2-page Summary for NEPTUNIUM SOLUBILITY IN THE NEAR-FIELD ENVIRONMENT OF A
PROPOSED YUCCA MOUNTAIN REPOSITORY

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The total system performance assessment (TSPA) for the proposed repository at Yucca Mountain, NV, includes a wide variety of processes to evaluate the potential release of radionuclides from the Engineered Barrier System into the unsaturated zone of the geosphere. The principal processes controlling radionuclide release and mobilization from the waste forms are captured in the model to assess the dissolved concentrations of radionuclides in the source-term. The TSPA model of the source-term incorporates the far-from-equilibrium dissolution of, for example, spent nuclear fuel (SNF) to capture bounding rates of radionuclide availability as the SNF degrades. In addition, for individual radionuclides, the source-term model evaluates solubility constraints that are more indicative of longer-term, equilibrium processes that can limit the potential mass transport from the source term in those cases. These solubility limits represent phase saturation and precipitation processes that can occur either at the waste form as it alters, or at other locations in the near-field environment (e.g., within the invert) if chemical conditions are different. Identification and selection of applicable constraints for solubility-limited radionuclide concentrations is a primary focus in formulating the source-term model for the TSPA.

Neptunium is a long-lived radionuclide that becomes a larger fraction of the potential dose as radioactive decay of other radionuclides proceeds. To delineate appropriate long-term source-term controls on dissolved neptunium concentrations, a number of alternative models have been defined. The models are based on data both collected within the Yucca Mountain Project and taken from published literature, and have been evaluated against independent data sets to assess their applicability. The alternative models encompass ones based on precipitation of neptunium within its own separate oxide phases (i.e., "pure" Np-phases), and those where neptunium is incorporated into the secondary (tertiary, quaternary, etc.) uranyl phases forming as alteration products of SNF (secondary phases). The constraints on dissolved neptunium concentrations from "pure" Np-phase models provide more elevated bounds compared to the values derived from models of trace incorporation of Np into secondary uranyl phases. Such secondary phase models depend on a larger set of processes and variables compared to more idealized solubility models for Np-oxides, and therefore, secondary phase models generally will have more complex bases to define adequately the expected behavior.

The three alternative models for solubility-limited neptunium concentrations that have been evaluated are: (a) the Np_2O_5 model based on precipitation of pentavalent neptunium phases, specifically Np_2O_5 saturation at low to moderate pH that transitions to $\text{NaNpO}_2\text{CO}_3$ saturation at high pH; (b) the NpO_2 model based on precipitation of that thermodynamically stable tetravalent neptunium oxide; and (3) the secondary phase model based on trace incorporation of Np into a primary formed secondary uranyl phase. At the relatively oxidizing conditions evaluated (at and slightly below atmospheric oxygen), the dissolved Np concentrations in equilibrium with any of these solid phases are dominated by the neptunyl ion (NpO_2^+) and its complexes in solution (i.e., pentavalent Np species). The Np_2O_5 model represents a conservative bounding model that results in concentrations of dissolved Np about 15 to 20 times higher than those for the NpO_2 model at neutral to slightly acidic pH values. As the oxidation potential decreases but remains relatively oxidizing, the dissolved Np concentration for the NpO_2 model decreases because of the change in oxidation state and widens the difference relative to the redox insensitive Np_2O_5 model. The secondary phase model is also relatively redox insensitive in this range for the system but produces concentrations that are the lowest of the three models at atmospheric oxygen conditions. Lower oxidation potentials favor the NpO_2 model because the solid phase becomes even more stable relative to the oxidized Np in the other solids. The NpO_2 model also exhibits retrograde solubility, decreasing by about 2 orders of magnitude between 25°C and 90°C.

Initial Project studies of Np solubility measured precipitation of Np-phases in dilute bicarbonate solutions that were highly Np-supersaturated via a neptunyl salt. The precipitates observed were found to be hydrated forms of Np_2O_5 and $\text{NaNpO}_2\text{CO}_3$ (at higher pH and Na concentrations). These oversaturation studies were reversed to confirm the solubilities of these phases. These studies are the primary basis for the

development of the Np_2O_5 model. However, because the thermodynamic data indicate that NpO_2 is more stable, these appear to be metastable phases that precipitated more readily than the stable solid because of the lack of a reduction step in their formation. Based on more recent studies, such kinetic barriers may not be large enough to limit formation of NpO_2 over longer times for a number of reasons. One study has already demonstrated NpO_2 precipitation from solution at 200°C in about two to three months (Roberts et al., 2003). In a study of humid air alteration of Np-doped U_3O_8 under oxidizing conditions, crystalline NpO_2 was produced in less than 3 weeks at 150°C and had started forming in about 16 weeks at 90°C for samples with Np:U ratios of 1:8 (Finch, 2002). These results suggest that NpO_2 formation rates may be high enough to control dissolved Np concentrations via the thermochemically stable solid.

Consideration of the conditions specific to altering SNF also provides additional support for this model, as it is likely that Np occurs within SNF in a tetravalent state and may exist as a very dilute solid solution within the UO_2 structure. As such, a thermochemical drive would exist for enrichment of the NpO_2 component in the remaining solid solution as the spent fuel alters. This process could limit the dissolved Np concentration as SNF alters and would progress naturally to saturation with NpO_2 . Such a mechanism would not involve any reduction kinetics as the NpO_2 would simply remain in the solid phase as the oxidatively unstable UO_2 component is altered. Project studies of SNF dissolution, both batch and drip tests, indicate that there are mechanisms limiting the dissolved Np on time-scales of up to about 9 years. The NpO_2 model solubilities provide a reasonable upper bound to the concentrations measured in these series of tests. Either slightly reduced conditions or NpO_2 enrichment as a solid solution in the unaltered SNF rim would decrease model solubilities into the observed range of values. The Np_2O_5 solubility model is demonstrably conservative by at least an order of magnitude.

Given that Np is a minor constituent of SNF, trace incorporation into uranyl alteration phases may be the most realistic constraint on its long-term behavior. An initial version of the secondary phase model was based on Np incorporation into schoepite. Schoepite is expected to be the initial uranyl alteration phase that forms directly on SNF based on observations from both experiments and from natural analogue (uraninite) alteration. Recent work (Burns et al., 2004) indicates that substantial removal of Np from solution clearly occurs only with formation of uranyl phases that have interlayer cation sites and that only minor association of Np with uranyl phases lacking interlayer cations (e.g., schoepite) was observed and was easily reversible by washing the solids. If Np is only efficiently removed by the tertiary and quaternary uranyl alteration phases that form as overgrowths on schoepite, then Np sequestration may depend on the relative timing of Np transport as those phases form. Because those uranyl alteration phases tend to form concentric layers beyond the schoepite, they will likely be along the transport path of Np away from altering SNF and may be able to effectively limit Np mobilization at that point. Quantification of this model would be facilitated by clarification of the mechanism for Np removal by these uranyl phases, as well as delineation of the compositional dependencies of that process. Compared to the secondary phase model, the NpO_2 model provides a slightly idealized, bounding approach that can be implemented more directly. If expanded to include solid solution within unaltered SNF, the NpO_2 model could represent constraints on dissolved Np as low as those for the secondary phase model, but only during the active alteration of the SNF.

In order to provide additional corroboration of the applicability of the NpO_2 model, the Project is conducting a series of kinetic experiments (similar to those of Roberts et al., 2003) to measure the precipitation rate and solubility of NpO_2 as functions of temperature. Initial tests will be performed at higher temperatures to estimate rates at more applicable lower temperatures, with confirmatory testing to follow. The data will also be used to reduce uncertainty in thermochemical data at higher temperatures for the NpO_2 model. Additional work is underway to investigate the mechanisms limiting Np concentrations in the drip tests. This will focus on further characterization of the solid phases from the drip tests to clarify the location and form of Np in the SNF and uranyl alteration phases. The data from these studies should allow discrimination among the possible controls on dissolved Np during alteration of SNF, including identification of any enrichment of Np in the remaining unaltered SNF.

Burns et al., *Radiochimica Acta* 92, 151–159, 2004.

Finch, *Mat. Res. Soc. Symp. Proc.*, 713, 639-646, 2002.

Roberts et al., *Radiochimica Acta*. 91, 87-92, 2003.