REQUEST FOR ADDDITIONAL INFORMATION (RAI)
Volume 3—Postclosure Chapter 2.2.1.3.4—Radionuclide Release Rates and Solubility Limits—2nd Set (RAIs 1 through 11)
(DEPARTMENT OF ENERGY'S SAFETY ANALYSIS REPORT Section 2.3.7—Waste Form Degradation and Mobilization and Engineered Barrier System and Flow and Transport)

Topics: Availability and Effectiveness of Colloids and Engineered Barrier System Radionuclide Transport

RAI #1

Clarify under what conditions the forward rate constant that governs irreversible attachment of Pu and Am onto mobile iron oxide colloids is (i) computed based on a sampled target flux-out ratio, or (ii) set to the upper or lower bounds of the physically acceptable range. Clarify whether the rate constants are ever sampled directly from a log-uniform distribution and if so under what conditions. Clarify whether there are differences in the abstraction between seep and no-seep conditions.

Basis: Information provided in SNL (2007a, b) on approaches for calculating the forward rate constant of Pu and Am on mobile iron oxide colloids contains apparent inconsistencies. Staff believes the abstraction involves a comparison of results of an inverse model of the target flux-out ratio with a range of physically reasonable values, but ambiguity in the descriptions should be resolved. In addition, it is not clear whether the same approach for the forward rate constant applies to both seep and no-seep conditions. This information is needed to verify compliance with 10 CFR 63.21(c)(11-15) and 63.114(a) and (b).

RAI #2

Provide justification for excluding steel corrosion product (iron oxyhydroxide) colloids from the waste form domain for the EBS transport abstraction.

Basis: Within the EBS transport abstraction, the waste form domain is assumed to be free of corrosion product colloids; whereas steel corrosion products are assumed present in this domain in other abstraction models (water content and in-package chemistry). No basis for the assumption that corrosion product colloids are absent has been provided.

For radionuclides with low solubility, the dissolved concentration will be maintained at the concentration limit with or without colloids. If colloids are generated in or transported to the waste form domain, the total mobile mass (dissolved plus sorbed to mobile colloids) will be larger. Thus, neglecting iron oxide colloids in the waste form domain could cause radionuclide

release to be underestimated. This information is needed to verify compliance with 10 CFR 63.21(c)(9) and (11-15) and 63.114(e) and (g).

RAI #3

Identify the processes or features that limit colloid-facilitated transport in the EBS. Specifically, provide information on temporal variations in the stability and mass concentrations of colloids in the EBS and the corresponding aqueous chemical characteristics (pH and ionic strength) governing colloid stability for each colloid type in each domain. Summarize the information, explain how important modeled chemical conditions are to predictions of time-dependent colloid-associated release, and discuss confidence levels in predictions of colloid mass through time, given uncertainties in predictions of chemical conditions.

Basis: DOE did not demonstrate how often colloids would be unstable or stable in the EBS and which colloids would tend to be more stable and, hence, would be more important in dose calculations. This information is important to clarify the factors that influence the degree to which colloid–facilitated transport affects radionuclide release from the EBS. This information is needed to verify compliance with 10 CFR 63.21(c)(9) and (11-15) and 63.114(b) and (g).

RAI #4

Clarify how mean mass concentrations and stability conditions of SNF colloids, iron oxide colloids, and DHLWG colloids change in TSPA under the igneous intrusion and seismic scenarios.

Basis: Although DOE presented some information about potential changes in chemical environments under seismic and igneous scenarios for a single realization and provided explanations for potential impacts on colloidal suspensions, DOE did not provide quantitative information on if or how mean colloid mass concentrations and stability conditions would change under seismic and igneous intrusion scenarios. This information is needed to verify compliance with 10 CFR 63.21(c)(9) and (11-15) and 63.114(a), (b), and (g).

RAI #5

Provide justification for treating the corrosion product domain as a homogenous single-continuum porous medium with no preferential flow paths.

Basis: The information is needed to determine if radionuclide retention in the corrosion product domain is appropriately represented. The TSPA conceptualization of the corrosion product domain as a uniform granular porous medium maximizes access to sorption sites, which would serve to minimize or decrease release. However, the long-term configuration of the corrosion

products is uncertain. An alternative conceptualization in which part of the corrosion products form a contiguous mass with tight pore space and low permeability (SNL, 2007b, p. 6-47) could lead to preferential flow paths, preferential pathways for diffusive releases, reduced sorption in the EBS, and greater release of radionuclides. A basis for choosing between these two competing conceptualizations of the corrosion product mass has not been provided. This information is needed to verify compliance with 10 CFR 63.21(c)(11-15), and 63.114(a), (b), (f), and (g).

RAI #6

Provide additional justification for including amorphous hydrous ferric oxide (HFO) in the calculation of specific surface areas for stationary corrosion products. In particular, provide a basis that addresses repository-relevant time frames.

Basis: For the calculation of the surface area available for sorption on corrosion products, the TSPA abstraction considers corrosion products to be a mixture of HFO and goethite. HFO has a large specific surface area. Overestimating the HFO fraction would cause the release of plutonium, neptunium and other radionuclides to be underestimated. Although newly formed corrosion products are expected to be mostly HFO, HFO is unstable with respect to goethite and hematite (Schwertmann and Cornell 1991, Section 4.2.2); after long periods of time, goethite will most likely be the dominant phase (SNL, 2007b, pg 6-52).

The basis provided in the SAR for neglecting the transformation from HFO to goethite relies on studies of steel materials that had been undergoing corrosion for relatively short time periods. Specifically, the time periods of the cited studies were at most tens of years and were generally much shorter. However, radionuclides released from the waste form many years after waste package breach will likely encounter corrosion products that are much older. A basis for neglecting the HFO-to-goethite transformation on repository-relevant time frames (e.g. tens of thousands of years) has not been provided. This information is needed to verify compliance with 10 CFR 63.21(c)(11) and (12), and 63.114(b) and (f).

RAI #7

Describe and provide quantitative information on the movement of key radionuclides through the various components of the engineered barrier system. Quantitative information should include radionuclide mass in and flux between the physical domains. In particular, quantitatively describe the movement of isotopes of neptunium, plutonium and a highly mobile element such as technetium for the nominal and igneous modeling cases. For each combination of radionuclide and modeling case, identify one realization that contributes significantly to mean dose for that combination and one realization that represents typical EBS releases and provide the following

- Radionuclide flux (dissolved and, for plutonium, irreversibly associated with each colloid type) from the waste form domain, corrosion product domain, and invert as functions of time.
- Sorbed, precipitated, and dissolved mass in the waste form domain, corrosion product domain, and invert as functions of time.

Basis: Information on radionuclide retention in individual components of the EBS abstraction is needed to verify that the TSPA results are consistent with the process abstractions. This information is needed to verify compliance with 10 CFR 63.21(c)(11) and (12), and 63.114(a) and (b).

RAI #8

Justify the assumption that a single-rate first-order kinetic model appropriately represents Am and Pu sorption onto stationary and colloidal corrosion products.

Basis: This information is needed to determine if (i) radionuclide retention in the corrosion product domain and (ii) irreversible attachment to colloids are appropriately represented. The TSPA abstraction assumes a single-rate first-order kinetic model without providing a basis for that assumption. Data from experiments on plutonium sorption onto goethite are analyzed and compared with a two-site model and a non-first-order model (Elovich rate model) in SNL (2007b), where it is concluded "The data do not show the smoothly decaying exponential curve that sorption onto a single site would produce" (SNL, 2007b, p. 6-301). Consequences of using a single-rate first-order kinetic model to represent a more complex sorption process are not clear. This information is needed to verify compliance with 10 CFR 63.21(c)(11) and (12), and 63.114(b), (c) and (g).

RAI #9

Demonstrate that the procedure for establishing the range of forward rate constants from sorption data does not result in EBS releases of plutonium being underestimated.

Basis: The range of forward rate constants for sorption of americium and plutonium onto corrosion products was estimated from plutonium sorption experiments in SNL (2007a). The rate constants were calculated from the plutonium sorbed fraction at the end of the experiments. Rapid early uptake of plutonium was ignored when estimating the rates. Had the rates been estimated from the early part of the time series, the estimated rate constants would be larger. Larger forward rate constants would result in larger transfer of radionuclide mass to mobile corrosion product colloids and possibly to larger colloid-associated plutonium and americium releases from the EBS. In addition, because rate constants for desorption from stationary corrosion products are proportional to the forward rate constants in the abstraction, underestimating the forward rate constants would also result in the desorption rates being

underestimated, with potential implications for EBS releases of plutonium and americium. This information is needed to verify compliance with 10 CFR 63.21(c)(11) and (12), and 63.114(b).

RAI #10

Clarify the technical basis for validating the calculated sorption coefficients for iron corrosion products through comparison to previous compilations over the entire pH range considered in the EBS transport abstraction.

Basis: The competitive surface complexation model (C-SCM) used to calculate K_d values for radionuclide sorption onto stationary corrosion products (iron oxides or Fe-Ox) is supported by comparing the range in calculated values to recent EPA compilations of soil K_ds obtained in the laboratory (SAR, Section 2.3.7.12.3.4; SNL, 2007b, Section 7.2.3). For the purposes of this comparison, DOE compares values over a pH range from 6 to 9 (SAR, Section 2.3.7.12.3.4). DOE provides reasons for potential discrepancies at pH < 7, but there seems to be a consistent bias of C-SCM calculated K_d values to the high end of the EPA ranges at pH >8. For example, for moderately sorbing radionuclides such as neptunium and uranium, the calculated K_d values for 8 <pH< 9 are about 1 to 3 orders of magnitude above the lower limit for the EPA compilation at similar pH. The potential reasons for the bias in distributions and a discussion of potential consequences from using higher calculated values should be described clearly. This information is needed to verify compliance with 10 CFR 63.21(c)(11), (12) and (15), and 63.114(b) and (g).

RAI #11

Describe conditions where diffusion towards the EBS occurs in TSPA and explain the responsible physical and chemical processes. Describe the impact of the conceptual model, as noted in the basis, on radionuclide transport between the engineered barrier system and the unsaturated zone. Specify the modeling cases in which this occurs. Conditions may include dripping versus non-dripping, and magnitude of waste package failure.

For representative high-mobility, low-mobility, and colloid-associated radionuclides, quantitatively describe and explain the impact of diffusion towards the waste package on:

- EBS radionuclide release characteristics (e.g., net and gross release rates) and
- length of time and magnitude of contribution to dose (e.g., peak-spreading effects, changes in dose).

Basis: The conceptual model in SAR Figure 2.3.7-47 shows that unidirectional advective radionuclide flux (release from EBS) and bidirectional diffusive flux (both into and out of the EBS) could occur. Staff needs to understand under what repository conditions radionuclide transport from the UZ back to the EBS can occur, since this phenomenon could limit release to

the UZ. This information is needed to verify compliance with 10 CFR 63.21(c)(11), (12), and 63.114(a).

References:

Schwertmann, U. and R.M. Cornell. *Iron Oxides in the Laboratory: Preparation and Characterization.* New York, New York: VCH Publishers. 1991.

SNL. "Waste Form and In-Drift Colloids-Associated Radionuclide Concentrations: Abstraction and Summary." MDL-EBS-PA-000004 REV 03. Las Vegas, Nevada: Sandia National Laboratories. 2007a.

SNL. "EBS Radionuclide Transport Abstraction." ANL-WIS-PA-000001 REV 03. Las Vegas, Nevada: Sandia National Laboratories. 2007b.