas the maximum reactivity of the Case 2 transient is 1.2 β , which can be seen in Fig. 26.

Regarding the Case 1 transient, the larger power spike produces a large amount of dissolved hydrogen in the first 10 s, as depicted in left-hand graph of Fig. 27. Fig. 28 shows that, when the critical concentration is exceeded, this dissolved hydrogen nucleates into around 10 billion, relatively small, gas bubbles, the majority of which advect out of the system by around 52 s. As shown in Fig. 29, these bubbles create a system which is 23% voidage by volume, and results in the drop in total reactivity to -14.6β (as seen in Fig. 26).

Table 15

Basic system properties for the presented case study.

Property	Symbol	Value	Unit
Pu concentration	c_{Pu}	14.0	g L^{-1}
Plutonium nitrate concentration	$c_{\text{Pu}(\text{NO}_3)_4}$	0.05850	mol L^{-1}
External temperature	T_{ext}	293.6	K
System pressure	p	0.101325	MPa
Initial solution volume	$V(0)$	0.63	m^3

For the Case 1 transient, when the advection of gas bubbles out of the system dominates over the generation of more bubbles, the total reactivity increases, as shown in Figs. 26 and 28. This, coupled with a 0.4 β reactivity feedback due to an increased temperature, means that the total reactivity of the Case 1 transient exceeds 0 for a second time at around 43 s (as demonstrated in Fig. 26), causing the power to increase slowly to 2.5 MW, which in turn causes an increase in radiolytic gas generation (such that it dominates over gas loss due to bubble advection) and temperature increase, until boiling is observed (as demonstrated in Fig. 25).

For the Case 2 transient, the smaller initial power peak means the generation of radiolytic gas is delayed until 534 s, with the build-up of aqueous hydrogen occurring gradually until this point, as demonstrated in Fig. 27.

As shown in Fig. 28, the first onset of bubble nucleation in the Case 2 transient gives rise to fewer bubbles which have a larger radius (and thus advection velocity) than the initial bubbles of the Case 1 transient. The result is a smaller void fraction (as shown in Fig. 29), which corresponds to a smaller negative reactivity feedback (as shown in Fig. 26) when comparing the Case 2 transient to the Case 1 transient.

During the Case 2 transient, the oscillations in the bubble population, radius, and advection velocity (depicted in Fig. 28) are due to cycles of voidage loss due to advection dominating over voidage gain due to radiolysis, such that void fraction decreases, increasing reactivity (and thus power), resulting in voidage gain dominates over voidage loss, which reduces reactivity, and so on.

9. Effect of acidity on transient behaviour

9.1. System characteristics

Table 15 details the basic system properties used in this investigation. Several simulations were run, using solutions of various nitric acid concentrations.

All transients began with the same initial solution volume, with the following prescribed solution input and output from the vessel:

$$\dot{M}_{\text{in}}(t) = \begin{cases} 7.5 & \text{when } 0.0 \leq t \leq 100.0 \\ 0 & \text{otherwise,} \end{cases} \quad (142)$$

$$\dot{M}_{\text{out}}(t) = \begin{cases} 12.5 & \text{when } 50.0 \leq t \leq 100.0 \\ 0 & \text{otherwise,} \end{cases} \quad (143)$$

where $\dot{M}$ is measured in kg s^{-1} and t in seconds. Again, all transients used a 50-cell discretisation for the 1D thermal hydraulics and radiolytic gas models.

9.2. Results

Fig. 30 depicts the power profiles for the range of solution acidities investigated; it can be seen that the transients can be split into three separate behaviours.

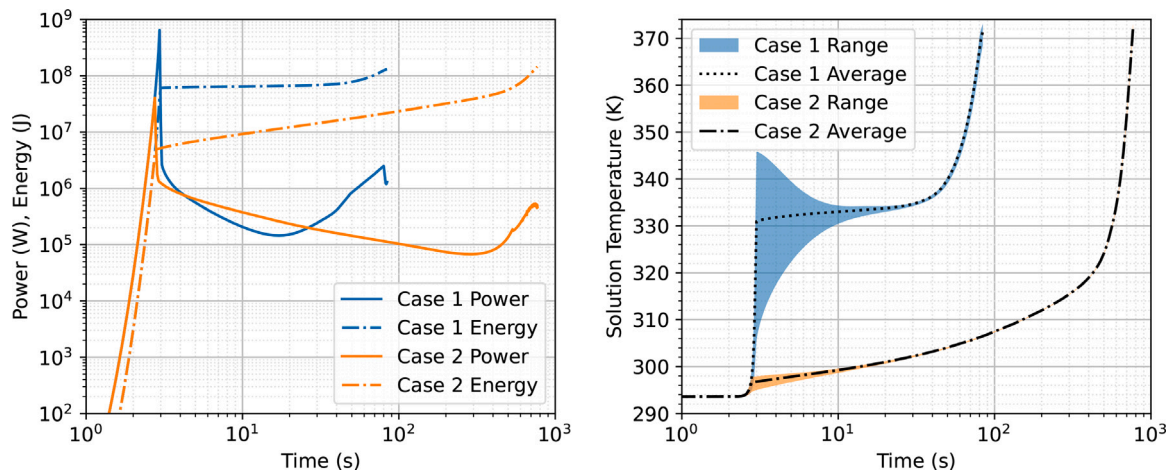


Fig. 25. The variation in fission power, fission energy, and solution temperature for both cases.

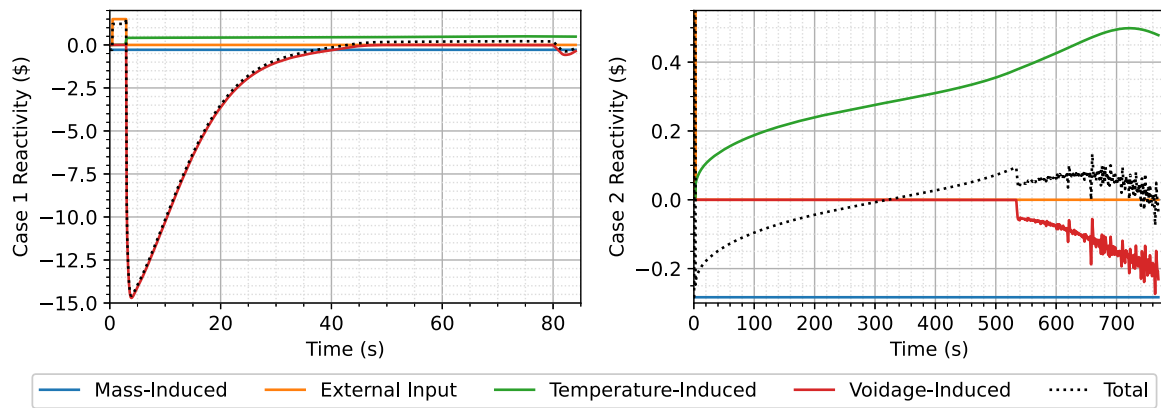


Fig. 26. The variation in reactivity components for both cases.

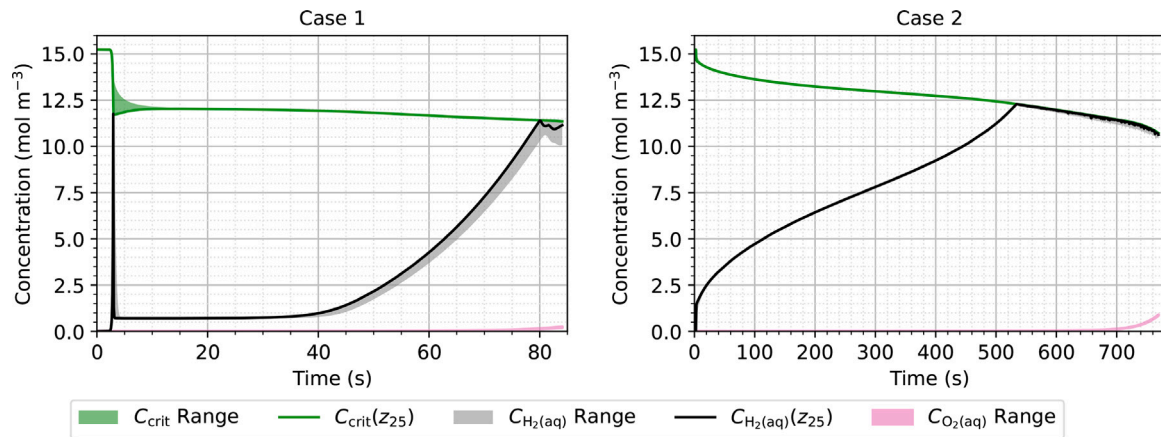


Fig. 27. Temporal variation in aqueous concentrations of hydrogen and oxygen, and the critical concentration, for both cases.

9.2.1. High-dilution behaviour

The left-hand graph of Fig. 30 shows that, for the most dilute solutions ($c_{\text{HNO}_3} \leq 0.2 \text{ mol L}^{-1}$), there is an initial power spike of between 0.50 and 1.37 GJ, occurring between 3.50 and 7.65 s of the simulation start time.

The initial power spike is due to the ingress of solution increasing the reactivity above 1 \$, as demonstrated by Fig. 31. The sudden decrease in reactivity which follows is due to the generation of radiolytic gas, as shown in Fig. 32.

As the radiolytic gas advects out of the system, the reactivity increases, until 50 s into the transient. At this point, the combined draining of void-bearing solution and ingress of void-free solution acts to decrease the overall voidage in the solution from 50 s to the end of the simulation, as demonstrated by Fig. 32.

For the solutions containing 0.1 and 0.2 mol L⁻¹ of HNO₃, the simulation is terminated when the solution starts to boil, at around 66 s, as shown in Fig. 33.

For the solution containing no excess acid ($c_{\text{HNO}_3} = 0.0 \text{ mol L}^{-1}$), the simulation continues until 81.6 s (when boiling begins, as shown in

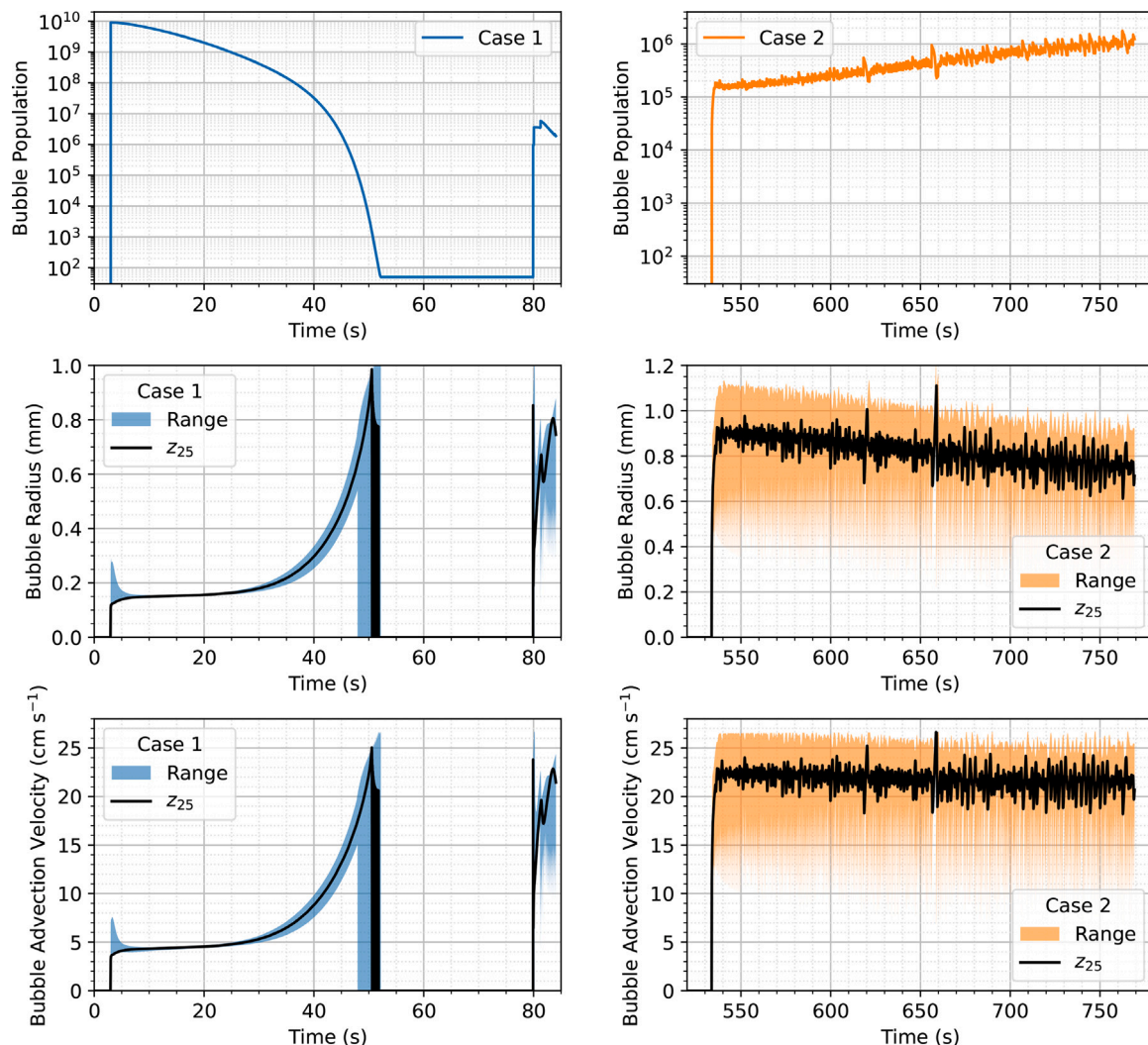


Fig. 28. Temporal variation in the properties of gaseous bubbles within the fissile solution for Case 1 (left-hand graphs) and Case 2 (right-hand graphs).

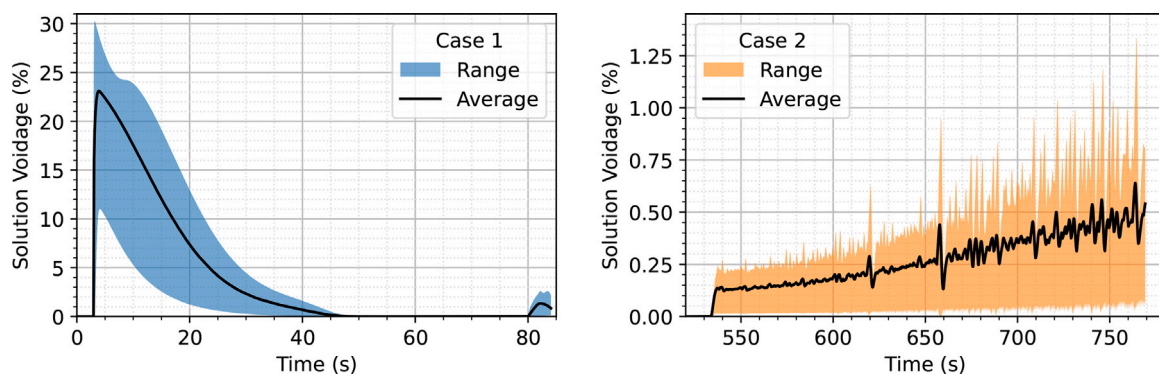


Fig. 29. Temporal variation in solution voidage for both cases.

Fig. 33). Between 60 and 81.6 s, oscillations in power, reactivity and voidage occur.

This is a result of the continued solution ingress/egress, and the cyclical loop of alternating voidage generation and voidage advection dominating over the other process (previously described in Section 8.2).

9.2.2. Mid-Dilution behaviour

For solutions of acidity in the range $0.3 \leq c_{\text{HNO}_3} \leq 1.5 \text{ mol L}^{-1}$, the transient is much simpler.

As solution enters the vessel, the reactivity increases, to a maximum of 2.106–3.067 \$ (depicted in Fig. 31), inducing a power spike in the range 0.04–36.62 GJ (depicted in Fig. 30). Due to the magnitude of the initial power peak, the simulation is almost immediately terminated due to the rapid onset of boiling (as shown in Fig. 33).

In most cases, the generation of radiolytic gas does not occur, due to the decrease in G_{H_2} , and increase in $H_{2\text{sol}}$, with increased solution acidity. However, for solutions containing 0.3 and 0.7 mol L⁻¹ of HNO₃,

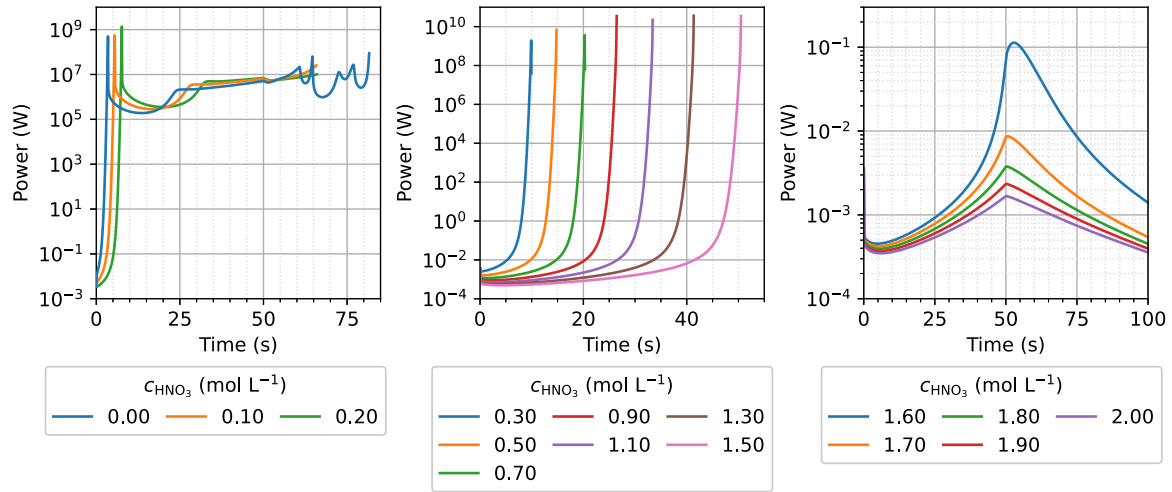


Fig. 30. Temporal variation in fission power with time, for a selection of acid concentrations.

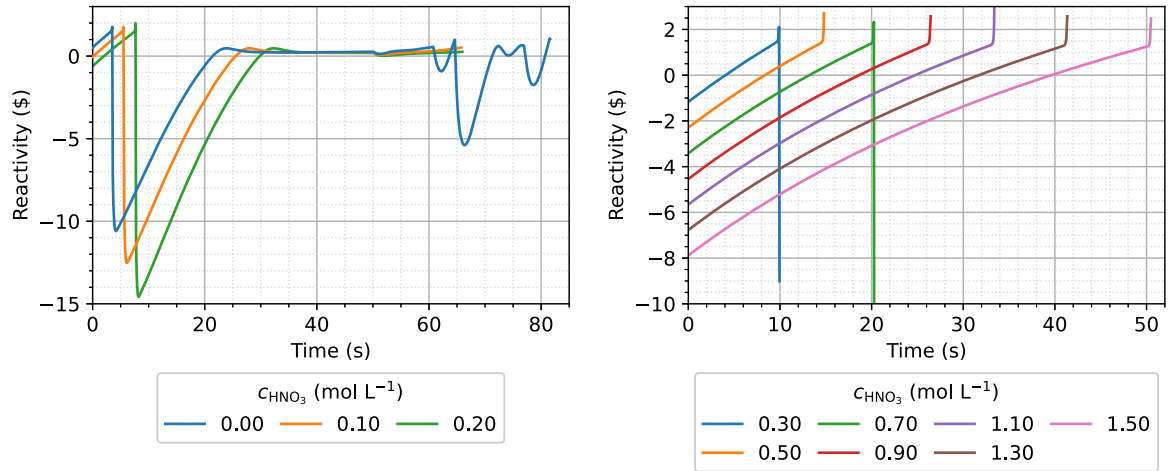


Fig. 31. Temporal variation in total reactivity with time, for a selection of acid concentrations.

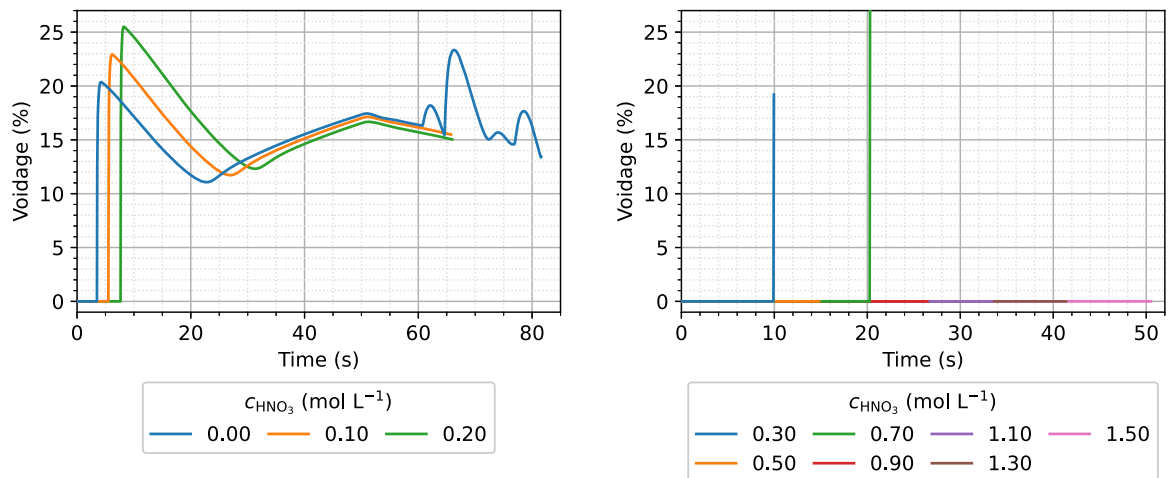


Fig. 32. Temporal variation in solution void fraction, for a selection of acid concentrations.

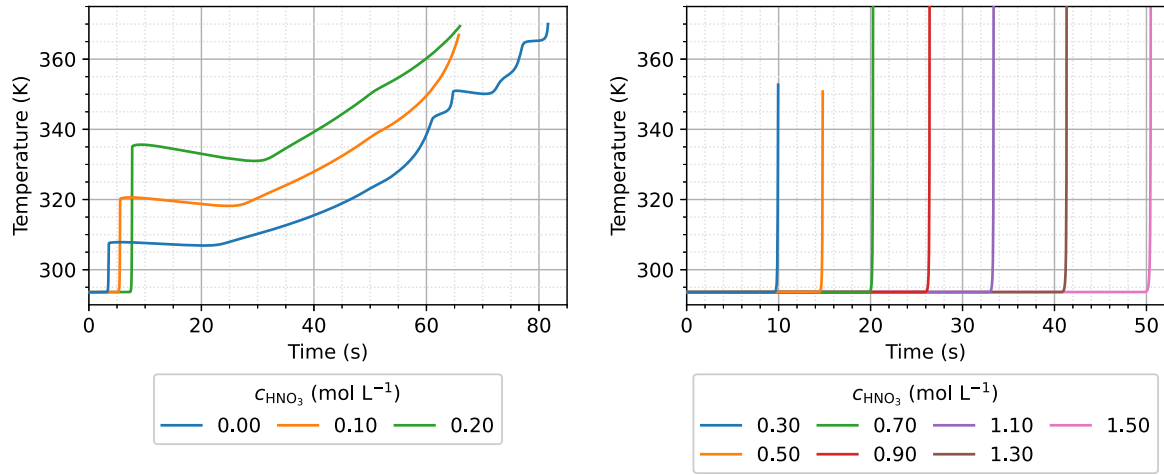


Fig. 33. Temporal variation in solution temperature, for a selection of acid concentrations.

Table 16

Basic system properties for the presented case study.

Property	Symbol	Value	Unit
Pu concentration	c_{Pu}	15.0	g L^{-1}
Nitric acid concentration	c_{HNO_3}	0.1	mol L^{-1}
Plutonium nitrate concentration	$c_{\text{Pu}(\text{NO}_3)_4}$	0.06268	mol L^{-1}
Mass fraction of HNO_3	m_{HNO_3}	0.00631	–
Mass fraction of H_2O	$m_{\text{H}_2\text{O}}$	0.99369	–
Hydrogen gas generation coefficient	G_{H_2}	1.096055×10^{-7}	mol J^{-1}
External temperature	T_{ext}	293.6	K
System pressure	p	0.101325	MPa
Initial solution volume	$V(0)$	0.465	m^3

radiolytic gas is generated, due to the smaller power spike increasing the time between peak power and the onset of boiling.

9.2.3. Low-Dilution behaviour

As shown in Fig. 30, solutions containing at least $1.6 \text{ mol L}^{-1} \text{ HNO}_3$ do not yield a significant amount of fission energy.

This is because increasing the acid molarity of a plutonium nitrate solution will result in a decrease in reactivity. As such, the addition of solution to the vessel results in a maximum reactivity of $0.691 \$$ when $c_{\text{HNO}_3} = 1.6 \text{ mol L}^{-1} \text{ HNO}_3$, decreasing to $-1.497 \$$ when the molarity increases to $2.0 \text{ mol L}^{-1} \text{ HNO}_3$. Due to the low fission yield, not enough energy is deposited into the solution to create radiolytic gas voids, or cause a notable temperature increase.

10. Effect of ramp reactivity insertion

10.1. System characteristics

Table 16 details the basic system properties used in this investigation. Several simulations were run, with ramp reactivity insertions described by:

$$\Delta \epsilon_{\text{ext}}(t) = \begin{cases} \frac{\xi_{\text{in}}}{t_{\text{in}}} t & \text{when } 0.0 \leq t \leq t_{\text{in}} \\ -\frac{\xi_{\text{in}}}{t_{\text{in}}} (t - t_{\text{in}}) & \text{when } t_{\text{in}} \leq t \leq 2t_{\text{in}} \\ 0 & \text{otherwise,} \end{cases} \quad (144)$$

where ξ_{in} is equal to $1.4 \$$, and t_{in} is varied between simulations. Again, all transients used a 50-cell discretisation for the 1D thermal hydraulics and radiolytic gas models.

10.2. Results

The behaviour of the transients can be categorised into four distinct groups: Group 1 has $t_{\text{in}} \leq 11 \text{ s}$, Group 2 has $t_{\text{in}} \approx 12 \text{ s}$, Group 3 has $13 \lesssim t_{\text{in}} \lesssim 42 \text{ s}$, and for Group 4, $t_{\text{in}} \geq 45 \text{ s}$.

Between groups 3 and 4, i.e. when $42 \lesssim t_{\text{in}} \lesssim 44 \text{ s}$, there is a region where transient behaviour transitions from Group 3 behaviour to Group 4 behaviour. For $t_{\text{in}} > 11 \text{ s}$, simulations terminated when the solution reaches 373.15 K (i.e. starts to boil).

10.2.1. Group 1

When $t_{\text{in}} \leq 11 \text{ s}$, as shown in Figs. 34 and 35, transients are characterised by a single, small ($<0.3 \text{ MW}$) power peak, occurring during the time range $t_{\text{in}} < t \leq 2t_{\text{in}}$, with no production of radiolytic gas, and a small increase in solution temperature.

10.2.2. Group 2

The second behaviour, occurring when $t_{\text{in}} \approx 12 \text{ s}$, has a slightly larger power peak (around 1.6 MW , demonstrated in Fig. 34), which induces a temperature increase significant enough to induce a positive reactivity feedback loop, demonstrated in Fig. 35.

For these transients, the production of radiolytic gas is delayed until some time after the initial power peak, due to the gradual build-up of aqueous hydrogen, demonstrated in Fig. 36. When gas begins to be produced, the trends in the gas properties, such as bubble quantity, average radius and average velocity, are accompanied by small oscillations or fluctuations with a relatively short time period.

When radiolytic gas begins to be generated, it is gradually produced up until the simulation is terminated (due to the onset of boiling), as demonstrated in Fig. 37. In addition, Fig. 38 shows that, once radiolytic gas bubbles are produced, their velocity remains relatively constant, though their average radii slightly decreases.

Fig. 39 shows that the solution temperature increases smoothly during the transient, corresponding to the roughly constant power and reactivity profiles presented in Figs. 34 and 35.

10.2.3. Group 3

As shown in Fig. 34, for the transients with $13 \lesssim t_{\text{in}} \lesssim 42 \text{ s}$, the power profiles are characterised by a relatively large ($\sim 100 \text{ MW}$) initial power peak, followed by a series of smaller power peaks, starting between 30 and 60 s after the initial peak, and lasting until the transient terminates due to the onset of boiling.

For these transients, the initial power peak induces the production of a large amount of radiolytic gas, with the subsequent peaks producing significantly less, as demonstrated by Figs. 37 and 38, and the corresponding negative reactivity feedback depicted in Fig. 35.

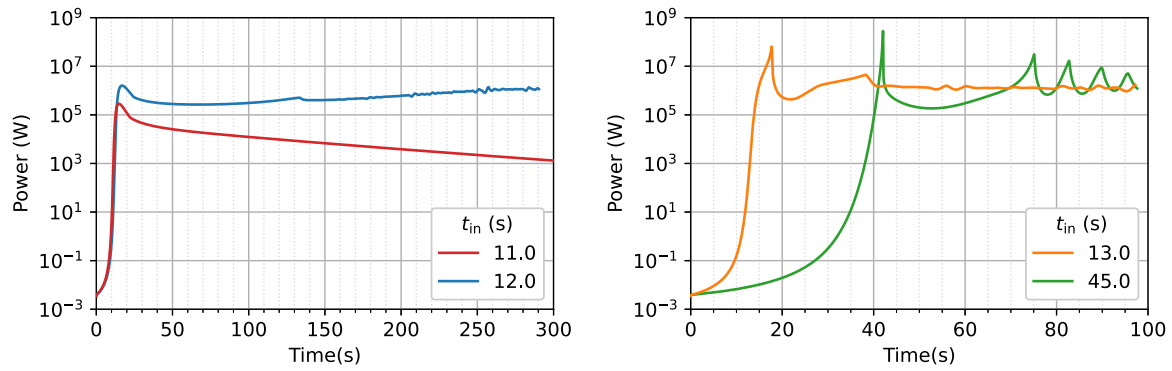


Fig. 34. Power profiles for transients displaying the four different behaviours.

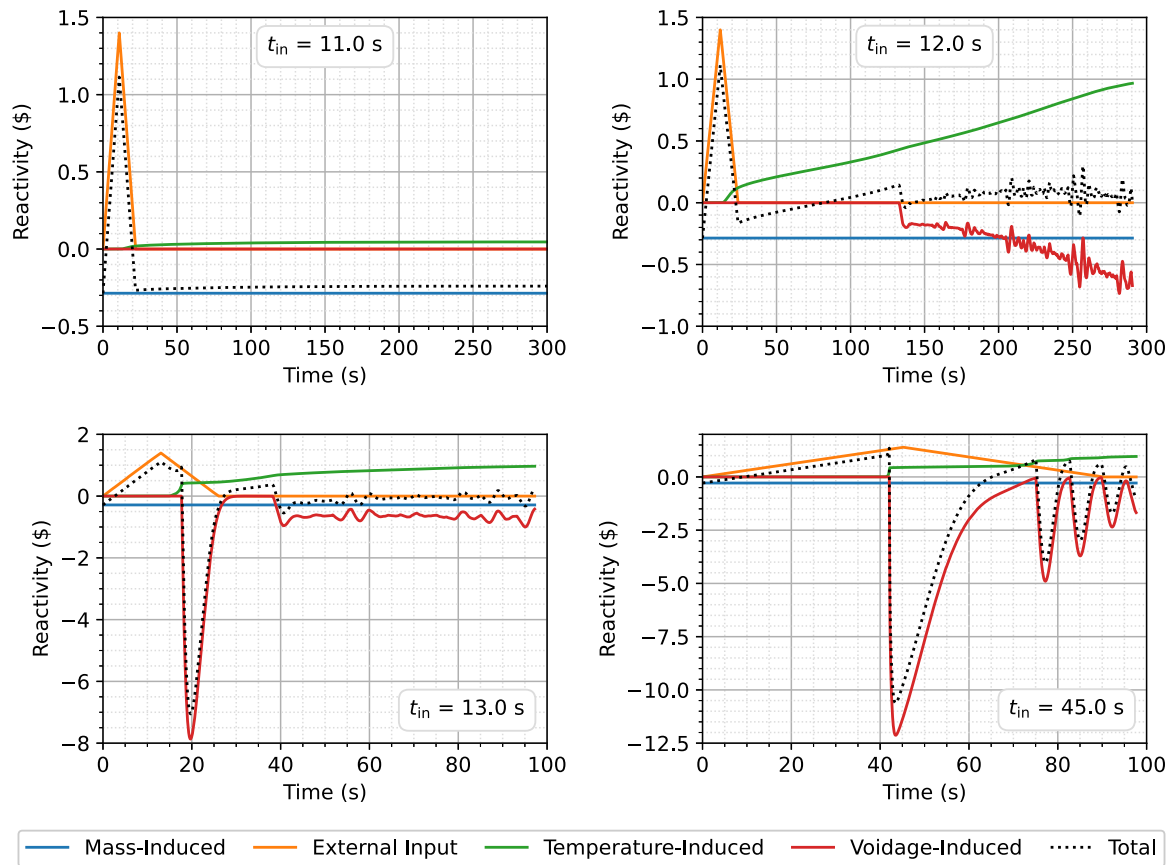


Fig. 35. Variation in total reactivity, and its constituents, for examples demonstrating the four groups of transient behaviour.

As shown in Fig. 36, once the critical hydrogen concentration has been exceeded the second time, the average hydrogen concentration remains very near the critical concentration for the remainder of these transients.

Finally, as shown in Fig. 39, these transients show two sharp increases in temperature, which occur during the first and second power peaks, followed by a steady increase in temperature until solution boiling begins.

10.2.4. Group 4

The transients with $t_{in} \geq 45$ s experience the largest initial power peaks (~ 280 MW), which produce the largest amount of radiolytic gas, causing the solution to reach around 20% voidage, as demonstrated by Fig. 37. This is because the solution spends more time at a reactivity > 1 \$, as shown in Fig. 35. Fig. 35 also shows that the initial peak in

reactivity occurs before the complete insertion of external reactivity, i.e. when $t < t_{in}$.

As shown in Fig. 34 these transients are characterised by larger (both in period and magnitude) oscillations in power, leading to distinct peaks in the concentration of aqueous hydrogen and solution voidage, in addition to bubble population, radius and velocity, as shown in Figs. 36–38, and a noticeably stepped temperature profile, displayed in Fig. 39.

11. Conclusion

This paper presented a novel methodology for simulating transient nuclear criticality excursions in aqueous solutions of dilute plutonium nitrate.

In Section 2, previous research regarding the positive temperature effect in dilute solutions was examined. This positive temperature effect

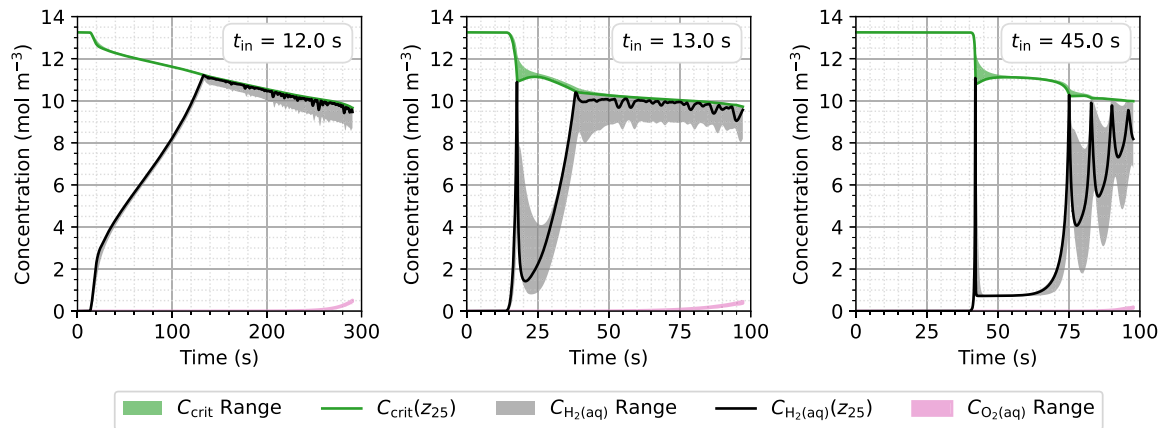


Fig. 36. Variation in aqueous concentrations of hydrogen and oxygen for the three example transients.

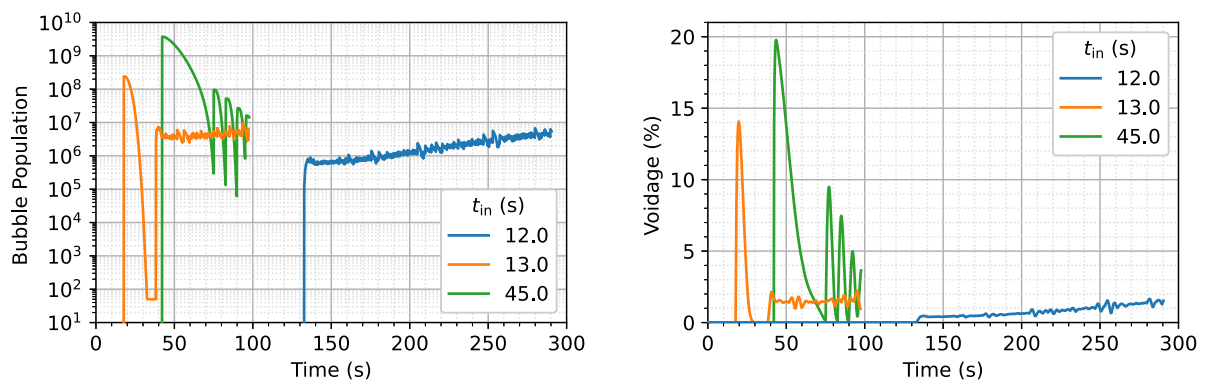


Fig. 37. Variation in bubble population and solution voidage for the three example transients.

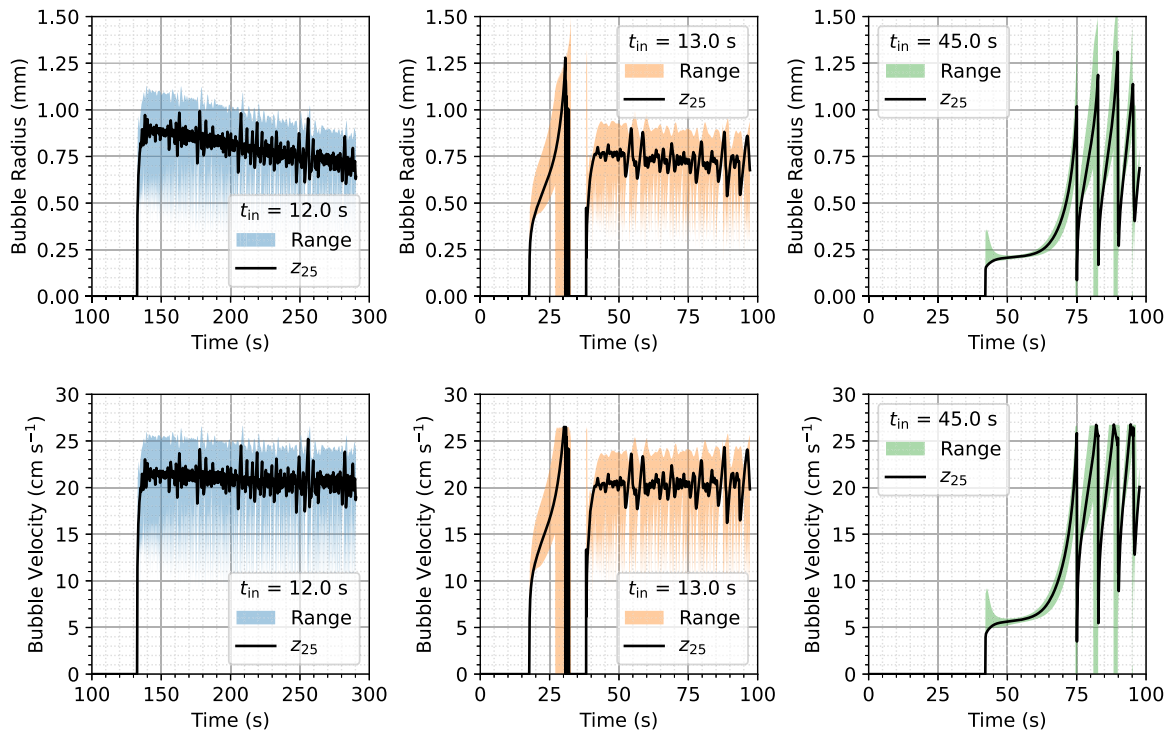


Fig. 38. Variation in bubble radius and velocity for the three example transients.

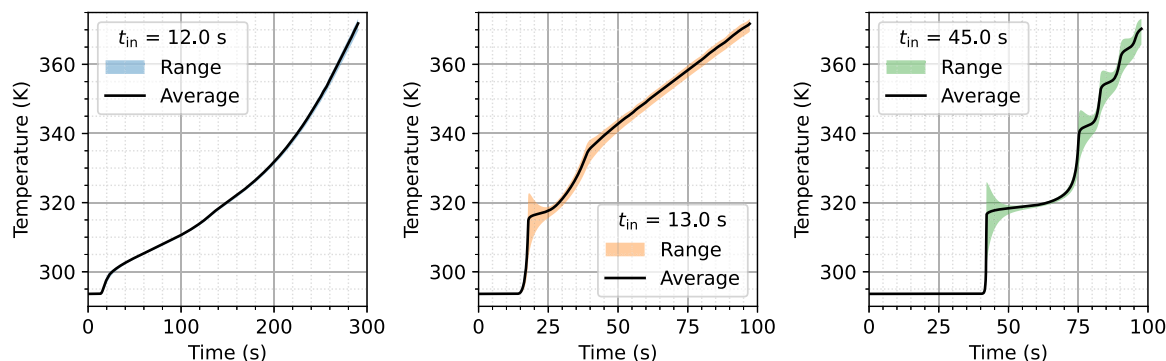


Fig. 39. Variation in solution temperature for the three example transients.

is due to a resonance at ≈ 0.3 eV in ^{239}Pu 's microscopic fission neutron cross section, and the shift of the neutron energy spectrum into this region when the temperature increases.

Simulations using MCNP revealed that increasing the plutonium or excess acid concentration reduced the positive temperature effect, and negative temperature effects were seen at the highest concentrations (e.g. 20 g L^{-1} of plutonium, or 4 mol L^{-1} of excess acid). This is because increasing either of these concentrations decreased the relative concentration of hydrogen in the system, reducing neutron moderation such that the neutron energy spectrum is already shifted beyond the cross section resonance at ≈ 0.3 eV. The same effect was had when increasing the inner radius of the solution vessel relative to the outer radius; increasing the vessel's outer radius decreased the rate of leakage from the well-moderated solution, whilst increasing the vessel's inner radius replaced the solution with air, making neutron moderation less effective. Decreasing the isotopic abundance of ^{239}Pu increased the positive temperature effect, due to the decrease in the relative probability of fission compared to other neutron interactions, effectively increasing neutron moderation such that the neutrons' energy spectrum was shifted into the range of the ≈ 0.3 eV resonance, increasing the positive temperature effect.

The transient model phenomenology was developed in Section 3. In addition to power and solution temperature, the concentration of radiolysis products in both the aqueous and gaseous phase, and the number of stable bubbles, were tracked. In this section, correlations describing the rates of hydrogen peroxide decomposition and stable radiolytic gas bubble formation were employed. As these correlations were derived from experimental data from uranium solutions, they impart some uncertainty in the results. As such, further research to perform sensitivity analysis and uncertainty quantification regarding these variables would increase the understanding of the model and subsequent results.

Sections 4 and 5 presented the determination of solution material properties and system heat transfer coefficients, which are needed by the transient model. Details regarding radiolysis, including radiolytic gas bubble nucleation (also needed by the transient model) were presented in Section 6. It was seen that the bubble nucleation radius varied notably with the acidity, temperature and pressure of the solution, and the LET of fission fragments, meaning the critical concentration of dissolved gas was also sensitive to these parameters. In later analysis, it was shown that the critical concentration greatly influenced the time and magnitude of initial power peaks in nuclear criticality transient scenarios, having implications for criticality safety.

The nuclear properties needed by the transient model were presented in Section 7. The mean neutron generation time decreased with increased plutonium concentration because of the corresponding increase in the fraction of fissile atoms. For the same reason, the reactivity and intrinsic neutron source increased with increased plutonium concentration. Conversely, increasing the solution's acidity had a negligible effect on the mean neutron generation time and intrinsic neutron

source because the abundance of fissile atoms remained constant. The reactivity decreased with increased solution acidity because the relative decrease in the abundance of hydrogen atoms decreased the rate of neutron moderation. Equations describing the change in mean neutron generation time and reactivity with solution temperature and voidage were derived.

For 38.5 L of solution with plutonium and excess acid concentrations of 16.0 g L^{-1} and 0.2 mol L^{-1} respectively, the effect of a step reactivity insertion on transient behaviour was investigated in Section 8. Increasing the step size from 2.25 to 2.50 s increased the initial power peak from 41 to 650 MW, and decreased the time to boil from 769 to 84 s. For the larger step size, the transient was characterised by an initial surge in radiolytic gas production, whilst the smaller step size induced a more constant (but lower) bubble population throughout the remainder of the transient.

In Section 9, the effect of solution acidity on transient behaviour was presented, for solutions with 14.0 g L^{-1} plutonium, with the same initial volume, and exposed to the same mass flow rates into and out of the system. As previously discussed, increasing the acidity of a plutonium nitrate solution decreases its reactivity. In addition, the amount of radiolytic gas produced per unit of fission energy decreases with increasing acidity because a higher proportion of the energy from the fission fragments were transferred to HNO_3 molecules (which have a lower tendency to decompose into gaseous molecules), compared to H_2O molecules, which decompose to give H_2 (directly) and O_2 (through the decomposition of H_2O_2). Thus, the solutions with acidity between 0.3 and 1.5 mol L^{-1} experienced the highest initial power peak due to the suppression of radiolytic gas production by the acid molecules. The initial power peak was smaller in solutions with lower acidity because of the decrease in reactivity caused by radiolytic gas production. The initial power peak was fully suppressed in solutions of higher acidity due to the reactivity never exceeding 0.7 \$.

As such, for solutions with an acidity $\leq 0.2 \text{ mol L}^{-1}$, the transient was characterised by an initial power spike, inducing a large amount of voidage which delayed the onset of boiling. When the acidity was increased to 0.3 to 1.5 mol L^{-1} , the solution boiled during the initial power peak, due to a lack of radiolytic gas required to reduce the system's reactivity. Increasing the acidity further meant the mass added to the solution was not enough to induce prompt criticality in the system (as such, the initial power peak was $< 0.2 \text{ W}$), and no radiolytic gas was produced.

Finally, Section 10 presented the effect of a ramp reactivity input rate on the criticality transient in a solution with plutonium and excess acid concentrations of 15.0 g L^{-1} and 0.1 mol L^{-1} . Four distinct behaviours of criticality transient were observed. For the steepest ramps, criticality was not maintained long enough (due to the rapid insertion/removal of reactivity) for an energetic transient with the production of radiolytic gas to occur. For slightly shallower ramps, the reactivity insertion induced a temperature increase, inducing the positive temperature effect, and giving rise to the delayed production

Table A.17

Isotopic composition of plutonium, as in Haeck et al. (2008).

Isotope	Weight (%)
²³⁸ Pu	0.1936
²³⁹ Pu	76.8064
²⁴⁰ Pu	20.7779
²⁴¹ Pu	1.1203
²⁴² Pu	1.1018

Table A.18

Isotopic compositions of plutonium used in the Fig. 6.

Isotope	Weight (%)	Weight (%)	Weight (%)	Weight (%)	Weight (%)
²³⁸ Pu	0.2	0.2	0.2	0.2	0.2
²³⁹ Pu	90.0	87.5	85.0	82.5	80.0
²⁴⁰ Pu	7.6	10.1	12.6	15.1	17.6
²⁴¹ Pu	1.1	1.1	1.1	1.1	1.1
²⁴² Pu	1.1	1.1	1.1	1.1	1.1

Table B.19The values of a_i in Eq. (115) used to determine $\Lambda(t)$.

i	a_i	i	a_i	i	a_i
1	1.812657E+02	10	-6.424223E-01	19	-4.746979E+04
2	5.233099E+03	11	-4.118703E+04	20	-5.438304E-03
3	-1.070060E+01	12	2.273030E+05	21	-2.257679E+04
4	5.450787E+00	13	6.779886E+00	22	-8.351378E+00
5	6.700835E+05	14	1.808841E-02	23	-8.895890E+01
6	2.093451E-01	15	7.796177E+02	24	5.882781E+02
7	-1.662971E+00	16	1.927435E-01	25	5.453529E+03
8	-3.311924E+02	17	2.990706E+02	26	2.479486E+00
9	-2.530037E+03	18	8.757540E+02	27	-1.497284E+02

Table B.20The values of a_i in Eq. (115) used to determine $\xi(t)$.

i	a_i	i	a_i	i	a_i
1	-1.912334E+02	10	9.205146E-01	19	-5.930783E+03
2	-1.617200E+04	11	1.825769E+05	20	1.729330E-03
3	2.116949E+01	12	-4.067347E+05	21	2.342249E+04
4	-1.404666E+01	13	-1.174410E+01	22	1.618644E+00
5	-3.830348E+06	14	-2.054794E-02	23	1.768618E+01
6	-4.231017E-01	15	-1.464126E+02	24	-5.385500E+02
7	5.639278E-01	16	-6.004816E-02	25	-4.921170E+02
8	5.403236E+02	17	-3.371154E+01	26	-5.760121E-01
9	-4.786210E+02	18	-3.596777E+03	27	2.788604E+01

of radiolytic gas. The shallowest ramps gave rise to more radiolytic gas being produced during the initial power spike, due to the reactivity insertion being maintained. Due to the large amount of radiolytic gas produced, the cyclical nature of the competing radiolytic gas generation and advection processes (i.e. clearer oscillations in solution voidage, power and bubble properties) were observed.

CRediT authorship contribution statement

J.R. Daniels: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **M.D. Eaton:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

In accordance with EPSRC funding requirements, all supporting data used to create figures in this paper may be accessed at the following DOI: [10.17632/696gzfd6py.1](https://doi.org/10.17632/696gzfd6py.1).

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Appendix A. Plutonium isotopic composition

See [Tables A.17](#) and [A.18](#).

Appendix B. Coefficients for determining Λ and ξ using Eq. (115)

See [Tables B.19](#) and [B.20](#).

Appendix C. Coefficients for determining $\Delta\Lambda_{th}$, $\Delta\Lambda_{rg}$, $\Delta\xi_{th}$ and $\Delta\xi_{rg}$ using Eq. (121)

See [Tables C.21–C.24](#).

Table C.21The values of b_i in Eq. (121) used to determine ΔA_{th} .

i	b_i	i	b_i	i	b_i	i	b_i	i	b_i
1	2.163504E-01	12	-2.224001E+04	23	9.403087E+00	34	-1.612640E-03	45	-3.784821E-01
2	-1.379168E+02	13	-5.141844E-01	24	-7.340364E+01	35	-2.417494E-01	46	-5.153258E+01
3	-3.010176E-02	14	-2.103773E-03	25	-6.480428E+02	36	-3.344172E+00	47	-5.569792E-06
4	-6.114934E-01	15	-7.998948E+01	26	-2.696837E-01	37	-7.703136E-04	48	-2.678667E+01
5	4.471650E+03	16	-1.905756E-02	27	1.828843E+01	38	1.216803E+01	49	-1.159924E-02
6	9.476253E-04	17	-3.718025E+01	28	-2.827157E-03	39	2.274922E+02	50	-9.592194E-02
7	1.623018E-01	18	1.898254E+01	29	1.945435E+00	40	7.352106E-03	51	7.639097E-01
8	1.703250E+01	19	5.577188E+03	30	4.118996E-04	41	2.243915E-05	52	6.047360E+00
9	3.157768E+02	20	5.473855E-04	31	6.460293E-03	42	8.054881E-01	53	2.778945E-03
10	7.281009E-02	21	2.593014E+03	32	-9.389590E+01	43	1.917944E-04	54	-1.712806E-01
11	-6.003514E+02	22	1.068317E+00	33	-1.314892E-05	44	3.990749E-01		

Table C.22The values of b_i in Eq. (121) used to determine ΔA_{rg} .

i	b_i	i	b_i	i	b_i	i	b_i	i	b_i
1	1.477844E+02	12	-5.433299E+06	23	1.609419E+03	34	-5.997951E+01	45	-4.600722E+04
2	7.069029E+03	13	-7.260016E+00	24	-2.125803E+04	35	-4.292881E+03	46	-6.265119E+06
3	-7.186775E+00	14	-2.053520E-01	25	-1.932893E+05	36	-1.477507E+05	47	-2.129184E-01
4	-5.218722E+01	15	-1.303828E+04	26	-4.835538E+01	37	-1.714388E+01	48	-2.800876E+06
5	2.212455E+06	16	-2.419642E+00	27	5.897516E+03	38	1.532336E+06	49	-5.280477E+02
6	1.240951E-01	17	-5.176101E+03	28	4.829836E+02	39	2.284741E+07	50	-5.706896E+03
7	1.954743E+01	18	8.471591E+03	29	3.730892E+04	40	1.282929E+02	51	8.376395E+04
8	-1.495998E+02	19	1.543946E+06	30	-3.465711E+01	41	5.027299E-01	52	7.718378E+05
9	4.136308E+04	20	7.275762E-02	31	1.410836E+02	42	4.701663E+04	53	1.690653E+02
10	6.685118E+00	21	6.917162E+05	32	-1.207495E+07	43	7.246905E+00	54	-2.322629E+04
11	-2.694620E+05	22	1.568023E+02	33	7.771354E-01	44	1.792099E+04		

Table C.23The values of b_i in Eq. (121) used to determine $\Delta \xi_{th}$.

i	b_i	i	b_i	i	b_i	i	b_i	i	b_i
1	1.603405E-01	12	1.510325E+03	23	-1.264308E+00	34	2.216210E-04	45	-8.512986E-02
2	-1.649100E+01	13	-4.234446E-02	24	1.171799E+01	35	-3.656695E-02	46	1.312523E+01
3	-1.273375E-02	14	2.620725E-04	25	1.511063E+02	36	1.442293E-01	47	1.008695E-06
4	5.219849E-02	15	8.683166E+00	26	4.277386E-02	37	6.826133E-05	48	3.688948E+00
5	-2.822544E+02	16	2.765307E-03	27	-5.111285E+00	38	3.109635E+00	49	1.060425E-03
6	2.602005E-04	17	2.968800E+00	28	-5.798110E-04	39	-2.011664E+01	50	1.473218E-02
7	-2.031708E-02	18	3.405696E+00	29	3.447266E-01	40	9.794328E-04	51	-1.382278E-01
8	1.653849E+00	19	-1.037302E+03	30	5.079778E-05	41	-2.395527E-06	52	-1.899592E+00
9	-1.723205E+01	20	-9.041063E-05	31	-4.353354E-04	42	-1.004658E-01	53	-4.991136E-04
10	-7.732993E-03	21	-3.036714E+02	32	-2.777460E+01	43	-3.071455E-05	54	6.377612E-02
11	-9.275485E+01	22	-1.095264E-01	33	-1.464075E-06	44	-2.771329E-02		

Table C.24The values of b_i in Eq. (121) used to determine $\Delta \xi_{rg}$.

i	b_i	i	b_i	i	b_i	i	b_i	i	b_i
1	-7.462113E+01	12	1.253115E+06	23	-3.861758E+02	34	2.026584E+01	45	-1.084744E+04
2	-3.943824E+03	13	-7.171266E+00	24	3.943118E+03	35	-2.021839E+03	46	7.759729E+05
3	3.479118E+00	14	1.178504E-01	25	3.203838E+04	36	4.573446E+04	47	6.422232E-02
4	3.299497E+01	15	3.389475E+03	26	1.088695E+01	37	1.179174E+01	48	4.608265E+05
5	1.492102E+05	16	9.016697E-01	27	-8.546809E+02	38	3.502502E+05	49	1.375396E+02
6	-7.142739E-02	17	1.776495E+03	28	-1.916743E+02	39	-4.415897E+06	50	9.214045E+02
7	-7.743888E+00	18	1.464471E+03	29	1.464794E+04	40	6.881087E+01	51	-1.178586E+04
8	2.614394E+02	19	-2.979221E+05	30	1.014951E+01	41	-3.331362E-01	52	-7.320388E+04
9	-1.541304E+04	20	-2.622807E-02	31	-1.048434E+02	42	-8.755953E+03	53	-2.388463E+01
10	-4.004812E+00	21	-1.425588E+05	32	-3.238736E+06	43	-2.293691E+00	54	1.641956E+03
11	-4.050066E+04	22	-5.067911E+01	33	-2.354336E-01	44	-5.061592E+03		

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