# An alternative conceptual model for radiolysis effects on chemical conditions in salt repositories

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***Abstract***

*The accurate prediction of actinide solubility in a deep geological repository is crucial for performance assessment (PA) calculations and the safety case. Previous assessments have relied on simplifying assumptions, such as the negligible impact of radiolysis on chemical conditions. However, the large plutonium inventory expected at the Waste Isolation Pilot Plant (WIPP) necessitates evaluating this assumption. Radiolysis in the WIPP repository can significantly alter chemical conditions, affecting the actinide source term and potentially compromising the chemical condition safety function. This study aims to evaluate the impact of radiolysis on chemical conditions and the actinide source term in the WIPP repository. We used the Geant4-DNA extension of the Geant4 Monte Carlo simulation toolkit to simulate the alpha radiolysis of water and the subsequent chemistry in the presence of scavengers. Time-dependent primary yields of radical anions and molecular species and the effects of scavenger species were quantified. Results show that nitrate, a known component in transuranic waste, decreased hydrogen yield and increased hydrogen peroxide relative to pure water. Current PA calculations ignore hydrogen peroxide generation and could be overestimating hydrogen yield.*

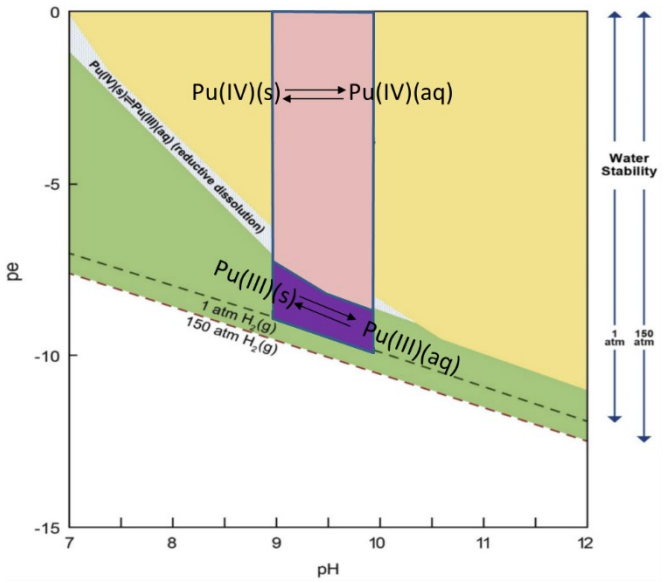
## Introduction

Performance assessment (PA) modelling is crucial for demonstrating compliance of the US Department of Energy's (DOE) Waste Isolation Pilot Plant (WIPP) with the US Environmental Agency's (EPA) radioactive waste disposal standards. This modelling must identify and evaluate significant events and processes that could impact repository performance, estimate radionuclide releases, and incorporate various uncertainties into a probability distribution function to meet regulatory standards. The WIPP PA includes various conservatisms to ensure that the assessments remain robust and reliable, even under uncertain conditions. Over time, PA must evolve from relying on professional judgment and simplified, scientifically acceptable, conservative models to evidence-supported ones that use more robust models and empirical data to reduce uncertainties.

Radiolysis, initially considered a minor concern, is one conservatism still in the WIPP PA. Radiolysis was screened out of the features, events, and processes (FEPs) in WIPP's first compliance certification application (CCA) because of the low consequence on long-term performance. The low consequence resulted from the much smaller amount of radiolytic hydrogen ($H_2$) generated compared to the anoxic corrosion of metallic iron ($Fe^0$) and the carbon dioxide ($CO_2$) from the microbial degradation of cellulose, plastic, and rubber (CPR). By extension, any radiolysis effect on the repository's chemical conditions was deemed negligible.

Anticipated changes in waste form, containers, radionuclide activity due to an additional 34 MT of plutonium slated for disposal, and facility design initiated a reassessment of the FEPs screening arguments on radiolysis. The radiolysis of brine and CPR was screeded into PA calculations but only as a source of $H_2$, with the impact limited to the water flow solution (Day, 2019). However, the radiolysis of water ($H_2O$) is known to generate several

other species besides $H_2$. Intermediate species may recombine to form $H_2O$ and different molecular species like $H_2$ and hydrogen peroxide ($H_2O_2$). Groundwater solutes and TRU waste components (e.g. organic complexants and oxyanions) may also act as scavengers and react with the intermediates to form new radical ions, altering the rate of generation




of $H_2$ and $H_2O_2$. Some radiolysis products are reducing species, and others are oxidising. Therefore, these species and their reactions could alter the engineered chemical conditions (e.g. $E_h$, pH) and thereby redox-sensitive reactions. Current predictions of actinide solubility and releases may be incomplete due to a limited understanding of the chemical conditions (Ward et al., 2024). A reassessment of the conceptual model governing chemical conditions is warranted.

## Current conceptual model

### *Chemical conditions*

In addition to geologic isolation by the salt host rock and shaft seals, the WIPP safety case depends on maintaining favourable thermodynamics. Favourable thermodynamics results from a pH "engineered" to be mildly alkaline ($9 \leq pH \leq 10$) and reducing conditions due to the anoxic corrosion of $Fe^0$. The lower redox boundary is defined by a negative logarithm of the electron activity ($pE \leq -7.5$). In contrast, the upper boundary is a $pE \leq 0$ (Fig. 1). Under these conditions, the most crucial long-term oxidation states for plutonium (Pu), the dominant actinide in WIPP TRU waste, are Pu(III) and Pu(IV) (Fig. 1).

**Figure 1. Plutonium aqueous and solid-phase stabilities under alkaline, reducing conditions in NaCl (3 m) and Pu (10-8 m), modified from Schramke et al. (2020).**

Table 1 shows the predicted solubilities of actinides (An) in the 3+ (An(III)) and 4+ (An(IV)) oxidation states for various brine volumes in the disturbed repository. The Salado and Castile brines represent end-member compositions used in experimental studies and PA calculations. Of these two brines, the Salado is more concentrated (I = 7 M) and less basic (pH = 6.5), with a lower concentration of magnesium ($Mg^{2+}$ = 1.02 M) and higher bromide ($Br^-$ = 0.027 M) and borate ($B(OH)_4^-$) = 0.158 M). The Castile brine is more dilute (I=5 M) and more basic (pH=8.9) with higher $Mg^{2+}$ (10.02 M), lower $Br^-$ (0.011 M), and $B(OH)_4^-$ (0.062 M).

**Table 1: Predicted solubility (mol/L) of Th(IV) and Am(III) for five brine end-member volumes.**

| WIPP Brine | Element | 1 × Minimum[3] | 2 × Minimum | 3 × Minimum | 4 × Minimum | 5 × Minimum |
|---|---|---|---|---|---|---|
| [1]Salado | Th(IV)(aq) | 5.34E-08 | 5.34E-08 | 5.34E-08 | 5.34E-08 | 5.34E-08 |
| | Am(III)(aq) | 3.40E-06 | 1.86E-06 | 1.33E-06 | 1.07E-06 | 9.09E-07 |
| | | | | | | |
| [2]Castile | Th(IV)(aq) | 5.73E-08 | 5.74E-08 | 5.75E-08 | 5.75E-08 | 5.75E-08 |
| | Am(III)(aq) | 3.51E-06 | 1.93E-06 | 1.39E-06 | 1.13E-06 | 1.33E-06 |

1. Brine from the Salado Formation at the repository level
2. Brine from the Castile Formation beneath the repository.
3. Based on a minimum brine volume of 33 804 $m^3$

In experiments to parameterise geochemistry models, Am(III) and Th(IV) are used as analogs for An(III) and An(IV), respectively. The mean An(III) solubility used in PA is one to two orders of magnitude higher than the mean An(IV) solubility (Table 1). The increase in Am(III) solubility with volume while Th(IV) remains constant is remarkable. The dominant Th(IV) complex for all brine volumes is $Th(OH)_4(aq)$, which contributes 85 percent to the total Th, with $Th(OH)_3(CO_3)^-$ contributing 15 percent. Neither complex is affected by dilution; only the organic complexes are. In the case of Am(III), AmEDTA- accounts for 92 percent of the total Am, whereas $Am(OH)_2^+$ accounts for 7 percent at the minimum brine volume. However, $AmEDTA^-$ accounts for 71 percent, whereas $Am(OH)_2^+$ accounts for 28 percent at the 5× dilution. Because EDTA is a much stronger complexant than hydroxide, the Am concentration decreases as the EDTA concentration decreases (Domski et al., 2023).

The EPA hypothesises that $H_2$ leads to extreme reducing conditions, causing Pu(III) to dominate (Shramke et al., 2020). However, PA calculations take no credit for the factors that could affect the upper redox boundary, pE ≤ 0 (Bynum et al., 2024). The current model assumes that primary radiolysis products react quickly with iron corrosion products and do not affect redox conditions. The model assumes that α radiolysis of brine generates $H_2$ at an average rate of 1.4 molecules per 100 eV (G-value); the G ($H_2O$) is then -1.4 molecules per 100 eV with the dissociation energy provided by $^{241}Am$, $^{238}Pu$, $^{239}Pu$, $^{240}Pu$ and $^{242}Pu$ (Day, 2019).

Researchers have modelled the system in the presence of $Fe^0$ and $H_2$ iron and hydrogen and concluded that the system is highly reducing, such that only Pu(III) exists (Bynum et al., 2024). The question then becomes whether Pu(III) or Pu(IV) controls the solubility within the thermodynamic model (Fig. 1).

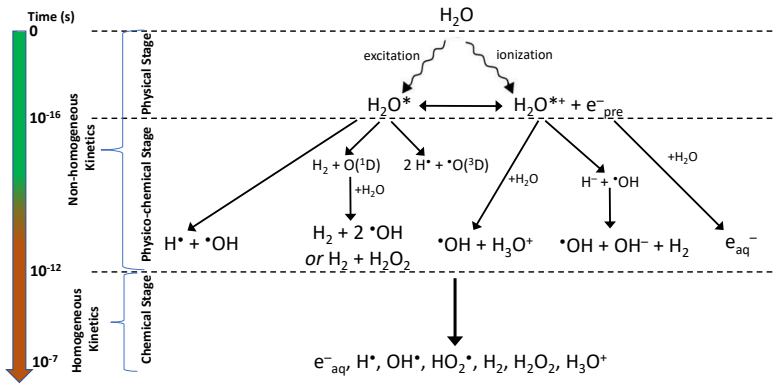
## Proposed conceptual model

### *Radiolysis effects on chemical conditions*

Radiolysis of water consistently produces a variety of chemical species, including hydrated electrons ($e_{aq}^-$) hydrogen radicals ($H^\bullet$), hydroxyl radicals ($^\bullet OH$), and hydronium ions ($H_3O^+$). These species may recombine to form $H_2O$ and molecular species like $H_2$ and $H_2O_2$ (Fig. 2). Water vapor in residual air shortly after repository closure may generate oxygen ($O_2$), nitrogen dioxide ($NO_2$), nitrogen monoxide ($^\bullet NO$), and nitric acid ($HNO_3$) (Morco et al., 2017). Solutes in groundwater may act as scavengers and react with the primary products in radical-transfer reactions to form dichloride ($Cl_2^{\bullet -}$), carbonate ($CO_3^{\bullet -}$), and sulphate ($SO_4^{\bullet -}$) radical anions. In the presence of dissolved oxygen ($O_2$), superoxide ($O_2^{\bullet -}$) and hydrogen dioxide ($HO_2^\bullet$) radicals may form (Spinks and Woods, 1990). Some products are reducing, e.g. $e_{aq}^-$, $H^\bullet$, $H_2$, and $O_2^{\bullet -}$ whereas others are oxidising, $^\bullet OH$, and $HO_2$, and $H_2O_2$. The ratio of radicals to molecular species depends on the linear energy transfer (LET) of the radiation with higher LET (e.g. α-radiation)

increasing the concentration of radicals and the probability of recombination, which leads to higher concentrations of molecular species (Laverne, 1996).

**Figure 2. Schematic of reactions and transient species produced by the irradiation of water without solutes after Ward et al. (2024).**




Transuranic waste contains oxyanions (e.g. $NO_3^-$, $PO_4^{3-}$, $SO_4^{2-}$) that can react with radicals and affect the formation of $H_2$ or $H_2O_2$. Aqueous nitrate ($NO_3^-$) scavenges $e_{aq}^-$ and is reduced to $NO_2$, which may react with oxidising species such as $^{\bullet}OH$ and $H_2O_2$ to regenerate $NO_3^-$. Organic solutes in aqueous solutions can also affect radical generation, forming $H_2$ and $H_2O_2$. When $Cl^- > 20$ mgL$^{-1}$, then $Cl^-$, rather than $H_2$, absorbs most of the energy to generate reactive radical (e.g. $Cl^{\bullet}$, $ClO^{\bullet}$) and non-radical (e.g. $Cl_2$, $Cl_3^-$, HClO, $ClO^-$, $ClO_2^-$, and $ClO_2$) species (Büppelmann et al., 1988).

The corrosion of $Fe^0$ releases $Fe^{2+}$ into the solution, and the resulting $Fe^{2+}/Fe^{3+}$ redox couple is critical to the chemical conditions. The $Fe^{2+}/Fe^{3+}$ couple is vital to both oxidising and reducing reactions with radiolysis products (Sutherland et al., 2017; Ward et al., 2024), i.e.

$$Fe^{2+} \underset{e_{aq}^-,\ O_2^{\bullet-},\ H^{\bullet},\ H_2}{\overset{OH^{\bullet},\ O_2,\ H_2O_2}{\rightleftharpoons}} Fe^{3+} \qquad \text{(Eq.1)}$$

Increasing evidence shows that the $Fe^{2+}/Fe^{3+}$ redox couple is essential in determining the Pu oxidation state. In synthetic WIPP brines, $Fe^0$ maintained reducing conditions, and $Pu(OH)_3$ solids were in equilibrium with dissolved Pu(III). As the system became less reducing, Pu(III) solids oxidised to Pu(IV), but Pu(III) remained in solution. In the presence of magnetite ($Fe_3O_4$), the system became more oxidising, and Pu(IV) became the dominant oxidation state. The persistence of less-reducing conditions is due to the accumulation of radiolysis products and organic complexants. An improved understanding of the effect of scavengers on the yields and time dependencies of radiolysis products is needed to account for the effects of radiolysis on chemical conditions.

## Simulating scavenger reaction with Geant4-DNA

Several proprietary codes have been developed, with slightly different capabilities, to simulate radiolysis. All require G-values as input, but data are sparse for repository conditions, which include high-ionic strength aqueous solutions at a mildly alkaline pH. The Geant4-DNA Monte Carlo toolkit is an extension of the open-source Geant4 simulation framework designed to model the interactions of ionising (alpha (α), beta (β), and gamma (γ)) radiation with biological matter.

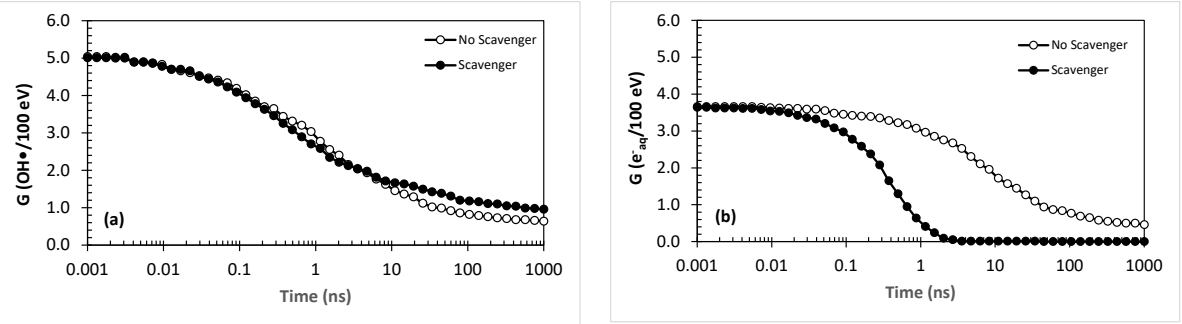
Geant4-DNA provides detailed modelling of electron elastic and inelastic interactions in $H_2O$, which is essential for simulating the initial physical interactions with radiation (Incerti et al., 2010). Geant4-DNA simulates the initial production of reactive species (Fig. 1) resulting from the interaction of radiation with $H_2O$ molecules. This stage significantly impacts the initial radiochemical yields of transient species. The toolkit models the diffusion of these species and their subsequent chemical reactions, leading to the formation of secondary radiolytic products (e.g. $H_2$, $H_2O_2$). Of particular importance to this work is the ability to incorporate the presence of various scavengers to study their influence on the radiolysis process (Chappuis et al., 2023). Geant4-DNA has incorporated independent reaction times (IRT), validation against experimental data, and updated pre-chemical models to simulate scavenger effects. These simulations are crucial for understanding the yields of reactive species under different radiation types, qualities, and scavenger concentrations. Although the two end-member WIPP brines are rich in chloride ions ($Cl^-$), known to scavenge radiolysis products, $Cl^-$ is not considered in this study. The focus is $NO_3^-$, a known component of TRU waste whose effect on chemical conditions and actinide releases is currently not considered in PA.

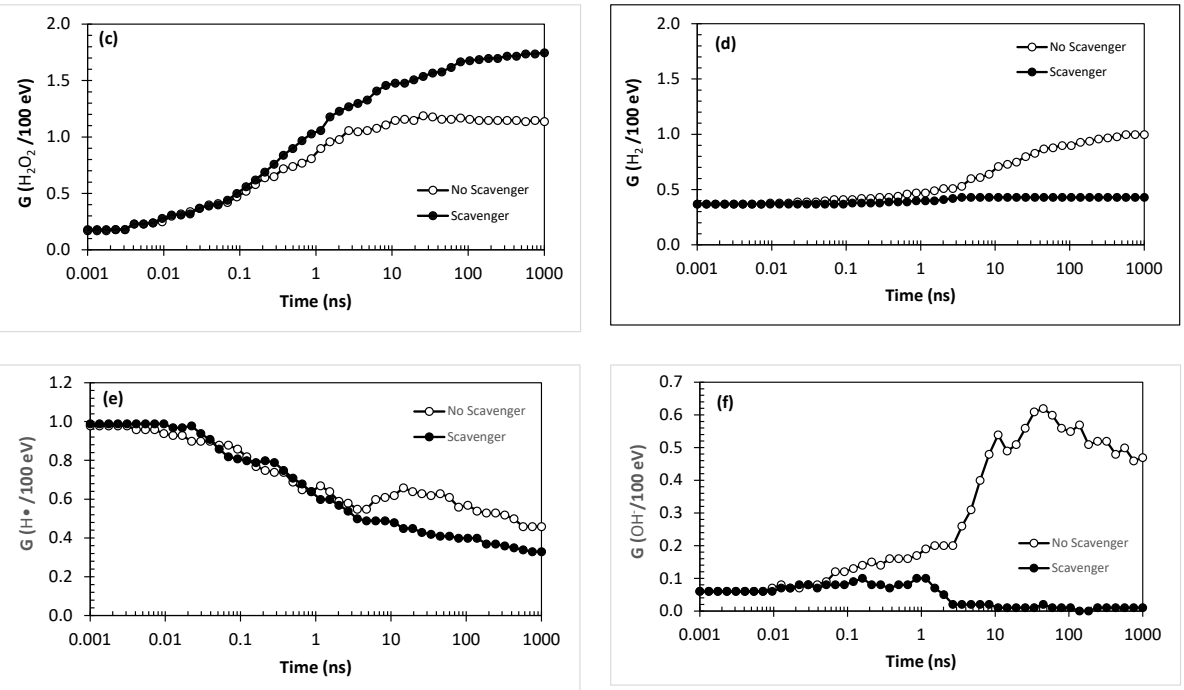
Geant4-DNA was used to assess the effect of nitrate ($NO_3^-$) on yields of radiolysis products, which could ultimately help to establish redox conditions in the closed repository. Following an intrusion, five volumes of brine dissolve the $NO_3^-$ inventory ($3.60 \times 10^5$ kg) for a direct brine release. The five brine volumes comprise factors of 1, 2, 3, 4, and 5 times the minimum volume of 33 804 $m^3$.

## Results

Figure 3 shows computed time-dependent G-values for selected radiolysis after α-irradiation with a $^{238}Pu$ (5.593 MeV) source. Each plot compares the G-value for pure water and an aqueous solution containing 0.18 mol/L of $NO_3^-$, which is the scavenger of interest. Nitrate had little effect on G(•OH) (Fig. 3a), but it is an effective scavenger for solvated electrons, $e_{aq}^-$ (Fig. 3b). The $e_{aq}^-$ typically reacts with the generated $H_2O_2$ to produce $OH^-$ and is responsible for most of its loss. However, aqueous $NO_3^-$ scavenges $e_{aq}^-$, protecting $H_2O_2$ from attack and increasing G($H_2O_2$) (Fig. 3c). The $e_{aq}^-$ also reacts with $H_2O$ to produce $H_2$ + $OH^-$ so scavenging by $NO_3^-$ reduces G($H_2$) (Fig. 3d) and G($OH^-$) (Fig. 3f). The decrease in G($OH^-$) resulted in an increase in $H_3O^+$ (not shown). Nitrate ions could compete with Pu in scavenging the precursors of $H_2$.

**Figure 3. Time evolution of G-values for α-particles (5.593 MeV) from $^{238}Pu$ in pure water and an aqueous solution containing $NO_3^-$, (a) •OH, (b) $e_{aq}^-$, (c) $H_2O_2$, (d) $H_2$, (e) H•, and (f) $OH^-$.**






## Conclusion

Current WIPP PA calculations account for the radiolytic generation of $H_2$ but ignore the generation of oxidising and reducing species. An incomplete chemical conditions model that ignores the contribution of oxidising and reducing products and the effect of scavengers on relative yield could influence predictions of actinide solubility and long-term releases. The proposed alternative conceptual model accounts for radiolysis, including the effects of scavengers on product yield and the effect of the radical and non-radical species on chemical conditions. Accounting for these effects requires an improved understanding of the effect of scavengers on the yields of radiolysis products as they will influence redox conditions.

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