

RAI Volume 3, Chapter 2.2.1.4.1, First Set, Number 2:

SAR Section 2.1.2.2 states that, “Sorption of dissolved radionuclides on corrosion products in the waste package... is a beneficial process of the EBS when the waste packages are breached.” Discuss the performance aspects of stationary corrosion products in terms of their impact on the timing and magnitude of plutonium release from the corrosion product domain. The discussion should include:

- The factors that control plutonium release from the stationary corrosion products and corrosion product domain. Controlling factors may include precipitation/dissolution reactions, solubility limits, sorption to colloids, pH, ionic strength, water flux, and mass of corrosion products
- A quantitative description of the timing and magnitude that these factors impact radionuclide release from the corrosion product and corrosion product domain
- Intermediate TSPA results corroborating the discussion of these interactions
- Release statistics/masses/concentrations for sorption to the corrosion products, release from the corrosion products and release from the corrosion product domain on a per waste package basis
- Consideration of the various scenarios (e.g. early failure, seismic, igneous, human intrusion)

This information is needed to better understand the role of corrosion products in limiting radionuclide release of plutonium in determining compliance with 10 CFR 63.114.

1. RESPONSE

In the total system performance assessment (TSPA) model, radionuclide transport through the waste package is conceptualized to occur in two spatially separated transport domains: the upstream waste form domain and the downstream corrosion products domain. Radionuclides from the waste form domain (also referred to as Cell 1) migrate via advection and/or diffusion into the downstream corrosion products domain (also referred to as Cell 2). The subsequent release of radionuclides from the corrosion products domain is predominantly to the invert, although there can be a small amount of back diffusion to the waste form domain (see Section 1.1.3 of the response to RAI 3.2.2.1.3.4-2-007).

Upon waste package breach, steel, which comprises a large fraction of the mass of the waste package, will begin to corrode. Within the corrosion products domain, steel degradation is

conceptualized to produce stationary corrosion products in the form of a porous medium. Stationary corrosion products primarily affect the timing and magnitude of plutonium release by:

- Sorption – Reversible sorption of plutonium onto the stationary corrosion products retards the release of plutonium from the corrosion products domain.
- pH Buffering – The presence of stationary corrosion products affects the in-package chemistry, primarily by preventing acidic pH values in the corrosion products domain after waste package breach. The correspondingly higher pH values in the corrosion products domain relative to the waste form domain causes plutonium to precipitate and plutonium-bearing colloids to become unstable and settle out in some realizations, both of which delay plutonium release.

Section 1.1 qualitatively discusses the effects of stationary corrosion products on plutonium release from the corrosion products domain. Section 1.2 presents selected TSPA results from the igneous intrusion and seismic ground motion modeling cases to demonstrate that sorption onto stationary corrosion products and pH buffering are the major processes impacting the release of plutonium from the corrosion products domain. These two modeling cases are the dominant contributors to the overall mean annual dose (SAR Figure 2.4-18). Analysis of results from early failure and human intrusion modeling cases would not add any additional insights.

1.1 PERFORMANCE ASPECTS OF STATIONARY CORROSION PRODUCTS

Iron oxyhydroxides comprise the great majority of the corrosion products and will dominate the sorptive properties of the corrosion products (SNL 2007, Section 6.3.4.2.1). Therefore, the corrosion products in the TSPA model are assumed to be iron oxyhydroxides, represented by a mixture of goethite and hydrous ferric oxide (SNL 2007, Section 6.3.4.2.3.1).

1.1.1 Sorption

The major factors affecting the sorption of plutonium to stationary corrosion products in the corrosion products domain are the model parameters directly used to represent the sorption of plutonium to the stationary corrosion products.

The degree to which plutonium sorbs to stationary iron oxyhydroxide corrosion products is determined in the TSPA model by a kinetic sorption model. The mass balance for the sorption of plutonium onto stationary iron oxyhydroxide corrosion products is given by:

$$\frac{\partial(\theta_w C_{sPu})}{\partial t} = Q_{is}^{kinetic} - Q_{iaq}^{kinetic} + i - d \quad (\text{Eq. 1})$$

where θ_w is the water content (volume of water per bulk volume), C_{sPu} is the sorbed plutonium concentration (mass of sorbed plutonium per volume of water), t is time, $Q_{is}^{kinetic}$ and $Q_{iaq}^{kinetic}$ are the plutonium sorption and desorption rates, respectively (mass of plutonium per (bulk volume \times time)), and i and d are terms representing plutonium ingrowth and decay, respectively

(SNL 2007, Equation 6.5.1.2-32). The sorption and desorption rates are calculated from the equations:

$$Q_{is}^{kinetic} = \rho_b \bar{s}_{CP} k_f C_{Pu} \quad (\text{Eq. 2})$$

and

$$Q_{iaq}^{kinetic} = \rho_b \bar{s}_{CP} k_r C_{sPu} \quad (\text{Eq. 3})$$

where ρ_b is the dry bulk density (mass of corrosion products per bulk volume), \bar{s}_{CP} is the specific surface area of the iron oxyhydroxide corrosion products (surface area per mass of corrosion products), k_f and k_r are the forward and reverse rates of the sorption reaction, respectively (volume of water per (surface area \times time)), and C_{Pu} is the aqueous plutonium concentration (mass of aqueous plutonium per volume of water) (SNL 2007, Equations 6.5.1.2-14 and 6.5.1.2-15).

The forward rate constant (k_f) is assigned a log uniform distribution with a range of 0.002 to 0.05 m³/m²/yr (SNL 2007, Section 6.5.2.4.6). This distribution is based on the results of time-dependent plutonium sorption experiments on colloidal suspensions of hematite and goethite. The reverse rate (k_r) is calculated by dividing the forward rate by the nondimensional plutonium distribution coefficient, K_d . The distribution coefficient is the ratio of the sorbed concentration to the aqueous concentration under equilibrium conditions. Because the K_d is also the ratio of the forward and reverse reaction rate constants, it also has a controlling influence on the ratio of the sorbed and aqueous plutonium concentrations under nonequilibrium conditions.

The plutonium distribution coefficient was estimated for the corrosion products domain using an equilibrium double-layer surface complexation model (SNL 2007, Section 6.5.2.4). This model was used to simulate competitive sorption of radionuclides onto goethite over the ranges of pH, CO₂ partial pressure, and concentrations of radionuclides and sorption sites expected in the domain. Conditions in the domain (e.g., surface site properties, carbon dioxide partial pressure, and aqueous radionuclide concentrations) were sampled across wide ranges using the Latin Hypercube Sampling methodology. This approach produced a set of 4,800 realizations that were evaluated by multiple regression to produce a function for calculating the sorbed plutonium concentration from the aqueous plutonium concentration and three other parameters. Based on the regression, the factors having a significant influence on the equilibrium sorbed plutonium concentration (C_{sPu}^{eq}) under the expected range of conditions are the concentration of sorption sites (C_s), the aqueous plutonium concentration (C_{Pu}), the aqueous concentration of uranium (C_U), and the partial pressure of CO₂ (P_{CO_2}). The resulting function is:

$$\log(C_{sPu}^{eq}) = a + b * pCO_2 + c * C_s + d * \log(C_U) + e * (\log(C_U))^2 + f * \log(C_{Pu}) \quad (\text{Eq. 4})$$

where:

$$p\text{CO}_2 = -\log(P_{\text{CO}_2} \text{ (bar)})$$

$$a = -2.0371$$

$$b = 0.6036$$

$$c = 0.9972$$

$$d = -0.9172$$

$$e = -0.0516$$

$$f = 0.9500.$$

Each aqueous and sorbed concentration in this equation has units of moles per liter of water (mol/L). The coefficient of variation (R^2) determined by the regression for this function is 0.946 (SNL 2007, Table 6.5-14). This model was validated by comparing the results to experimental measurements (SNL 2007, Section 7.2.3).

The independent parameters in the plutonium sorption equation affect the sorbed plutonium calculation in different ways. The concentration of aqueous plutonium (C_{Pu}) and the concentration of sorption sites (C_s) are strongly related to the sorbed plutonium concentration as indicated by the high values of the coefficients c and f . This relationship is expected because these parameters approximate the concentrations of the reactant species in the sorption reaction. The concentration of the product of the sorption reaction (C_{sPu}^{eq}) is directly and thermodynamically related to the reactant species concentrations. In addition, the concentration of sorption sites is important in limiting the amount of sorption that can occur. The sorption site concentration is a function of the steel corrosion rate, the corrosion product specific surface area, the sorption site density of the corrosion products, and the corrosion product mass per liter of water in the domain.

The aqueous concentration of uranium (C_U) in the plutonium sorption equation is important because under the expected conditions of the corrosion products domain, uranium effectively competes for sorption sites. Thus, this parameter is inversely related to plutonium sorption, as indicated by the negative signs of coefficients d and e .

The remaining parameter in the equation, $p\text{CO}_2$, affects the aqueous speciation of plutonium and uranium, which in turn affects their sorption to corrosion products. Consistent with the sign of the $p\text{CO}_2$ coefficient, as $p\text{CO}_2$ increases (i.e., as P_{CO_2} decreases), plutonium sorption increases. This relationship is the result of a lower proportion of aqueous plutonium carbonate species at higher $p\text{CO}_2$. The surface complexation model only simulates sorption of noncarbonate plutonium aqueous species (SNL 2007, Table 6.5-12).

Response surfaces defined by the equilibrium plutonium sorption equation are displayed in Figure 1.1.1-1 for the general ranges of values of the independent parameters in the TSPA realizations presented in Section 1.2. Figure 1.1.1-1(a) shows a strong dependence on the aqueous plutonium and surface site concentrations. It also shows, along with Figure 1.1.1-1(b), a limited but increasing inverse dependence on the aqueous uranium concentration as the aqueous uranium concentration increases. The increasing dependence with increasing aqueous uranium concentration is due to the second order term in the sorption equation. In addition,

Figure 1.1.1-1(b) shows the relatively small dependence on the CO₂ partial pressure. These response surfaces indicate that the sorbed plutonium concentrations exceed the aqueous plutonium concentrations by approximately three to five orders of magnitude for the ranges plotted.

Because the sorption and desorption of plutonium is described by a kinetic model, the ratio of the sorbed and aqueous plutonium concentrations in the corrosion products domain will not always correspond to the ratio established by the equilibrium distribution coefficient (K_d). Nevertheless, during periods in which the model predicts fairly steady sorbed and aqueous plutonium concentrations, the ratio of these concentrations will approximate the K_d . Under these conditions, ignoring ingrowth and decay, Equation 1 shows that the rates of sorption and desorption will be approximately equal.

During these periods of nearly steady concentrations of sorbed and aqueous plutonium, the retardation of plutonium in the corrosion products domain caused by sorption can be approximated. The retardation of plutonium in the corrosion products domain is a direct measure of the performance of the stationary corrosion products in delaying the release of plutonium. Figure 1.1.1-2 shows the calculated retardation of plutonium in the corrosion products domain under equilibrium or steady state conditions resulting specifically from sorption to stationary corrosion products for a CO₂ partial pressure of 10⁻³ bar and an aqueous plutonium concentration of 10⁻⁷ mol/L. The three lines in this figure correspond to the approximate minimum, maximum, and median surface site concentrations in the corrosion products domain. The retardation factor is calculated as one plus the ratio of C_{sPu}^{eq} (mol/L) to C_{Pu} (mol/L). Because the retardation factor due to sorption is a function of the ratio of the sorbed and aqueous plutonium concentrations and the sorbed and aqueous concentrations are highly correlated with one another, the retardation due to sorption has little sensitivity to the aqueous plutonium concentration. Figure 1.1.1-2 indicates that the surface site concentration and the aqueous uranium concentration are the major factors affecting the retardation of plutonium due to sorption in the corrosion products domain.

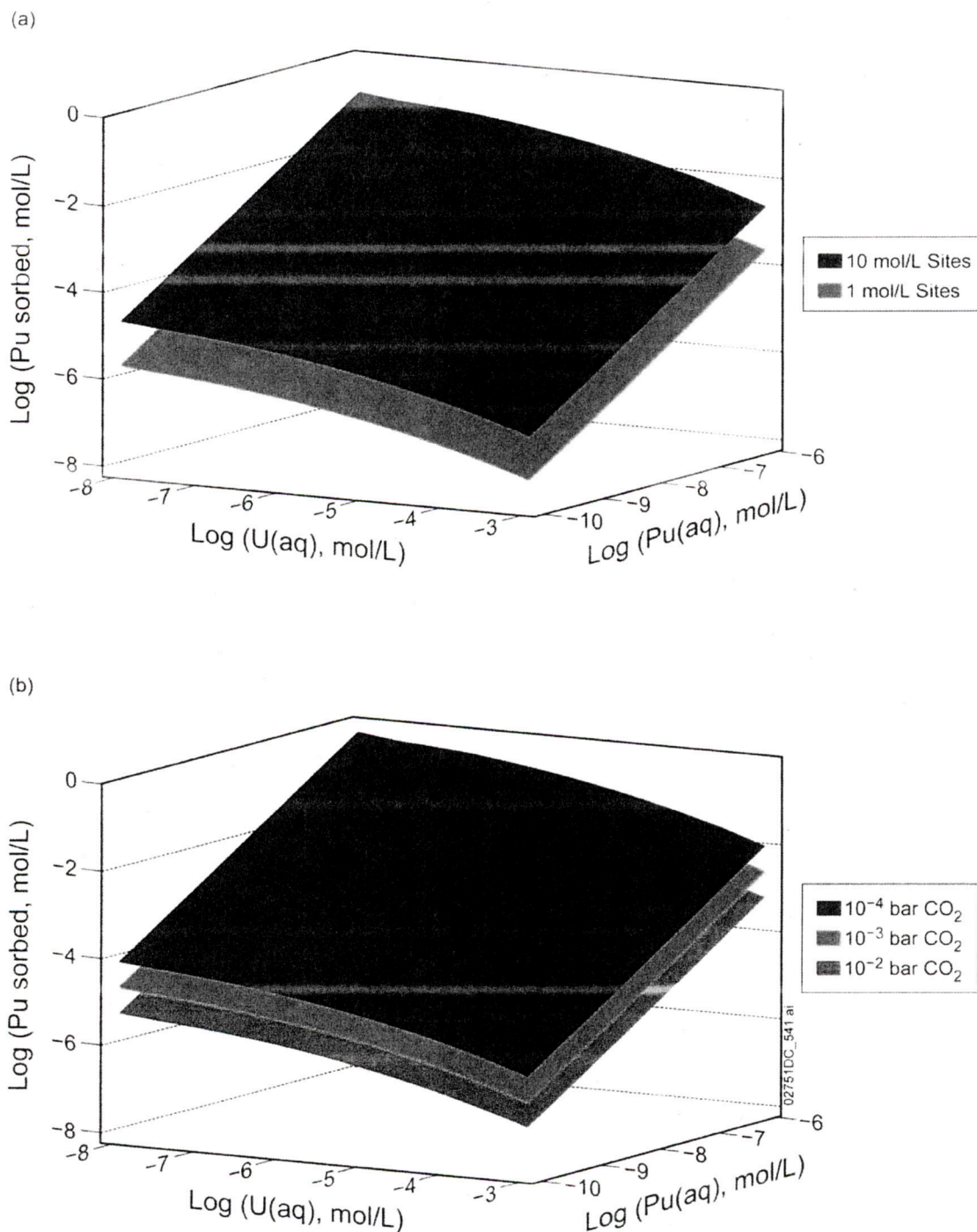


Figure 1.1.1-1. The log of the Equilibrium Sorbed Plutonium Concentration (a) as a Function of the logs of the Aqueous Concentrations of Uranium and Plutonium and the Surface Site Concentration ($P_{CO_2} = 10^{-3}$ bar) and (b) as a Function of the logs of the Aqueous Concentrations of Uranium and Plutonium and P_{CO_2} (surface site concentration = 10 mol/L)

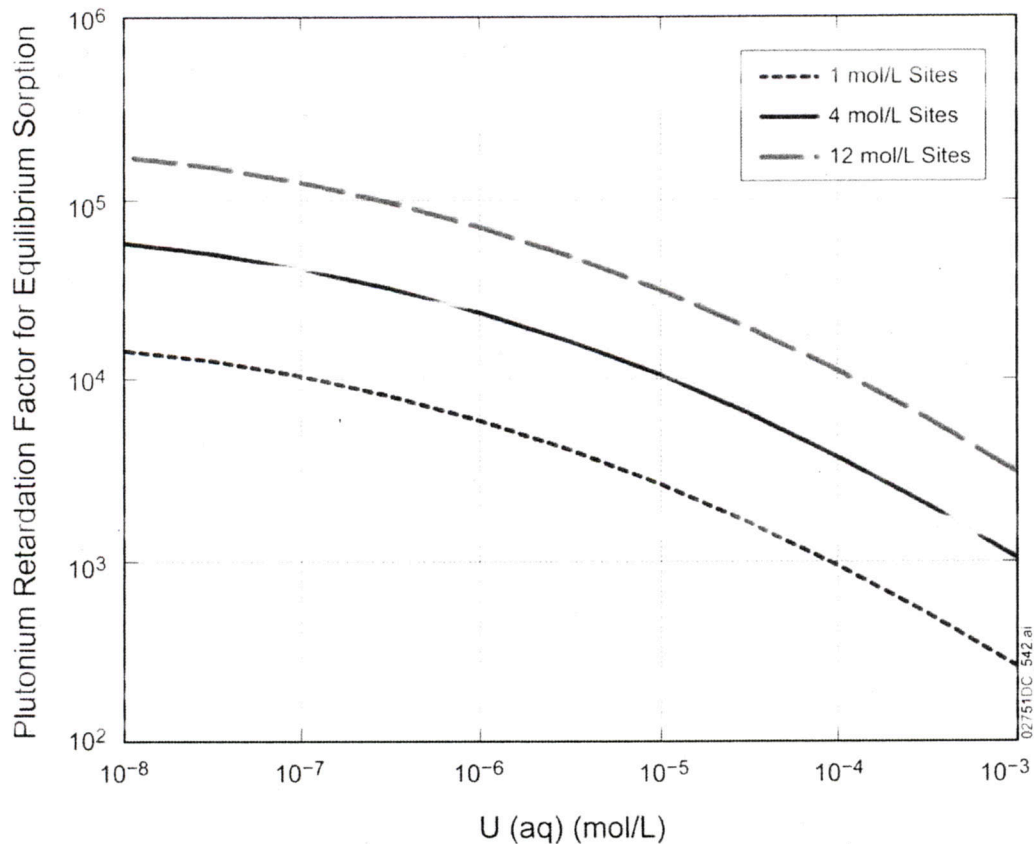


Figure 1.1.1-2. Plutonium Retardation Factor for Equilibrium (or Steady State) Sorption to Stationary Corrosion Products in the Corrosion Products Domain as a Function of Aqueous Uranium Concentration and Total Site Concentration for an Aqueous Plutonium Concentration of 10^{-7} mol/L and a Carbon Dioxide Partial Pressure of 10^{-3} bar

1.1.2 pH Buffering

In addition to sorbing radionuclides, the stationary corrosion products in the corrosion products domain sorb protons. The overall effect of this sorption is to buffer the pH in the corrosion products domain between approximately 7 and 8.4 when stationary corrosion products are present (see Figures 1.2.1-12 and 1.2.2-12). Under certain conditions in the corrosion products domain (i.e., in some TSPA realizations), this pH buffering causes plutonium entering from the waste form domain, where the pH range is about 4.9 to 8.3 (see Figures 1.2.1-11 and 1.2.2-11), to precipitate and plutonium-bearing colloids to become unstable and settle. In realizations where pH buffering increases the pH in the corrosion products domain relative to the waste form domain, these effects reduce the overall release rates of plutonium from the corrosion products domain.

Plutonium precipitation occurs when the equilibrium aqueous concentration would otherwise exceed the aqueous solubility of plutonium. Differences in pH between the waste form domain and the corrosion products domain can cause the solubility of plutonium to be lower in the

corrosion products domain than in the waste form domain. The excess aqueous plutonium will precipitate in the corrosion products domain and the aqueous plutonium concentration will be fixed at the solubility limit as long as the precipitate is present. The release of plutonium from the corrosion products domain is thus retarded by plutonium precipitation because the precipitated mass is immobile until it re-dissolves. However, significant sorption of plutonium to stationary corrosion products can limit plutonium precipitation in the corrosion products domain by reducing the plutonium aqueous concentration below the plutonium solubility. Plutonium precipitation over time is shown in Section 1.2 for specific realizations of the igneous intrusion and seismic ground motion modeling cases. The pH buffering effect of the stationary corrosion products on the commercial spent nuclear fuel (SNF) waste form and iron oxyhydroxide colloids is to reduce their stability (see the response to RAI 3.2.2.1.3.4-2-003). Plutonium-bearing commercial SNF waste form colloids that are mobile in the waste form domain settle in the corrosion products domain. These colloids are unstable in the buffered pH range of the corrosion products domain at any ionic strength. As described in the supplemental response to RAI 3.2.2.1.3.4-2-007, in certain realizations this effect results in the immobilization of a significant mass of plutonium irreversibly associated with commercial SNF waste form colloids in the corrosion products domain and decreases the overall plutonium release rates. Plutonium-bearing iron oxyhydroxide colloids are stable only at low ionic strength in the pH range of the corrosion products domain; however, only a small mass of plutonium is associated with iron oxyhydroxide colloids.

Plutonium precipitation and pH buffering also have lesser secondary effects on plutonium sorption to stationary corrosion products. The precipitation of plutonium limits the plutonium sorbed to stationary corrosion products by limiting the aqueous concentration to the plutonium solubility limit. Thus, plutonium precipitation sets an upper limit on the retardation due specifically to sorption to stationary corrosion products. However, precipitation does not limit the overall plutonium retardation in the domain because it increases the ratio of immobile to mobile plutonium in the domain above the ratio predicted by the distribution coefficient, K_d .

The pH buffering by stationary corrosion products also affects uranium solubility, which can limit the aqueous uranium concentration in the corrosion products domain. The aqueous concentration of uranium is important to plutonium sorption because uranium competes with plutonium for sorption sites (Figure 1.1.1-2). This effect is accounted for in the TSPA model by including the aqueous uranium concentration in the plutonium sorption equation. However, precipitation of uranium is rare in the corrosion products domain and therefore has little or no effect on plutonium sorption or release.

1.1.3 Secondary Effects

A secondary effect of stationary corrosion products that enhances plutonium transport is increased diffusion of plutonium from the waste form domain to the corrosion products domain. Sorption and precipitation of plutonium in the corrosion products domain increases diffusion from the waste form domain because these processes reduce or limit the aqueous concentration in the corrosion products domain. Lower aqueous concentrations generate larger concentration gradients to drive diffusive transport. This secondary effect can significantly increase the release

of plutonium from the waste form domain, especially when there is low or no advective transport from the domain.

The water flux is an independent factor that can affect the retardation of plutonium within the corrosion products domain. A high water flux can skew the shape of the plutonium release curves because plutonium sorption and desorption are kinetically limited. However, as shown in the response to RAI 3.2.2.1.3.4-2-009, the kinetic limitations on plutonium sorption and desorption are not significant enough to cause a significant departure from local equilibrium conditions in the TSPA model. Thus, in the TSPA model the water flux does not directly affect plutonium retardation in the corrosion products domain.

An indirect way the water flux can affect the sorption of plutonium is by affecting the ionic strength, which can affect the solubility of plutonium and uranium and the stability of plutonium-bearing colloids. However, effects on solubility are limited only to cases where aqueous concentrations are near or equal to solubility limits, and in those cases the effect is to set an upper limit on the sorbed concentration. The effects of ionic strength on colloidal stability are negligible for the narrow pH range of the corrosion products domain (see the response to RAI 3.2.2.1.3.4-2-003).

1.2 TSPA RESULTS

This section provides a quantitative description of the effects of stationary corrosion products on the timing and magnitude of plutonium release from the corrosion products domain using information extracted from the TSPA model, supplementing previously documented results. Specifically, TSPA results from the 1,000,000-year igneous intrusion modeling case and the 1,000,000-year seismic ground motion modeling case are described. These two modeling cases are the dominant contributors to the overall mean annual dose (SAR Figure 2.4-18).

For each modeling case, 300 realizations of the epistemically uncertain parameters are used with fixed event times (i.e., no aleatory uncertainty). For the 1,000,000-year igneous intrusion modeling case, the igneous intrusion event time is fixed at 100,000 years. For the 1,000,000-year seismic ground motion modeling case, the fixed event sequence is the same as for TSPA model realization 4,641; seismic events simulated in this realization are shown in SAR Figure 2.4-92. The sampled epistemically uncertain parameter values used for this analysis are the same as those used for the TSPA-LA analysis presented in *Total System Performance Assessment Model /Analysis for the License Application* (SNL 2008). Model results are typically shown as horsetails (all 300 realizations) with ensemble statistics (mean, median, 5th and 95th percentiles). These results include plutonium cumulative releases, plutonium release rates, plutonium mass distributions between mobile and stationary/immobile phases, mass of corrosion products, and pH.

In both modeling cases, plutonium behavior is represented by the transport of ^{242}Pu from commercial SNF waste packages in the seeping environment of percolation subregion 3. Percolation subregion 3 contains 3,285 commercial SNF waste packages, which is 40% of the total number of commercial SNF waste packages modeled to be in the repository. Locations in percolation subregion 3 are associated with the middle 40% of the expected range of percolation

values. The TSPA model segregates the waste packages in a percolation subregion into seeping and non-seeping environments. Waste packages in a seeping environment may experience dripping from seepage and condensation, whereas waste packages in a non-seeping environment may experience dripping from condensation only or may be in a non-dripping location.

The seepage fraction (i.e., fraction of waste packages in the seeping environments) varies over realizations, waste package types, and modeling cases. After an igneous intrusion event, percolation flux is applied to all waste package locations, including those previously identified as non-seeping, and the seepage model is no longer used. Thus, after the event, advective flux occurs in all locations, and the Engineered Barrier System (EBS) behavior in the seeping and non-seeping environments is similar. Therefore, mass fluxes and masses in place are reported only for waste packages in the seeping environment. Because the number of waste packages in this environment is defined by the seepage fraction, which varies between realizations, results are presented per waste package, to obtain quantities comparable among realizations.

For the igneous intrusion modeling case, the post-10,000-year mean (averaged over the 300 epistemic uncertainty values) seepage fraction for commercial SNF waste packages in percolation subregion 3 is 0.4369 (see SAR Table 2.1-7; note that the seepage fraction for the igneous intrusion modeling case is the same as for the nominal modeling case), corresponding to a mean value of 1,435 commercial SNF waste packages in the seeping environment of percolation subregion 3. For the seismic ground motion modeling case, the post-10,000-year mean seepage fraction is 0.7193 (see SAR Table 2.1-9), corresponding to a mean value of 2,363 commercial SNF waste packages in the seeping environment of percolation subregion 3.

Commercial SNF waste packages contain greater than 99% of the total initial ^{242}Pu inventory (SAR Table 2.3.7-5). The mean (averaged over the 300 epistemic uncertainty values) initial ^{242}Pu mass in a commercial SNF waste package is 6,142.5 g. ^{242}Pu has a half-life of 375,000 years; about 84% of the total mass of ^{242}Pu decays within 1,000,000 years. The ^{242}Pu mass released from the waste form partitions into several phases, including aqueous ^{242}Pu (dissolved and reversibly sorbed onto colloids), ^{242}Pu irreversibly attached to waste form colloids (designated Ic), and ^{242}Pu irreversibly attached to iron oxyhydroxide (FeO_x) colloids (designated If). Fractions of these ^{242}Pu masses may be immobile at various times—precipitated mineral phases in the case of aqueous ^{242}Pu and flocculated (settled or unstable) waste form and/or FeO_x colloids in the case of irreversibly sorbed ^{242}Pu .

1.2.1 1,000,000-Year Igneous Intrusion Modeling Case

In the igneous intrusion modeling case, all drip shields and waste packages are assumed to be completely failed as a result of the igneous intrusion event, and thereafter present no barrier to water flow. In addition, all waste forms are assumed to be instantaneously degraded (i.e., all of the mass is exposed) at the time of the event (SAR, pg 2.3.11-33). Immediately following the event, there is a short (100 years or less) thermal perturbation caused by the magma intrusion that prevents radionuclide releases for as long as the waste package temperature is greater than 100°C , the modeled boiling point of water (i.e., liquid water cannot contact the waste during this time).

For the 1,000,000-year igneous intrusion modeling case, the expected annual dose for each epistemic uncertainty vector is calculated from ten aleatory uncertainty vectors, corresponding to ten different igneous intrusion event times ranging from 250 years to 800,000 years, using the techniques outlined in *Total System Performance Assessment Model/Analysis for the License Application* (SNL 2008, Appendix J, Section J7.2). For this analysis, an igneous intrusion event time of 100,000 years was selected to best isolate key EBS behavior subsequent to an igneous intrusion event. All dependent variables or quantities analyzed in the following discussion (e.g., cumulative releases or release rates) are conditional on this aleatory event time, i.e., they are not expected values. These dependent variables are also plotted per failed waste package. Relevant additional discussion of the movement of radionuclide mass in the 1,000,000-year igneous intrusion modeling case, for a single realization with an igneous intrusion event at 10,000 years, may be found in Section 1.1 of the response to RAI 3.2.2.1.3.4-2-007.

Figure 1.2.1-1 shows the cumulative mass of ^{242}Pu released (accounting for radioactive decay) from the waste form matrix (also called the “source term”), the waste form domain, and the corrosion products domain, per failed waste package, conditional on the event time at 100,000 years. The cumulative releases in this figure and elsewhere in this response account for radioactive decay, which is why the cumulative release curves can show a decrease over time. Figures 1.2.1-1(b, c, d) show the epistemic uncertainty in cumulative mass release for each domain along with various statistics, such as mean and median, while Figure 1.2.1-1(a) shows a comparison across the three sources/domains of the mean over epistemic uncertainty, conditional on the event time of 100,000 years. The individual realizations in Figures 1.2.1-1(b, c, d) are for the “representative failed commercial SNF waste package” in the seeping environment of percolation subregion 3 in the TSPA model (SNL 2008, Section 6.3.2.2.2). Because all of the waste packages fail and all of the waste forms instantaneously degrade at the time of the igneous intrusion event (100,000 years), the cumulative release from the waste form matrix shown Figure 1.2.1-1(b) is equal to the initial per-package inventory (mean of 6,142.5 g) decaying over time.

As shown on Figure 1.2.1-1(a), the difference between the mean cumulative releases from the waste form matrix and from the waste form domain represents the ^{242}Pu mass retained in the waste form domain (e.g., precipitated as secondary mineral phases). Similarly, the difference between the mean cumulative releases from the waste form domain and the corrosion products domain represents the ^{242}Pu mass retained in the corrosion products domain (e.g., sorbed on corrosion products or flocculated as unstable colloids). The spread between the three curves in Figure 1.2.1-1(a) is due to the transport delay across the three sources/domains, caused by precipitation, sorption on corrosion products, and flocculation of commercial SNF waste form colloids. Uncertainty in these three processes can be seen by comparing the spread of the gray curves in each of Figures 1.2.1-1(b, c, d). The narrow spread shown by the 300 gray curves in Figure 1.2.1-1(b) is due to the uncertainty in the initial plutonium inventory, which is relatively small. However, the uncertainty in plutonium solubility, water volume, and in concentrations associated with commercial SNF waste form colloids creates additional spread in the release rates of ^{242}Pu from the waste form domain, as shown in Figure 1.2.1-1(c). Also, the uncertainty in various parameters affecting plutonium sorption onto stationary corrosion products, as well as uncertainty in the stability of commercial SNF waste form colloids, causes further spread in the release curves from the corrosion products domain, as shown in Figure 1.2.1-1(d). Note that the

small release prior to 100,000 years, as seen in Figures 1.2.1-1(b) and 1.2.1-1(c), is due to a few waste package failures by nominal corrosion processes.

Following the igneous intrusion event at 100,000 years, ^{242}Pu mass that is released from the waste form matrix is transported from the waste form domain to the corrosion products domain as either aqueous ^{242}Pu (Figure 1.2.1-2) or irreversibly attached to commercial SNF waste form colloids (Figure 1.2.1-3). While the mean values for these release rates are similar, the behavior in individual realizations is different. In about 38% of the realizations, commercial SNF waste form colloids are stable in the waste form domain (see the supplemental response to RAI 3.2.2.1.3.4-2-007); in these realizations significant ^{242}Pu mass is transported to the corrosion products domain as both aqueous ^{242}Pu and as irreversibly attached to commercial SNF waste form colloids. In the remainder of the realizations, transport to the corrosion products domain is overwhelmingly as aqueous ^{242}Pu (with very small amounts sorbed on commercial SNF waste form colloids at the minimum concentration used when these colloids are unstable). Note that the median and 5th-percentile curves are missing from Figure 1.2.1-3, as well as from other figures discussed later. This reflects either that the median and 5th percentile are zero because less than 50% of the realizations result in a positive quantity (the most likely reason), or that the curves are below the displayed y -axis scale.

^{242}Pu retained in the waste form domain is retained as precipitated mass (Figure 1.2.1-4). Precipitated mass remains in the waste form domain as long as there is sufficient ^{242}Pu available from the waste form matrix to maintain the dissolved concentration at the solubility limit. Release rates decline steeply when the precipitated mass is completely depleted. Note that the mean precipitated mass shows a more gradual decline than for any of the single realizations (Figure 1.2.1-4) because the mean includes all realizations, including those for which the precipitated mass has been depleted.

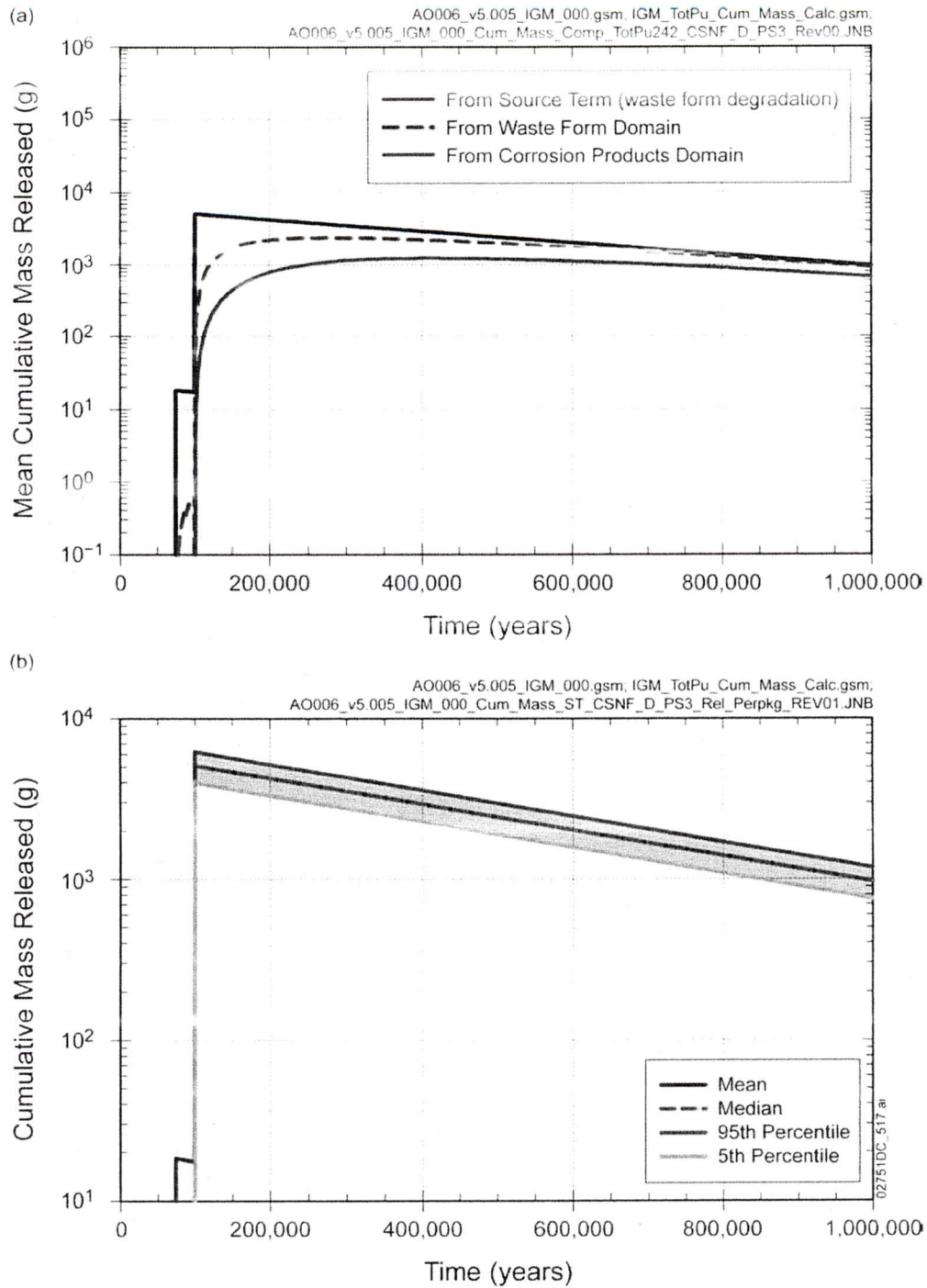


Figure 1.2.1-1. Cumulative Mass of ²⁴²Pu Released per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years: (a) Mean Releases; Mean Releases from (b) Source Term; (c) Waste Form Domain; (d) Corrosion Product Domain

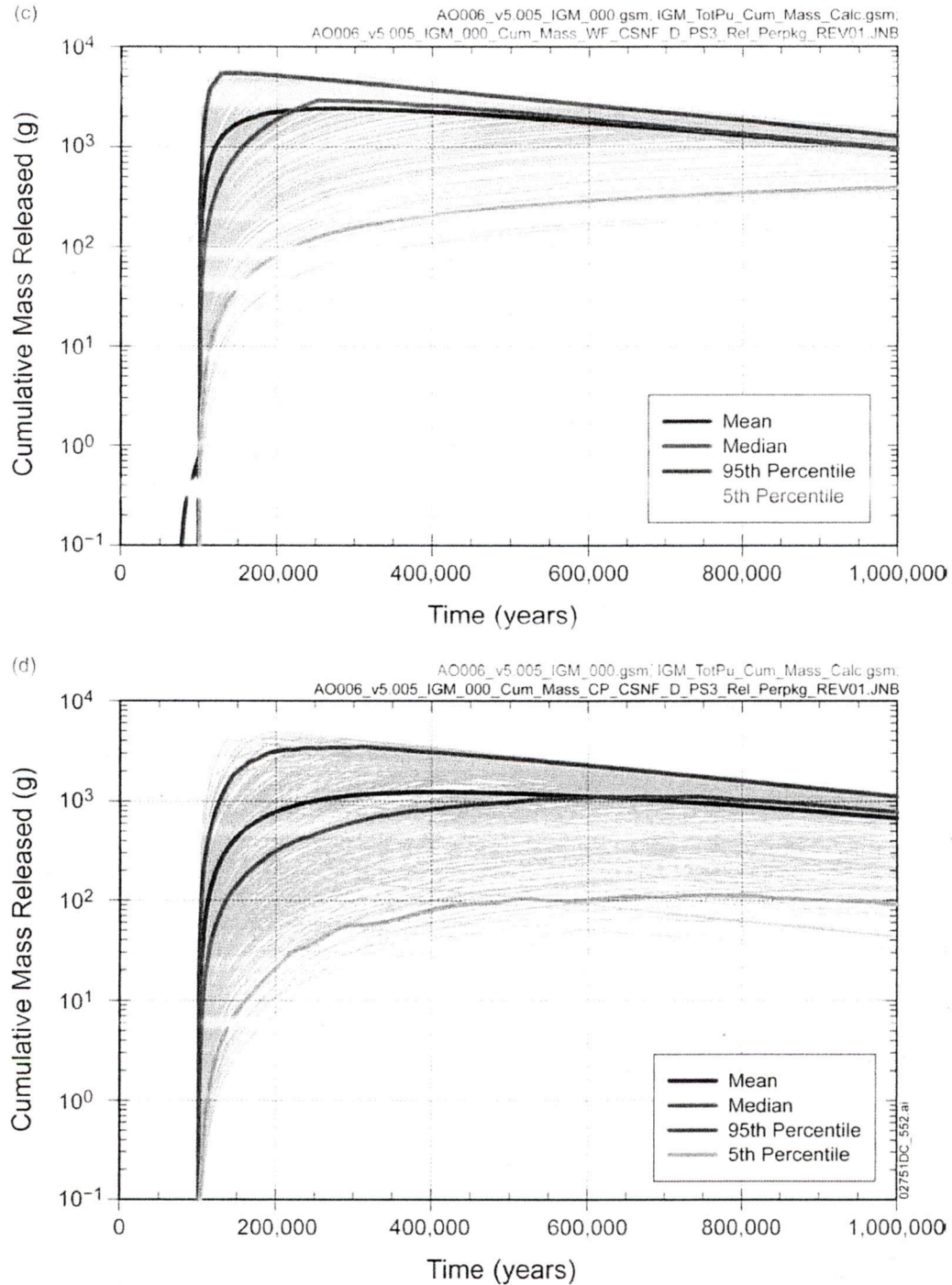


Figure 1.2.1-1. Cumulative Mass of ²⁴²Pu Released per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years: (a) Mean Releases; Mean Releases from (b) Source Term; (c) Waste Form Domain; (d) Corrosion Product Domain (Continued)

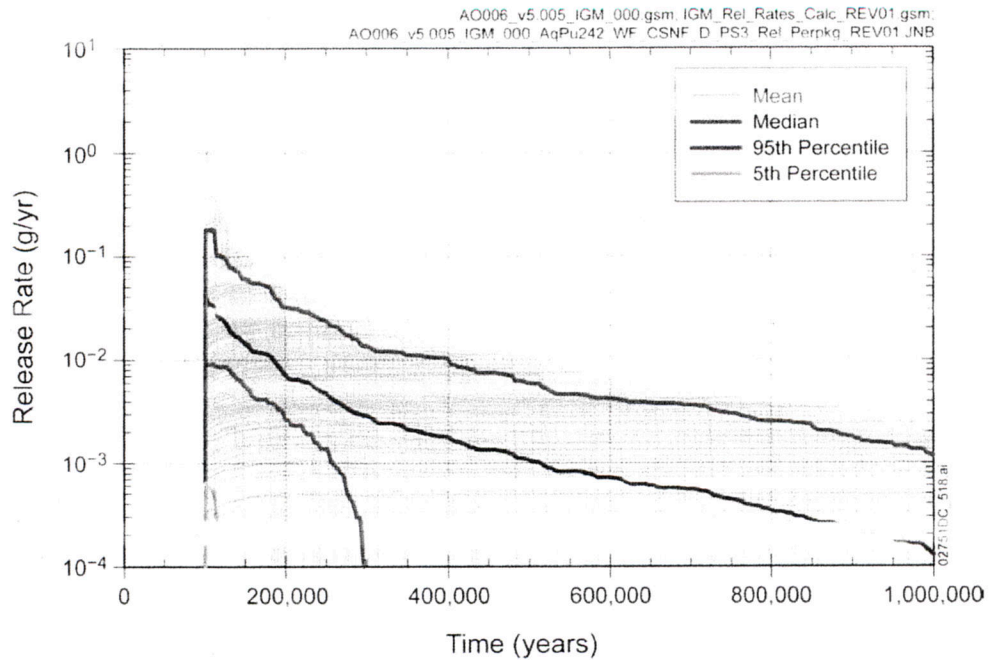


Figure 1.2.1-2. Release Rate of Aqueous ²⁴²Pu from the Waste Form Domain per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

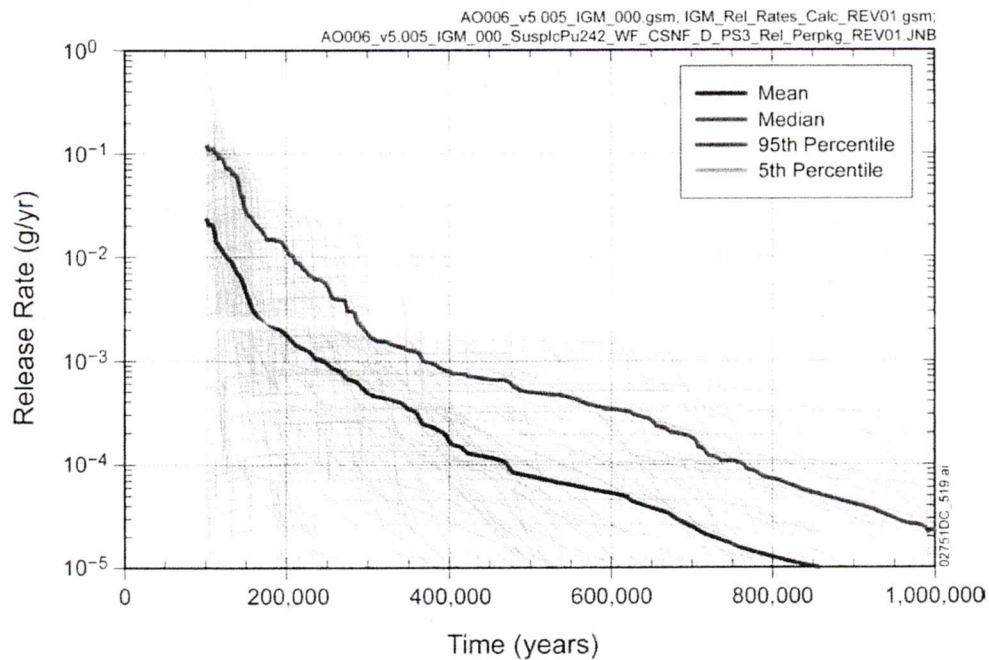


Figure 1.2.1-3. Release Rate of ²⁴²Pu Irreversibly Attached to Waste Form (lc) Colloids from the Waste Form Domain per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

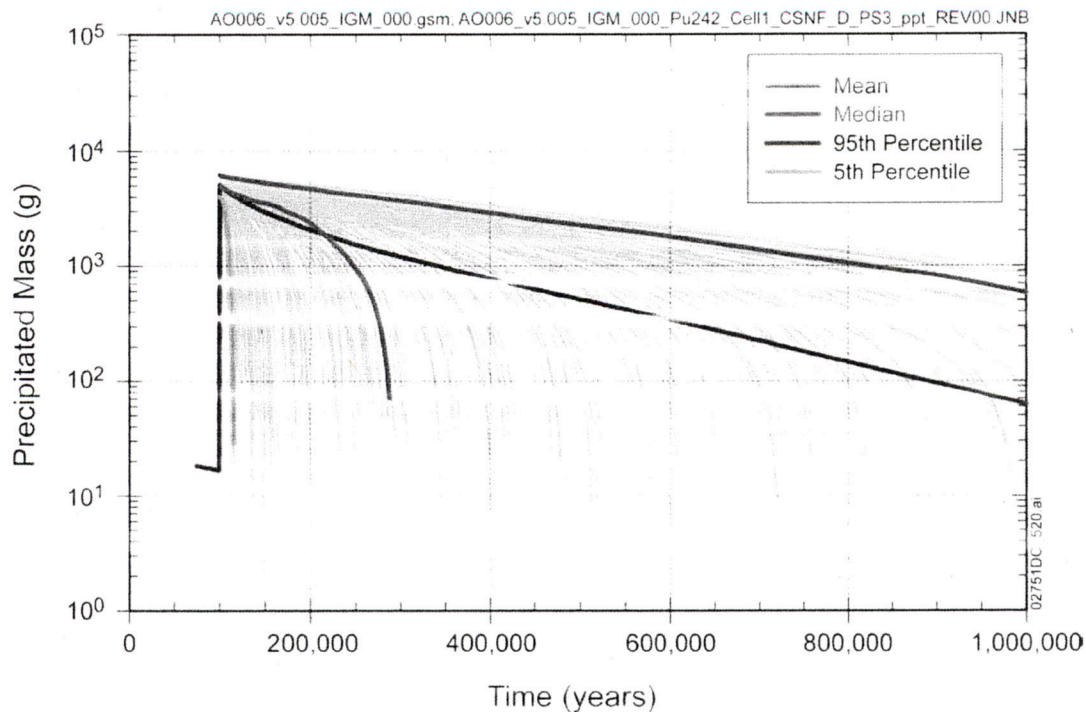


Figure 1.2.1-4. Mass of Aqueous ²⁴²Pu Precipitated in the Waste Form Domain per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

Mass that enters the corrosion products domain as aqueous ²⁴²Pu is:

- Transported through and released from the domain as aqueous ²⁴²Pu (Figure 1.2.1-5);
- Transported through and released from the domain irreversibly attached to FeO_x colloids (Figure 1.2.1-6);
- Immobilized in the domain by re-precipitation, and possibly re-mobilized by re-dissolution (Figure 1.2.1-7); or
- Retarded in the domain by reversible sorption onto stationary corrosion products (Figure 1.2.1-8).

Mass that enters the corrosion products domain irreversibly attached to commercial SNF waste form colloids is:

- Immobilized in the domain by the commercial SNF waste form colloids becoming unstable and settling, and re-mobilizing to sustain the minimum concentration of waste form colloids (Figure 1.2.1-9).

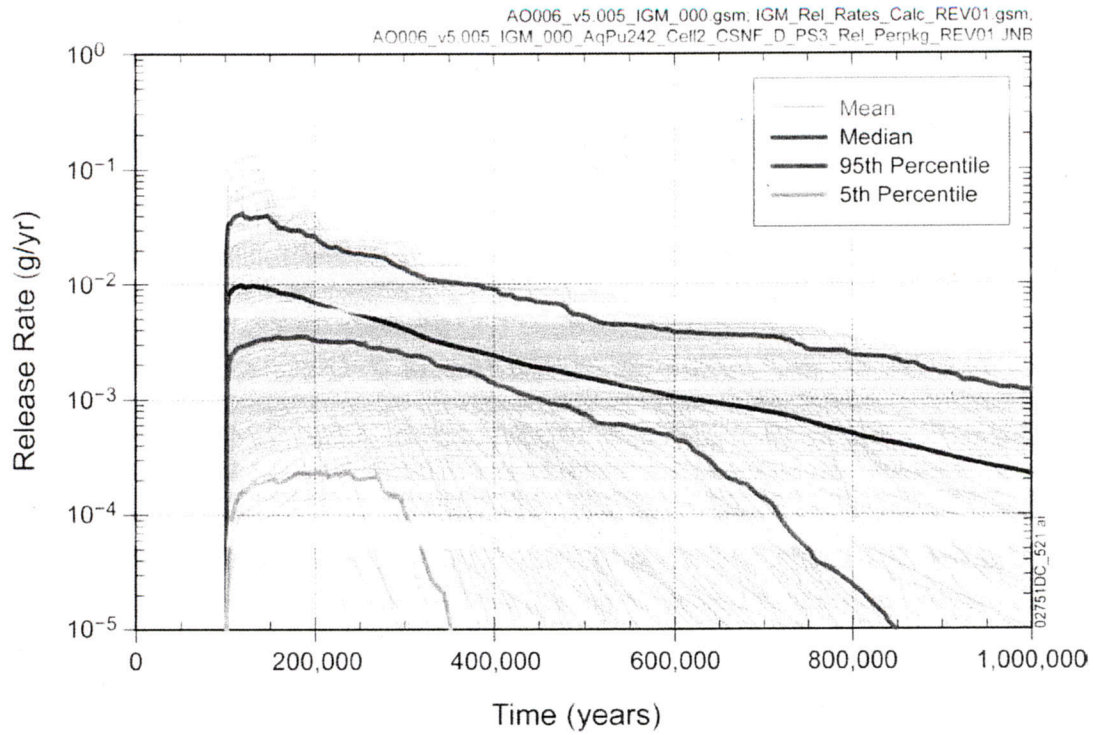


Figure 1.2.1-5. Release Rate of Aqueous ²⁴²Pu from the Corrosion Products Domain per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

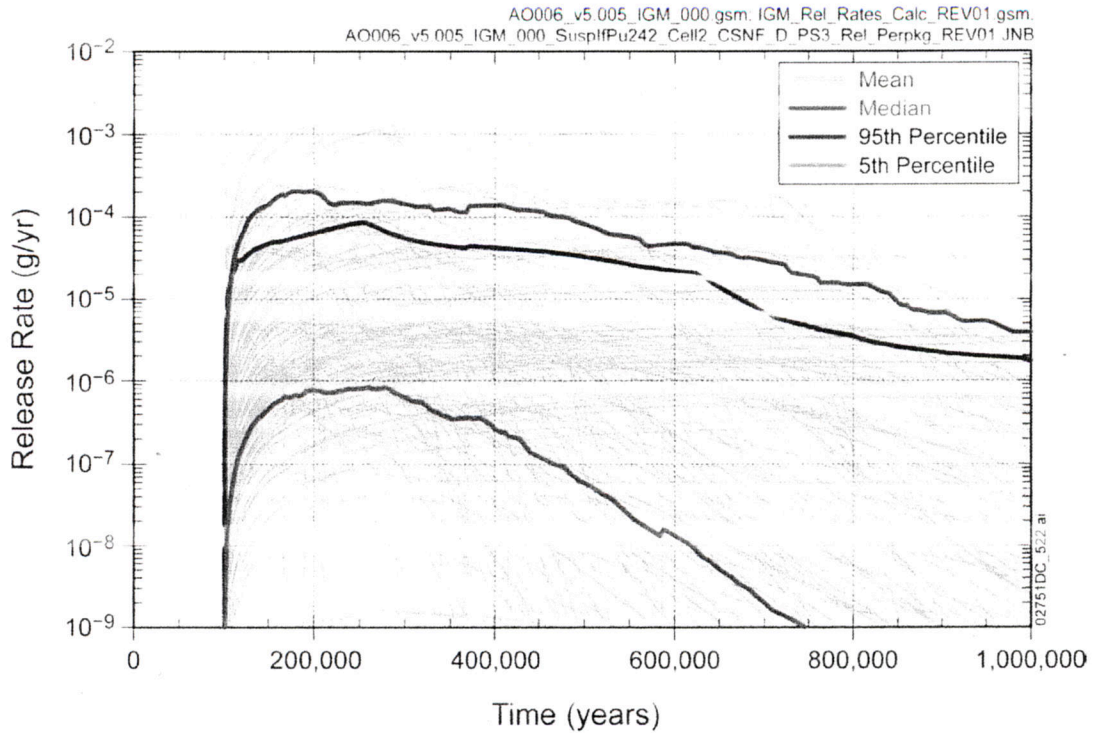


Figure 1.2.1-6. Release Rate of ^{242}Pu Irreversibly Attached to Iron Oxyhydroxide (If) Colloids from the Corrosion Products Domain per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

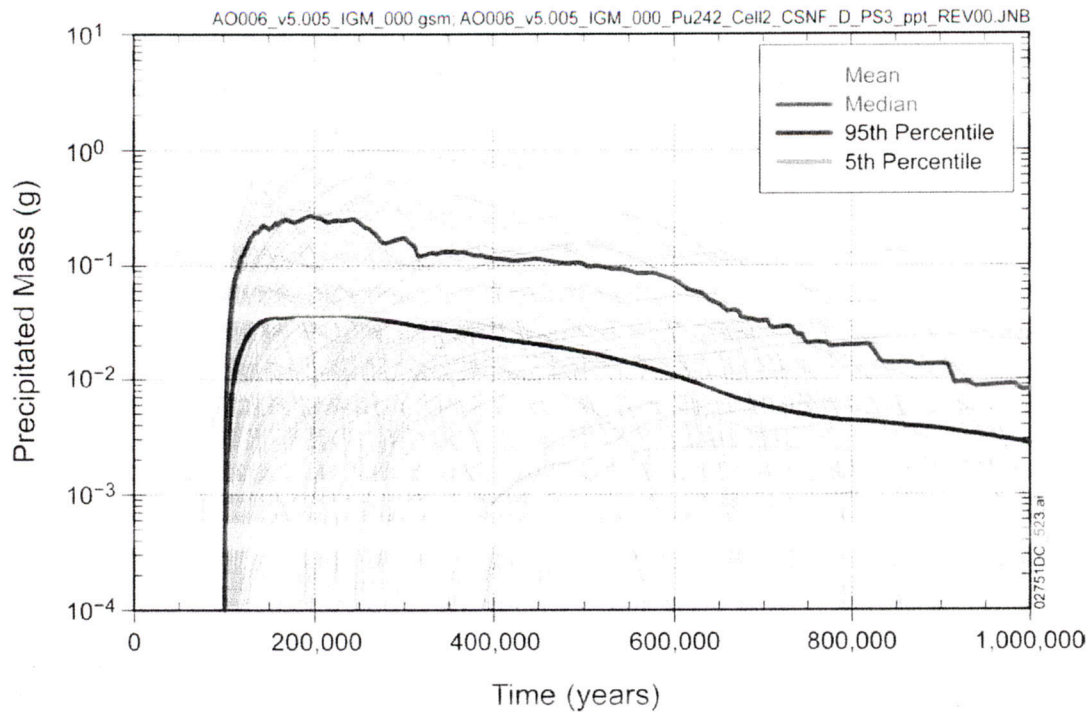


Figure 1.2.1-7. Mass of Aqueous ²⁴²Pu Precipitated in the Corrosion Products Domain per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

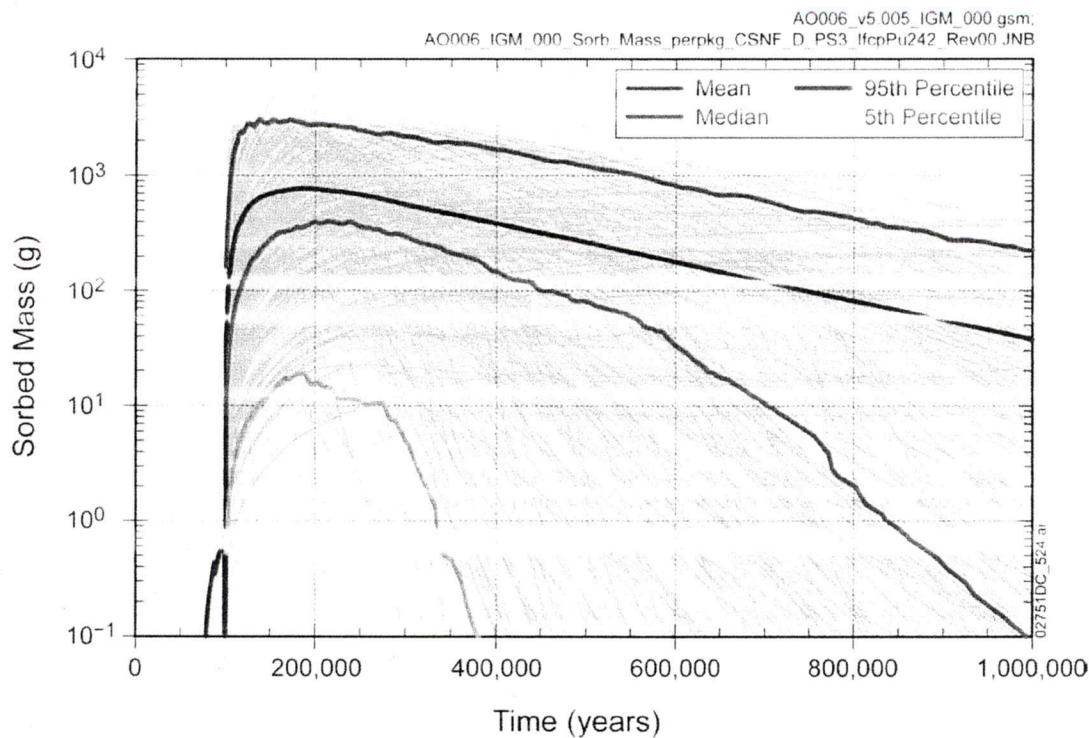


Figure 1.2.1-8. Mass of ²⁴²Pu Reversibly Sorbed onto Stationary Corrosion Products in the Corrosion Products Domain per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

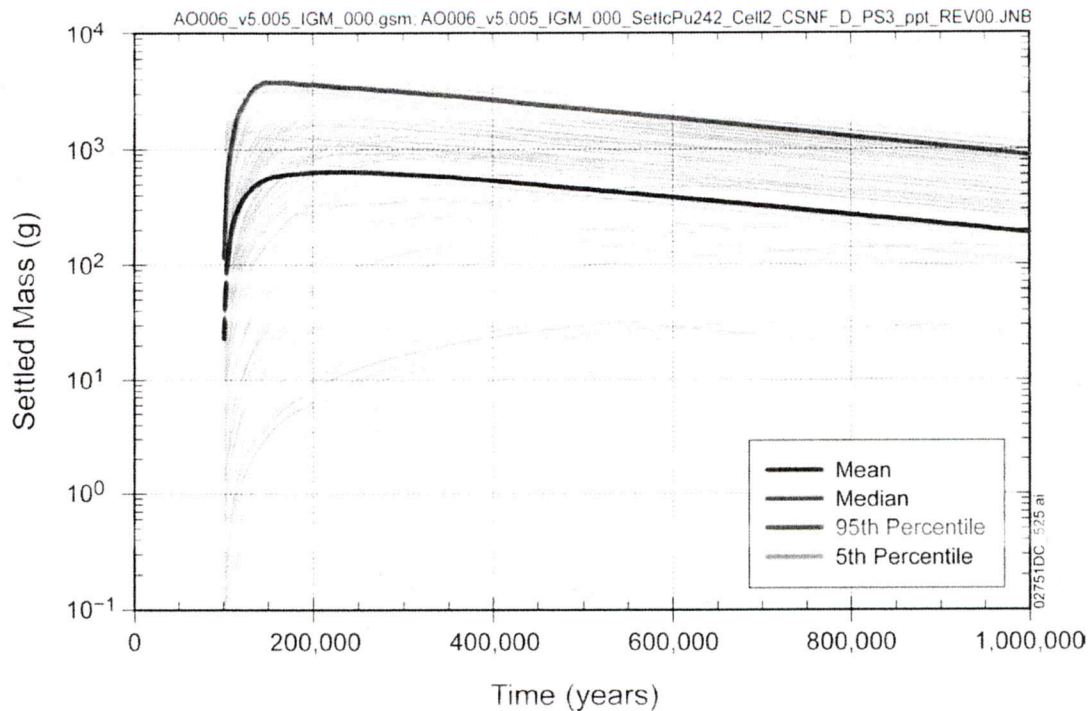


Figure 1.2.1-9. Mass of ^{242}Pu Irreversibly Attached to Waste Form (Ic) Colloids Settled (Unstable) in the Corrosion Products Domain per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

Table 1.2.1-1 summarizes the balance of mean mass at three different times (mean over epistemic uncertainty, conditional on an event time at 100,000 years), based on the results presented in Figures 1.2.1-1 through 1.2.1-9, to quantify the timing and magnitude of plutonium release from the three sources/domains per failed commercial SNF waste package. The following discussion is based on the behavior of the (epistemic) mean values of the masses. Where the mean behavior masks important behavior of individual realizations, discussion is added.

Table 1.2.1-1. Mean Mass of ²⁴²Pu per Failed Commercial SNF Waste Package in a Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

Time (years)		Unexposed (Waste Form Matrix)	Precipitate (Waste Form Domain)	Sorbed onto Stationary Corrosion Products (Corrosion Products Domain)	Attached to Settled Commercial SNF Waste Form Colloids (Corrosion Products Domain)	Cumulative Release to Invert	Cumulative Decay	Total ^a
200,000	Mass (g)	0	2,064	765	630	786	1,898	6,143
	% of Initial Mass	0.0	33.6	12.5	10.3	12.8	30.9	100.0
	% of Remaining Mass after Decay	0.0	48.6	18.0	14.8	18.5	N/A	100.0
600,000	Mass (g)	0	343	180	385	1,119	4,116	6,143
	% of Total Mass	0.0	5.6	2.9	6.3	18.2	67.0	100.0
	% of Undecayed Mass	0.0	16.9	8.9	19.0	55.2	N/A	100.0
1,000,000	Mass (g)	0	63	37	188	679	5,175	6,142
	% of Total Mass	0.0	1.0	0.6	3.1	11.1	84.3	100.0
	% of Undecayed Mass	0.0	6.5	3.8	19.4	70.2	N/A	100.0

^a Total may not equal 100.0% due to roundoff.

At 200,000 years, only 18.5% of the undecayed ^{242}Pu mass, on average (over epistemic uncertainty only), has been released from the corrosion products domain. The retained ^{242}Pu mass is present in the waste form domain as precipitated mass (48.6%), and in the corrosion products domain sorbed onto stationary corrosion products (18.0%) and irreversibly attached to settled commercial SNF waste form colloids (14.8%). In the corrosion products domain, the ^{242}Pu mass sorbed onto stationary corrosion products has already achieved a maximum value (Figure 1.2.1-8), due to the fact that the majority of the steel has corroded (Figure 1.2.1-10) and is available to provide sorption sites for ^{242}Pu . As described in the supplemental response to RAI 3.2.2.1.3.4-2-007, the settling of commercial SNF waste form colloids is caused by the change in colloid stability from the waste form domain to the corrosion products domain in some of the realizations. Comparison of the pH in the waste form domain (Figure 1.2.1-11) to the pH in the corrosion products domain (Figure 1.2.1-12) indicates the effect of pH buffering in the corrosion products domain. After the igneous intrusion event, there are several realizations with pH below 7 in the waste form domain (Figure 1.2.1-11), which can produce stable commercial SNF waste form colloids (see Figure 6(b) of the response to RAI 3.2.2.1.3.4-2-003). However, in the corrosion products domain, there are no realizations with pH below 7 after the intrusion event and the corresponding creation of corrosion products, and commercial SNF waste form colloids settle out (see Figure 6(c) of the response to RAI 3.2.2.1.3.4-2-003). As noted above, the mean ^{242}Pu mass associated with settled commercial SNF waste form colloids is similar to the mean ^{242}Pu mass sorbed onto stationary corrosion products, but results from colloid formation in the waste form domain in only about 38% of the realizations (see Figure 1(b) of the response to RAI 3.2.2.1.3.4-2-003).

At 600,000 years, 55.2% of the undecayed ^{242}Pu mass, on average, has been released from the corrosion products domain. The increase in release (as compared to 200,000 years) is primarily due to dissolution of precipitated ^{242}Pu in the waste form domain (which went from 48.6% to 16.9% of the undecayed mass) and net desorption of ^{242}Pu from stationary corrosion products in the corrosion products domain (which went from 18.0% to 8.9% of the undecayed mass) (Table 1.2.1-1). Net desorption occurs on average because precipitated mass is depleted in some of the realizations (Figure 1.2.1-7), resulting in a decrease in aqueous concentration in those realizations, which causes a subsequent reduction in sorbed mass (Equation 4). This net desorption is reflected in the observation that in realizations in which the precipitated mass is depleted the mass flux out of the corrosion products domain at this time (Figure 1.2.1-5) is larger than the mass flux into the domain (Figure 1.2.1-2).

At 1,000,000 years, 70.2% of the undecayed ^{242}Pu mass, on average, has been released from the corrosion products domain. The increase in release (as compared to 600,000 years) is due to depletion of precipitated ^{242}Pu in the waste form domain in additional epistemic realizations and net desorption of ^{242}Pu from stationary corrosion products in the corrosion products domain. The retained ^{242}Pu mass is present in the waste form domain as precipitated mass (6.5%), and in the corrosion products domain as sorbed onto stationary corrosion products (3.8%) and irreversibly attached to settled commercial SNF waste form colloids (19.4%) (Table 1.2.1-1).

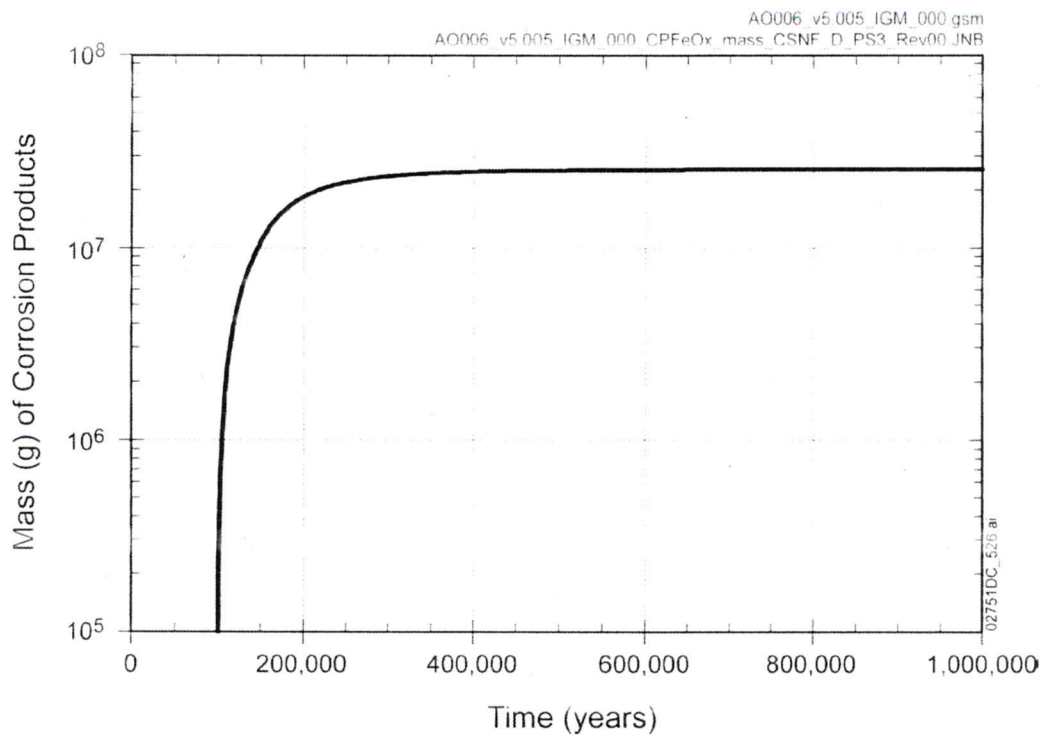


Figure 1.2.1-10. Mean Mass of Iron Oxyhydroxide Corrosion Products in the Corrosion Products Domain per Failed Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years

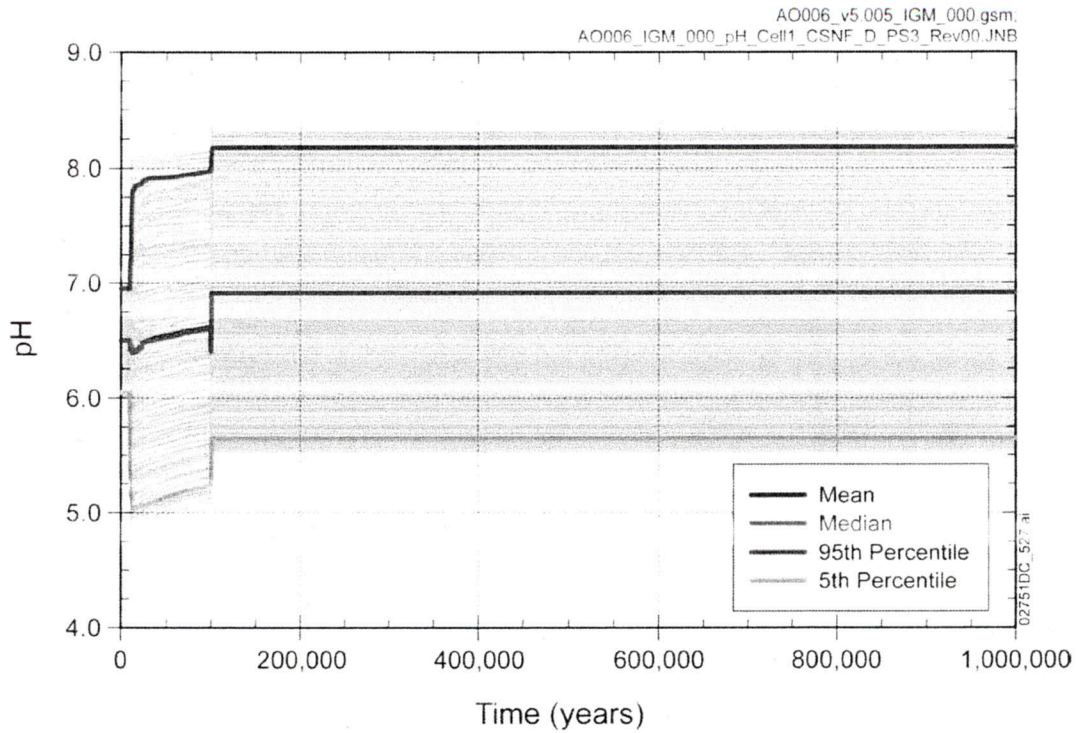


Figure 1.2.1-11. pH in the Waste Form Domain of a Commercial SNF Waste Package in the Seeping Environment of Percolation Subregion 3 after an Igneous Intrusion Event at 100,000 Years