LONG-TERM PASSIVITY OF ALLOY 22 AND NEAR-FIELD RADIONUCLIDE SEQUESTRATION IN A POTENTIAL YUCCA MOUNTAIN REPOSITORY OF SPENT NUCLEAR FUEL AND HIGH-LEVEL WASTE DISPOSAL

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ABSTRACT

This report summarizes some of the information on passive film stability of Alloy 22 container under repository conditions that the NRC staff used in evaluating DOE's Yucca Mountain License Application (NRC, 2014), particularly Alloy 22 passivity that dictates general corrosion rates. It also documents insights derived from DOE's analyses on actinide sequestration in the near field and used by NRC staff during the preparation of the Safety Evaluation Report (NRC, 2014), which showed stable sorption on corrosion products and, in conjunction with waste container longevity, resulted in delayed radionuclide releases. The passive film is a ~ 5 nm thick oxide layer formed on the Alloy 22 surface. Actinide sorption (mainly mono atomic layer) occurs primarily on the surface of iron oxide from the corrosion of Alloy 22 and other steel internals. Steady-state conformal chromium oxide on the Alloy 22 surface protects against passivity breakdown. Steady and stable chemistry and constant thickness of the protective conformal chromium oxide layer result in low general corrosion rates over a long period. Monitoring corrosion potential over an extended-time of years and shorter-time laboratory tests indicates the persistence of steady-state stable chromium oxide and fast repassivation. In a longer time, actinides will form secondary minerals or be sorbed on corrosion products of container or steel internals. The sorption of radionuclides to oxide or waste form surface is likely to be stable with time. Representative realizations in the DOE's Total System Performance Assessment (TSPA) for the potential Yucca Mountain Repository are used to illustrate the fraction of actinides sequestered in the in-package environments at various repository times. DOE's TSPA realizations indicate that actinide release is substantially delayed and, in some instances, reduced due to radioactive decay during the sequestration processes.

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INTRODUCTION

This report summarizes some of the information on passive film stability of Alloy 22 container under repository conditions used during the NRC and CNWRA staffs' evaluation of DOE's Yucca Mountain License Application (NRC, 2014). A passive film on the metal surface has a significant effect on the general corrosion rate. This report also captures knowledge used by NRC staff during the preparation of the Safety Evaluation Report (SER, NRC 2014) in evaluating DOE's license application regarding actinide sequestration in the near field that resulted in delayed radionuclide releases.

1. Passivity of Alloy 22

DOE (Safety Analysis Report Section 2.3.6.3.a and SNL 2007) indicated the stability of Alloy 22 passive film depends primarily on its physical and chemical properties, including microstructure, composition, and thickness. Jung, et al. (2007) summarized the stability of passive films on Alloy 22 under potential Yucca Mountain repository environments.

Composition and Microstructure

Multiple studies conducted to evaluate the composition and micro-structure of the passive film on Alloy 22 below 100 °C [212 °F] indicate that the main barrier for corrosion degradation processes is a conformal, chromium-rich oxide layer (Jung, et al., 2007; Orme, 2005). In this report, barrier oxide refers to the chromium-rich oxide unless otherwise specified. The chromium is in the +3 oxidation state, typically in the form of Cr_2O_3 or $NiCr_2O_4$. Other elements may play a role in the passive behavior for Alloy 22, such as molybdenum (reduces the anodic dissolution of the base metal) and tungsten (increases film thickness). These passive films showed a distinct layered structure, consisting of an inner layer rich in Cr and Ni, and an outer layer enhanced in Mo.

A point defect film growth model describes steady-state spatial and temporal compositions of alloying elements in passive films (Pensado, et al., 2002). A point defect film growth model here is a generic description of Point Defect Model (e,g,, Orme, 2005), because there are similar models with variations (e.g., with transport defects considered). The model by Pensado, et al. (2002) assumes that the conduction through the chromium-oxide film occurs mainly by interstitial cations, oxygen vacancies, or both. Figure 1.1 shows a chromium enriched oxide near surface.

The long-term stability of the passive film indicated by the thermodynamic data is difficult to assess by comparison to short-term tests. However, the results of the 9-month autoclave tests (Jung, et al., 2007; Orme, 2005) conducted on Alloy 22 in $NaCl$-$NaNO_3$-KNO_3 solutions at elevated temperatures, 120–220 °C [248–428 °F], indicated that a chromium-rich oxide film was present in most of the testing (i.e., is stable). This chromium oxide consisted mainly of a +3 oxidation state. The observation shows that the oxide could be Cr_2O_3, $Cr(OH)_3$, $CrOOH$, or possibly $NiCr_2O_4$. This is compatible with the thermodynamic data, where chromium is mainly stable in a +3 oxidation state. The consistency between low and high temperature data shows temporal stability of composition at longer time periods as the repository temperature decreases. Shorter high temperature data may represent longer low temperature behavior assuming a single activation process (to be discussed later) based on the observed compatible composition of the passive film. It was not until the temperature was much higher (i.e., at least 160 °C [320 °F]) and the nitrate-to-chloride ratio in the test solutions was high (around 6.7) that

the chromium reached an oxidation state of +6, which is expected to more readily dissolve the passive film.
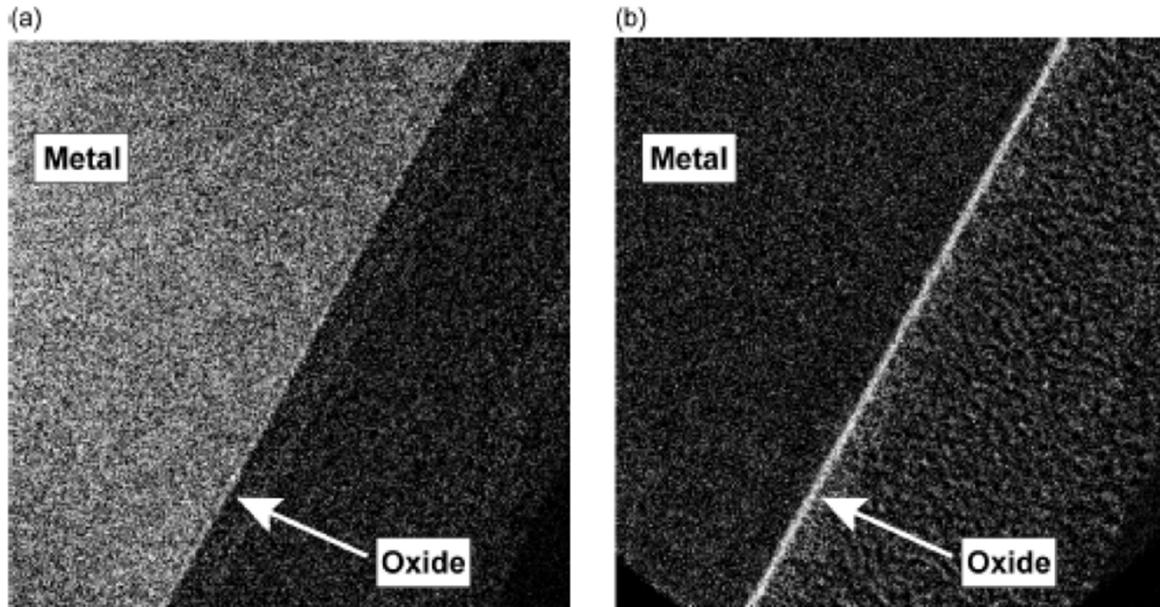
Figure 1.1. (a) Chromium and (b) Oxygen Energy Loss Spectroscopy Indicating a Chromium Oxide Film (Orme, 2005) from Immersion Tests of Alloy 22 at Varying Applied Potential in 1 mol/L NaCl Solutions near pH 3 at 90 °C [194 °F].

Two additional analog materials evaluated were Alloys 600 and 690. These two materials were chosen because of a chromium concentration similar to Alloy 22 as an analog and their use in elevated temperature processes (e.g., nuclear reactor components). Studies of these analog materials have been conducted at temperatures exceeding 320 °C [608 °F] (Montemor, et al., 2003). The results show that a passive chromium-rich oxide can form at elevated temperatures in solutions ranging in pH from 5 to 10.

Thickness

(1) Point Defect Film Growth Model and Supporting Data

SNL (2007) reviews and Pensado, et al., (2002) presents a point defect film growth model for the passive state on Alloy 22 under a few representative brine repository environments below 100 °C [212 °F]. The model recognizes both the growth of the barrier oxide into the metal via the generation of various types of point defect at the metal/film interface and the dissolution of the barrier layer at the film/solution interface, as well as the current carrier defects within the Cr_2O_3 barrier oxide.

Under open circuit conditions, the sum of rates of anodic oxidation cathodic reduction within the barrier layer are zero. When the growth rate of barrier layer is equal to the dissolution rate of

outer barrier layer, a steady state will be reached. The steady state is practically quasi steady-state with local reaction fluctuations.

While transients before the quasi steady-state are expected to persist for a considerable time (e.g., one year laboratory test time), the transient times are still short compared with the repository geological time (e.g., tens of thousands of years) and, therefore, the model concludes that the accumulated damage due to general corrosion can be assessed by using quasi steady-state models. In general, the model estimates that as the repository temperature decreases with time the corrosion potential drifts in the positive direction causing the corrosion rate to decrease. With the corrosion potential drift, the corrosion potential may exceed the transpassive potential. Depending on the dissolution rate of the outer barrier, the quasi-steady state remains. Details of this model provides the assessment for the quasi steady-state that agrees with experimental observations.

As stated above, the point defect film growth model states that in a geologic repository life time a quasi steady-state would be reached, primarily because the dissolution rate of the barrier oxide at the barrier layer/solution interface (outer layer) is nearly the same as the film growth rate at the metal/film interface. Thus, when an activation process for growth behaves as a single activation process it can persist in a wide range of temperatures. The presence of a single activation process means that many coupled processes in the point defect film growth model follow a general rule in kinetics: the fastest rate controls the parallel coupled processes, and the slowest rate controls the coupled series processes.

Based on the thermodynamic modeling results and literature short-term experimental results, a chromium-rich oxide passive film is stable at elevated temperatures. An example is given below assuming a single activation process. Jung et al. (2007) reviewed literature data including immersion tests of Alloy 22 in simulated groundwater of Yucca Mountain (Orme, 2005). The activation energy for general corrosion rates are 25 to 45 kJ/mol [23.7 to 42.7 Btu/mol] in Jung et al., (2007). Given the same barrier oxide thickness based on a single activation process, the time elapsed to get to the thickness at various temperatures can be approximated by an inverse Arrhenius relation.

If this data of activation energy is extrapolated, taking the activation energy of 35 kJ/mol [33.2 Btu/mol], to 90 ˚C [363 ˚f], the equivalent time will be 16 years by this simple Arrhenius relation. As the repository temperature decreases below boiling point after ~1000 years, the film is, then, expected to be stable over hundreds of years. This long-time barrier oxide stability from the simple estimates above shows: (i) a quasi steady-state is reached by balancing the corrosion rate of inner metal and the dissolution rate of outer oxide, or (ii) some oxide above a certain thickness may transform to be less protective microstructure (to be further discussed later), and therefore (iii) corrosion potential remains in a steady state below the transpassive potential.

Montemor et al. (2003) tested Alloys 600 and 690 for about 80 days in sodium hydroxide and sodium sulfate at 320 to 350 ˚C [608 to 662 ˚F]. With the same activation energy of 35 kJ/mol [33.2 Btu/mol] at 320 ˚C [608 ˚F], the time to develop the equivalent thickness of passive film at 90 ˚C [194 ˚F] would be about 20 years. Nuclear reactor experience of greater than 10 years in reactor water at ~ 300 ˚C [572 ˚F] indicates the film stability time would increase. Comparing to10 years at ~ 300 ˚C [572 ˚F], the film would be stable in an equivalent of ~ 700 years at 90 ˚C [194 ˚F]. At the lower repository temperatures at longer times (e.g., beyond 2,000 years), the film is expected to be stable.

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(2) Other Models

A similar approach was taken to assess the long-term stability of passive film (Brossia, et al., 2001). Steady-state composition and dissolution rates were postulated.

(3) Energetics for Barrier Oxide Formation

Bare alloy metals will have disequilibrium over-potential in groundwater from chemical equilibrium. This over-potential drives the dissolution of the alloy metal. The dissolution will form a barrier oxide and the barrier oxide will grow with time. The barrier oxide will have a steady-state thickness as described above.

The over-potential energy will be balanced with (i) chemical driving energy for oxide formation, (ii) strain energy associated with barrier oxide formation, and (iii) capacitance stored energy for dielectric or semiconducting barrier oxide. These values increase as barrier oxide becomes thicker. Generally for the stable oxide, chemical driving energy is dominant, compared with strain energy or capacitance energy.

The barrier oxide thickness will be limited either by (i) the dissolution of outer oxide surface or (ii) micro-structural instability or alteration of barrier oxide chemistry, as thickness increases. The dissolution of the outer surface of oxide is balanced with the inner metal surface dissolution as point defect film growth model theories predict. As aforementioned, oxide dissolution rates are closer to corrosion rates.

If strain or capacitance energy leads to the barrier oxide instability, the barrier oxide micro-structure or chemistry may be transformed into a non- or less-protective oxide, which does not contribute to the metal open-circuit potential. An example is aluminum or titanium anodization. Only a thin barrier layer of tens of nanometers formed under high voltage applied for aluminum anodization. On top of the barrier layer, porous oxide continues to grow. If strain or capacitance energy breaks the barrier layer, it is more frequent in localized areas, resulting in potential fluctuations, as shown in long-term tests (SNL, 2007). As the point defect film growth model models postulate, the barrier oxide is likely to be in quasi steady-state over long time periods (e.g., tens of thousands of years). If the passivity were to breakdown, repassivation will occur quickly, as discussed in the next section, which may not substantially affect overall corrosion rates.

Other Factors on Barrier Oxide Stability

Jung, et al. (2007) evaluated and summarized other effects of corrosion-related potential degradation processes on the long-term persistence of passive film on Alloy 22.   Other factors evaluated include tests that address:

   (i)   enhanced dissolution rate by anodic sulfur segregation
   (ii)   base metal chromium depletion on passive film stability
   (iii)   film spallation by void formation
   (iv)   anion-selective sorption
   (v)   large cathodic area development and increased cathodic kinetics
   (vi)   dry-wet cycle process

Jung, et al. (2007) concluded that these factors do not adversely affect long-term persistence of passive films in the Yucca Mountain repository environment.

<u>Corrosion Potential, Microstructure, Repassivation and General Corrosion Rate</u>

Oxide dissolution rates are in the range of long-term corrosion rates of Alloy 22 in most ceramic literature. The barrier layer thickness varies, primarily depending on solution compositions (Jung, et al., 2007). The point defect film growth model assesses the thickness to be less than 5 nm. This thickness was also reported in immersion tests (Jung, et al., 2007).

Results from longer-tem tests (>3 years) in Figures 1.2 and 1.3 below show the corrosion potential increases or stays constant with temperature below 60 to 90 °C [140 to 194 °F] (SNL, 2007). At constant temperature, the long-term tests (>3 years) in various repository environments show that corrosion potentials drifts after the initial transient period (~ 10 to 100 days). There appears to be a second transient period in the case of 1 M $CaCl_2$ + 1 M $Ca(NO_3)_2$ at 90 °C [194 °F]. The significance of potential shift is discussed later in terms of resulting general corrosion rates. Generally the long-term tests support the point defect film growth model prediction of quasi steady-state inner thickening and outer dissolution of the film.

Without an applied forced voltage in the repository, the growth of a barrier layer on Alloy 22 will be limited given the free corrosion potential. At this point while the outer surface of a barrier oxide dissolves either chemically or electrochemically, a new barrier oxide layer continues to form. In fact most chemical dissolution rates of oxide are in the range of long-term corrosion rates of Alloy 22 as addressed, resulting from 3 year immersion test results (SNL, 2007).

Over time below the chloride-induced pitting potential, dissolution will occur at local defects in the passive film. These sites will repassivate, leading to a restructuring of the passive film. The restructuring could affect both the inner or possibly outer layer. The role that the outer layer plays in corrosion resistance is less important than that of the inner compact layer. The corrosion of the inner layer has more complex atomic transport processes. The local dissolution and repassivation is likely to be stochastic due to high sensitivities of parameter values, which seems to be a cause of aforementioned potential drifts.

Repeated potentials are shown in Figures 1.2 and 1.3 above. An independent study shows that the repassivation time is rapid (seconds to hours) compared to longer time (of many days and longer) in passivation (Figures 1.2 and 1.3 above; He and Dunn, 2005; McMillion, et al., 2005; Pensado, et al., 2002; Brossia, et al., 2001). One notable observation of fast repassivation time compared to longer time in passivation is from the tests conducted for Alloy 22 galvanically coupled to a large Alloy 22 plate in 5 M NaCl solution with the addition of $2x10^{-4}$ M $CuCl_2$ at 95 °C [203 °F] (He and Dunn, 2005). Copper chlorides were added to increase the initial potential to an active state under the open-circuit condition. Data quoted above are from short-term tests (with initial high corrosion rates). If an oscillating process occurs, it is stochastic and would occur randomly on any place of the surface. Therefore, one single pit will not propagate continuously. Considering longer time for passive states, the net increase of corrosion rates would be minimal, which is in the uncertainty range of corrosion rates from immersion tests. A summary of up to 9.5 year corrosion test data on Alloy 22 is given below, without showing localized corrosion such as pitting.
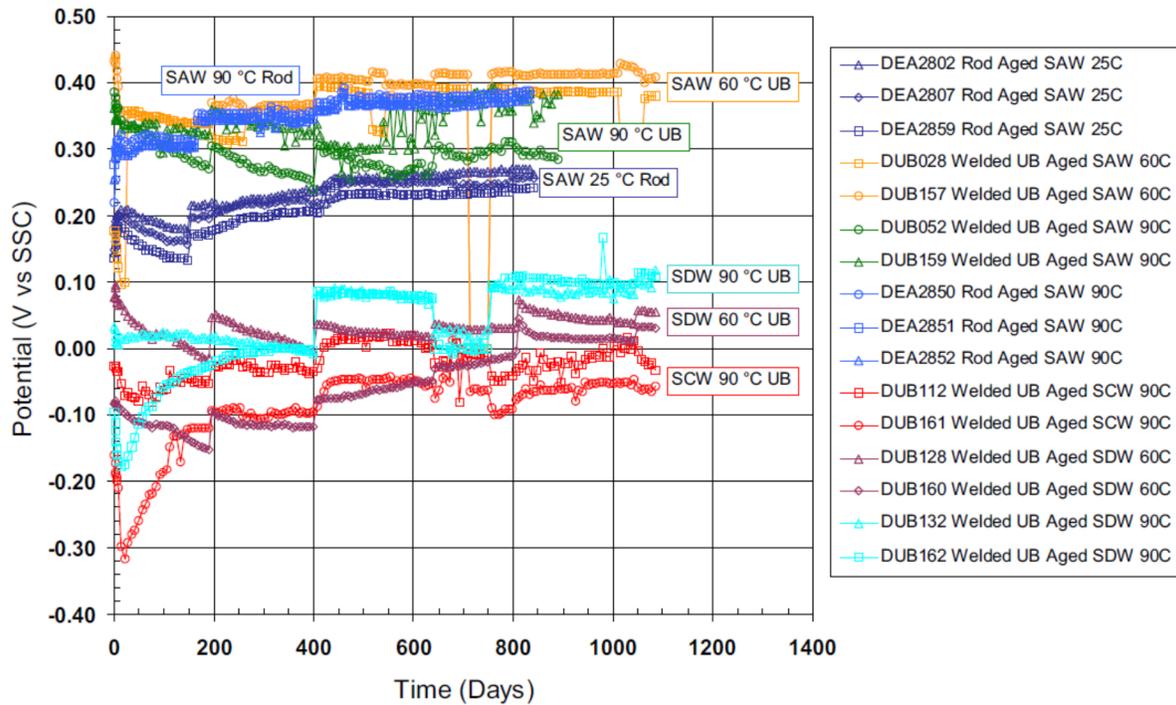
Figure 1.2. Open-Circuit Corrosion Potential of Alloy 22 Samples as a Function of Time in Different Types of Long-Term Corrosion Test Facility Solutions under Naturally Aerated Condition: SAW (Simulated Acidified Water), SDW (Simulated Dilute Water), SCW (Simulated Concentrated Water) (SNL, 2007).
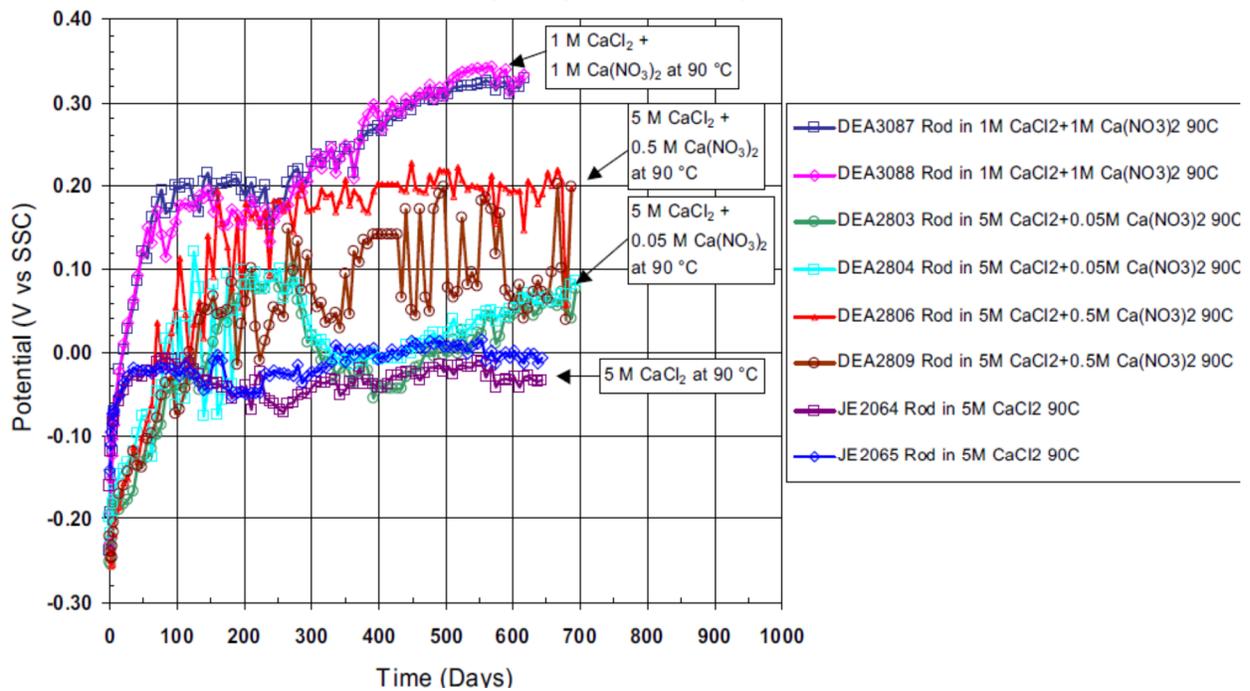
Figure 1.3. Open-Circuit Corrosion Potential of Alloy 22 Samples as a Function of Time in Differing Concentrations of CaCl$_2$ Solutions under Naturally Aerated Condition (SNL, 2007).

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Longer-Term General Corrosion Rate

In the previous review, Jung, et al. (2007) summarized longer-term general corrosion rate. Based on DOE's corrosion tests of Alloy 22 specimens for 5 years from the Long-Term Corrosion Test Facility, DOE measured a corrosion rate of 7.9 nm/year [3.11 x 10^{-7} in] for the 5-year specimens (Jung, et al., 2007). Lower values of corrosion rates were reported for the 9.5-year specimens (NRC, 2014). It is noted that the general corrosion rates have temporal and spatial distributions.

2. Long-Term Sequestration of Actinides

Under DOE's nominal and seismic scenario, a waste package can potentially last for hundreds of thousands of years or more before failure of the engineered barriers allows water flow into and out of the container. During this time, most short-lived radionuclides have decayed away. The remaining radionuclides that will be released would be long-lived fission products such as I-129 and Tc-99, and long-lived actinides such as Pu -242 and Np-237. In DOE's TSPA abstraction of radionuclide transport in the EBS, I-129 and Tc-99 are not retarded by EBS components or their corrosion products (e.g., DOE, 2009b). Pu-242 and Np-237, however, are adsorbed on the remaining spent nuclear fuel or HLW glass inside the waste package, corrosion products, e.g., iron oxides, or colloids in suspension or settled inside and outside the waste package (e.g., DOE, 2009b). Additionally, these actinides may also precipitate within the EBS. Although the remaining actinides may be eventually released, the overall release is substantially delayed.

Radiation strength may adversely affect the chemical equilibrium and stability of actinide and substrate (such as iron oxide from container corrosion). As the radiation level continuously decreases due to radioactive decay, the sorption process becomes more stable, along with less release of radionuclides.

Among the potential radionuclide release scenarios evaluated by DOE (2009a), the igneous intrusion scenario is particularly informative in terms of the role corrosion products play in sequestering Pu-242 and Np-237 within the EBS. The waste packages are assumed completely failed by the intruding magma. Seepage water is assumed to be infiltrating through the host rocks after the magma has cooled and reacts with waste package materials, resulting in corrosion of the waste package components and advective water flow into and out of the EBS.

Np-237, which may be reversibly sorbed onto stationary corrosion products, e.g., iron oxides, and colloids, has a relatively large inventory in spent nuclear fuel with a half-life over 2 million years. About 28% of the initial Np-237 mass, including ingrowth at 10,000 years, will decay within the first million years. Additionally, the amount of Np-237 that may be transported out of the EBS through groundwater may also be controlled by the solubility of Np-237, which in turn depends on the amount of seepage water and its chemistry.

In a realization extracted from the DOE's Total System Performance Assessment model (TSPA, see SNL, 2008) for the igneous intrusion scenario, the two mechanisms, precipitation and sorption onto stationary corrosion products in the corrosion product domains, account for about 5%, 85%, 65% and 3% of the initial inventory (including ingrowth at 10,000 years) at about 15,000, 50,500, 100,000 and 1 million years (Table 2.1). Near the time of the igneous event at 10,000 years, most of Np-237 is in the waste form domain and only a relatively small amount is retained in the solid phase of the corrosion production domain (Figure 2.1). Forty thousand years after seepage water enters the waste package and dissolves most of the inventory, the amount of mass retention becomes the opposite of that near the time of the igneous intrusion. By 100,000 years, 65% of the inventory remains retained in the waste package corrosion product domain.

Table 2.1. Percentage of Np-237 in the Solid Phase in the Waste Form (WF) Domain and Corrosion Product (CP) Domain from a Realization of the Igneous Intrusion Model[1]

Yeas	15,000	50,500	100,000	1,000,000
Percentage of mass in WF	92%[2]	-[3]	0%[2]	0%[2]
Percentage of precipitated mass in CP	2.2%[2]	47.6%	-[3]	0%[2]
Percentage of mass on stationary CP	2.8%[2]	37.6%	65%[2]	3%
Percentage of mass released from EBS	-[3]	13.7%	-[3]	88%

[1]The values are extracted from a TSPA realization of an epistemic uncertainty vector for the 1,000,000-year igneous intrusion modeling case (DOE, 2009b). The realization focuses on the seeping environment of a percolation region that contains 40% of proposed repository waste packages and represents the middle 40% of the expected range of percolation values of the proposed repository.

[2]The values were obtained by digitizing figures in DOE (2009b).

[3]Vaules not reported or too small to be accurately digitized are indicated by the minus (-) sign in the table.

The differences in chemical conditions (e.g., ionic strength and pH) in the WF and CP domains result in a lower Np-237 solubility in the CP domain and a relatively large fraction in the precipitated phase than the stationary corrosion product phase right after the igneous event at 10,000 years. As steel continues to corrode, the precipitated phase redissolves and the mass sorbed onto the stationary corrosion products continues to increase until 100,000 years in the CP domain. At this time, the concentration of Np-237 in the solution is lower than the solubility limit and all the precipitated Np-237 has redissolved. The mass released from the in-package environment plus the mass that has decayed account for about 35% of the inventory at 10,000 years. By 1 million years, only 3% of Np-237 remains inside the spent fuel waste package and 88% has be released from the EBS.

In addition to precipitation and sorption onto stationary corrosion products, Pu-242 can also be irreversibly adsorbed onto WF colloids, which can either suspend in solution or settle into solid phase, depending on chemical conditions in the WF and CP domains. In the WF domain, chemical conditions can be equally favorable to the suspension or settlement of the WF colloids (DOE, 2009c). If the chemical conditions in the WF domain is favorable to suspension of the colloids, a relatively large fraction of Pu-242 may be transported by seepage water to the CP domain, in which the fate of the Pu-242 irreversibly adsorbed onto WF colloids may depend on the chemical conditions in the CP domain. Because of the pH buffering effect by the iron-oxyhydroxide corrosion products in the CP domain, the WF colloids usually flocculate and settle in the CP domain. For the cases that chemical conditions in the WF domain favors settlement of WF colloids, transport of Pu-242 out of the WF domain is primarily through the aqueous

phase. The large iron-oxide surface area after the waste package materials completely corrode usually results in the Pu-242 adsorbed onto stationary corrosion products in the CP domain.

Pu-242 has a half-life of 375,000 years. About 84% of the total Pu-242 mass will decay within one million years. For the same realization as discussed above (under igneous intrusion scenario with an event at 10,000 years and within the same seeping environment of the same percolation region of the repository), the Pu-242 mass retained in the solid phase of the CP
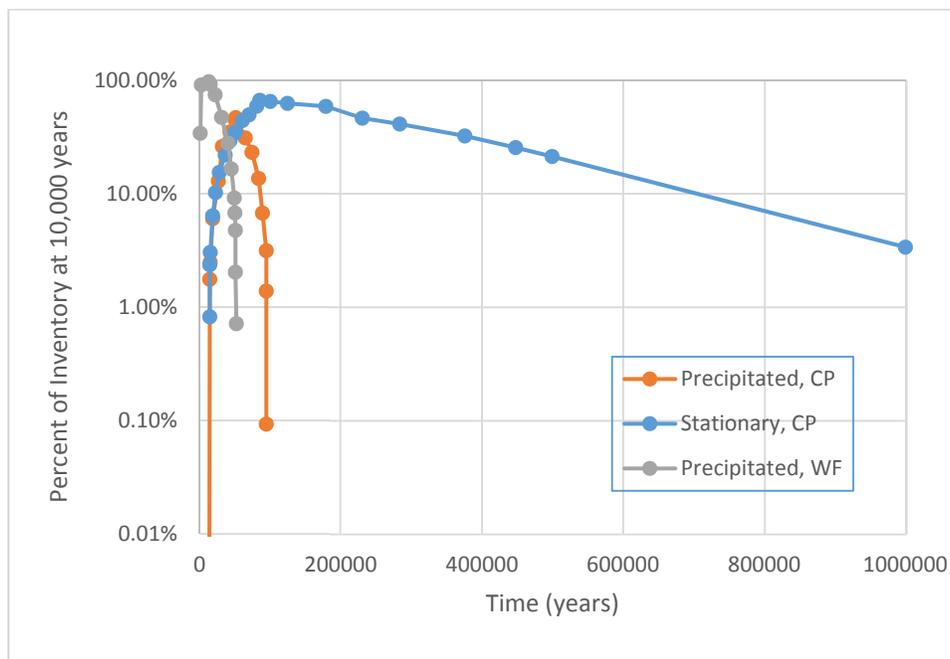
Figure 2.1. Np-237 Retained Inside the Waste Package, Including the Waste Form (WF) and Corrosion Production (CP) domains, in a Seeping Environment of a Percolation Subregion for a Realization of the TSPA Igneous Intrusion Modeling Case for 1,000,000 Years after Repository Closure. The Values Were Obtained by Digitizing Figures in DOE (2009b).

domain are about 5%, 59%, 26% and 11% of the initial inventory, including ingrowth at 10,000 years, at about 50,000, 204,000, 600,000 and 1 million years (Table 2.2). For this realization, most Pu-242 exists as precipitated oxide in the WF initially (Figure 2.2). The chemical conditions in the WF results in stable WF colloids with irreversibly absorbed Pu-242 in the WF domain, which are in turn transported into the CP domain and flocculate and settle into the solid phase due largely to the pH buffering effect of the waste package corrosion product or iron oxyhydroxide. As seepage water removes Pu-242 in solution and desorbs Pu-242 from steel corrosion products (stationary CP in Figure 2.2), the settled irreversibly adsorbed Pu-242 decays gradually over the lifetime of the repository. At 1 million years, only 11% of initial Pu-242 remains in the solid phase while 84% has decayed away.

Table 2.2. Percentage of Pu-242 in the Solid Phase in the Waste Form (WF) Domain and Corrosion Product (CP) Domain from a Realization of the Igneous Intrusion Model[1]

Yeas	50,000	204,000	600,000	1,000,000
Percentage of precipitated mass in WF	80%[2]	0%	0%	0%[2]
Percentage of mass on settled WF colloid in CP	4.2%[2]	51%[2]	26%[2]	11%[2]
Percentage of mass on stationary CP	1.2%[2]	8.2%[2]	0%[2]	0%[2]
Percentage of mass released from EBS	–[3]	11%	–[3]	–[3]

[1]The values are extracted from a TSPA realization of an epistemic uncertainty vector for the 1,000,000-year igneous intrusion modeling case (DOE, 2009b). The realization focuses on the seeping environment of a percolation region that contains 40% of proposed repository waste packages and represents the middle 40% of the expected range of percolation values of the proposed repository.

[2]The values were obtained by digitizing figures in DOE (2009b).

[3]Vaules not reported or too small to be accurately digitized are indicated by the minus (-) sign in the table.

Within an epistemic vector of DOE's TSPA realizations for the igneous intrusion scenario, the amount of Pu-242 irreversibly sorbed onto settled WF colloids and that sorbed onto stationary waste package corrosion products will be more evenly distributed among the realizations given the likelihood that chemical conditions in the WF domain may be equally favorable to suspension and settlement of the WF colloids (DOE, 2009d). The ensemble mean of the realizations may show a more evenly distributed Pu-242 mass among the solid phases in the CP domain. For example, in the igneous intrusion modeling case with an event at 100,000 years, the ensemble average of fractions of Pu-242 sorbed on settled WF colloids and stationary corrosion products are 10.3% and 12.5%, respectively (Table 2.3).

Compared to igneous intrusion scenario, behavior of mass release and retention in the seismic ground motion and nominal case is controlled by epistemic uncertainty in the timing of waste package failures. In DOE's abstraction of waste package damage, advective flux of seepage water through the stress corrosion cracks in the waste package is screened out in the seismic ground motion modeling case. As a result, high in-package ionic strength is maintained in the waste package. Thus, stable colloids are unlikely to form prior to the time of waste package failure that allows advective flux through large waste package surface openings to alter the in-package ionic strength. Most Pu-242 mass released from the WF matrix is previously retained as precipitated mass in the WF domain (DOE, 2009d). Therefore, Pu-242 immobilized by

irreversibly attached to settled commercial SNF waste form colloids in the corrosion products domain is less significant in comparison with the igneous intrusion modeling case.
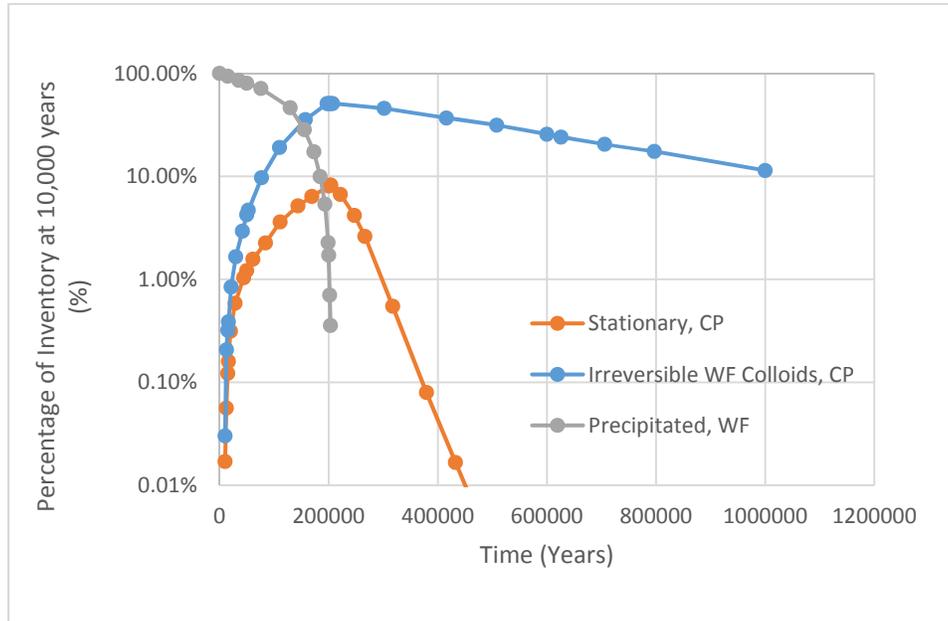
Figure 2.2. Pu-242 Retained Inside the Waste Package, Including the Waste Form (WF) and Corrosion Production (CP) domains, in a Seeping Environment of a Percolation Subregion for a Realization of the TSPA Igneous Intrusion Modeling Case for 1,000,000 Years after Repository Closure. The Values Were Obtained by Digitizing Figures in DOE (2009b).

Table 2.3. Mean Mass of Pu-242 per Failed Commercial SNF Waste Package in a Seeping Environment of a Representative Percolation Subregion for an Igneous Intrusion Event at 100,000 Years[1].

Year	200,000	600,000	1,000,000
Percentage of precipitated mass in WF	33.6%	5.6%	1.0%
Percentage of mass on settled WF colloid in CP	10.3%	6.3%	3.1%
Percentage of mass on stationary CP	12.5%	2.9%	0.6%
Percentage of mass released from the In-Package Environment	12.8%	18.2%	11.1%

[1]Values are extracted from Table 1.2.1-1 in DOE (2009d).

Because the times of waste package failure spread out through the 1-million-year period in the seismic and nominal case among individual realizations, comparing the ensemble per-failed-waste-package retention percentages of differing mechanisms to the igneous intrusion case, in which all waste packages fail at the same time, is not meaningful. Thus, a representative realization is more conducive to illustrating the individual effects of these mechanisms. For sorbing radionuclides such as Np-237 and Pu-242 under seismic and nominal scenarios, release from the EBS is controlled by the number of waste package failures and release rates from waste packages. The latter is in turn determined by waste package failure mechanisms, e.g., rupture and puncture, general corrosion patches, stress corrosion cracks (NRC 2014). In the following discussion, we examine a single realization under the nominal case with all drip shields fail by general corrosion at 304,000 years to demonstrate this risk insight used by NRC staff during the preparation of the SER. In the percolation subregion of interest here, waste packages also begin to fail intermittently at about 304,000 years (DOE, 2009b). All the waste package failures in the percolation subregion are failed by stress corrosion cracks. As a result, radionuclide transport in the WF and the CP domains is predominantly by diffusion. Nevertheless, the percolation subregion consists of both seeping and non-seeping environment, in contrast to the igneous modeling case in which the entire subregion is assumed seeping.

For the realization considered here, the cumulative Pu-242 release from the EBS at 1 million years from the seeping environment is less than a thousandth of a percent of the initial inventory. The release in the non-seeping environment is even smaller because the radionuclide is primarily transported through diffusion (85% of the released mass, see DOE, 2009b). At 1 million years, the amount of Pu-242 in the undegraded waste form and the amount of Pu-242 sorbed to stationary corrosion product in the CP domain account for approximately 1% and 15%, respectively (Table 2.4). Most of the initial Pu-242 inventory is removed through radioactive decay (84%).

After failure of the first waste package at 304,000 years, dissolved Pu-242 in the WF domain begins to precipitate until 800,000 years (Figure 2.3). In the CP domain, most Pu-242 sorbs on the surface of stationary corrosion products, but the concentration of Pu-242 in solution stays at the solubility limit because of the relatively small amount of seepage water that diffuses into the waste packages. At 1 million years, precipitated phase of Pu-242 remains in the CP domain (not shown in Figure 2.3 due to the relatively small amount). Compared to the igneous intrusion modeling case (Figure 2.2), the relatively smaller amount of water inside the waste packages result in smaller number of waste form colloids, which are unstable due to the high ionic strength.

The primary difference in retention of Np-237 to that of Pu-242 in the in-Package environment is the higher solubility and the absence of irreversible sorption to WF colloids. Though the solubility of Np-237 in the CP domain may be lower than that in the WF domain (e.g. see DOE, 2009b), the existence of corrosion products in the CP domain may remove a relatively large amount of Np-237 from the solution and result in Np-237 concentration lower than the solubility limit. For example, Figure 2.4 shows the solid phase distribution of Np-237 in a TSPA nominal case realization extracted by DOE (2009b). The absence of Np-237 precipitate after approximately 380,000 years indicates that corrosion products, once waste packages start to fail at around 304,000 years, continue to adsorb all the redissolved Np-237 as waste package materials continues to corrode. The sporadic appearance of a precipitated phase of Np-237 at around 304,000, 500,000, and 700,000 years indicates the first and the two peak failure times of

waste packages. The precipitated Np-237 redissolves relatively quickly in both the WF and CP domains in comparison with Pu-242 (Figure 2.3). At 1 million years 4% of Np-237 remains unexposed in the WF matrix and 68% has dissolved, diffused to the CP domain and sorbed onto stationary corrosion products (Table 2.5, or see DOE, 2009b).

Table 2.4. Percentage of Pu-242 in the Solid Phase in the Waste Form (WF) Domain and Corrosion Product (CP) Domain from a Realization of the Nominal Scenario Model[1]

Yeas	304,000	700,000	800,000	1,000,000
Percentage of unexposed mass in WF	61%[2]	17%[2]	4.3%[2]	1%
Percentage of precipitated mass in WF	0.3%[2]	4.1%[2]	0.4%[2]	0%
Percentage of mass on stationary CP	0%[2]	7.7%[2]	19%[2]	15%

[1]The values are extracted from a TSPA realization of an epistemic uncertainty ensemble for the 1,000,000-year nominal modeling case (DOE, 2009b). The realization focuses on the seeping environment of a percolation region that contains 40% of proposed repository waste packages and represents the middle 40% of the expected range of percolation values of the proposed repository.

[2]The values were obtained by digitizing figures in DOE (2009b).
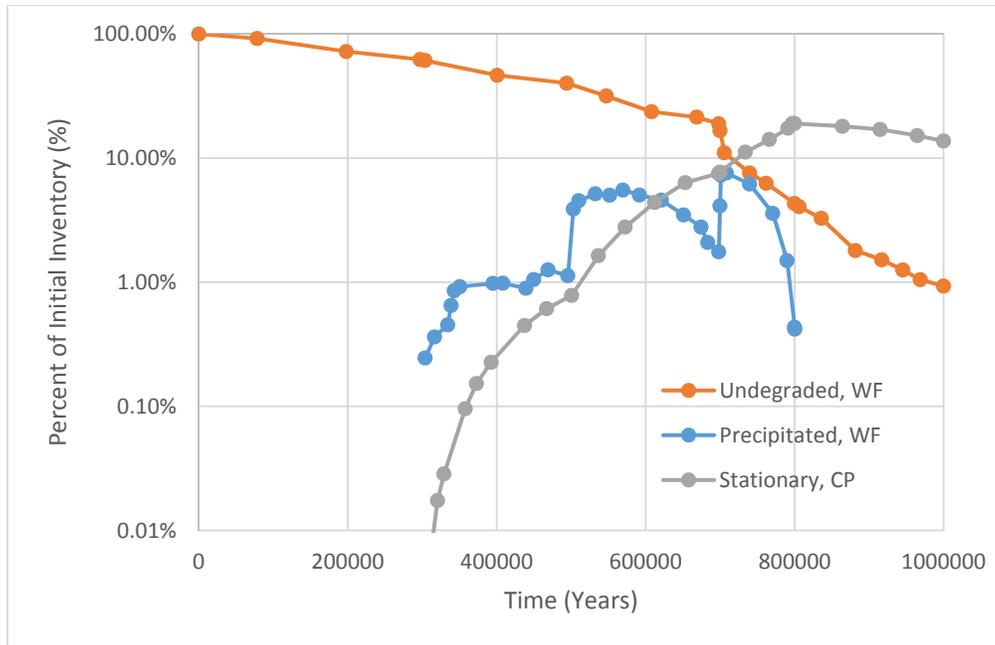
Figure 2.3. Pu-242 Retained Inside the Waste Package, Including the Waste Form (WF) and Corrosion Production (CP) domains, in a Percolation Subregion for a Realization of the TSPA Nominal Modeling Case for 1,000,000 Years after Repository Closure. The Values Were Obtained by Digitizing Figures in DOE (2009b).
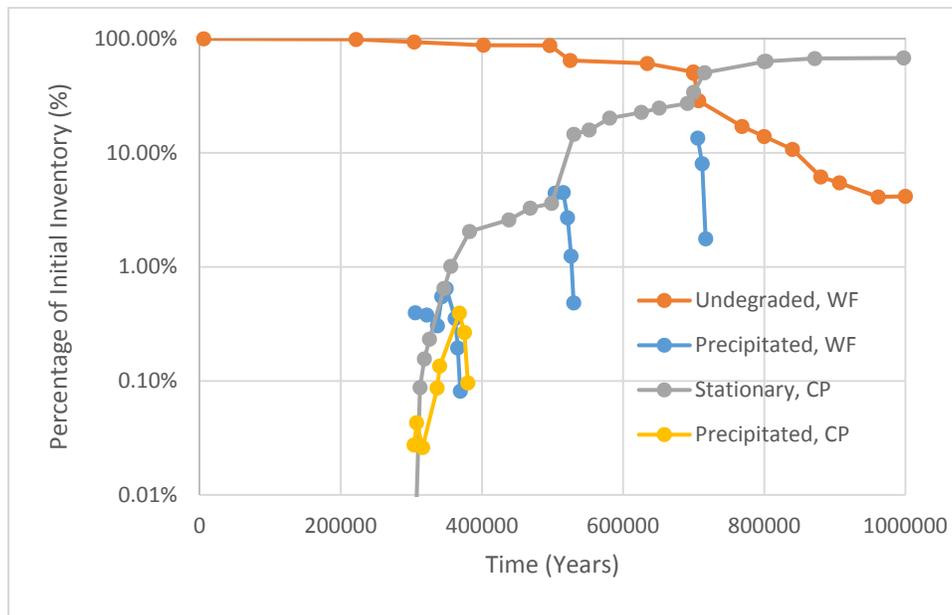
Figure 2.4. Np-237 Retained Inside the Waste Package, Including the Waste Form (WF) and Corrosion Production (CP) domains, in a Percolation Subregion for a Realization of the TSPA Nominal Modeling Case for 1,000,000 Years after Repository Closure. The Values Were Obtained by Digitizing Figures in DOE (2009b).

Table 2.5. Percentage of Np-237 in the Solid Phase in the Waste Form (WF) Domain and Corrosion Product (CP) Domain from a Realization of the Nominal Scenario Model[1]

Yeas	304,000	700,000	800,000	1,000,000
Percentage of unexposed mass in WF	94%[2]	50%[2]	14%[2]	4%
Percentage of mass on stationary CP	0%[2]	34%[2]	63%[2]	68%

[1]The values are extracted from a TSPA realization of an epistemic uncertainty ensemble for the 1,000,000-year nominal modeling case (DOE, 2009b). The realization focuses on the seeping environment of a percolation region that contains 40% of proposed repository waste packages and represents the middle 40% of the expected range of percolation values of the proposed repository.

[2]The values were obtained by digitizing figures in DOE (2009b).

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