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Subject: Revised Intermediate Milestone 20.06002.01.222.520
Effects of Spent Nuclear Fuel Uranyl Alteration Phases on Radionuclide Dissolved Concentration Limits

Dear Dr. Rubenstone:

This letter transmits the Revised Intermediate Milestone 20.06002.01.222.520, Effects of Spent Nuclear Fuel Uranyl Alteration Phases on Radionuclide Dissolved Concentration Limits. As per the email received from E. Whitt on December 1, 2005, the headers present in the original submittal (August 2005) have been removed in this revision.

If you have any questions about this report, do not hesitate to contact me (210.522.5540) or Dr. David Pickett (210.522.5582).

Sincerely,

English C. Pearcy
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EFFECTS OF SPENT NUCLEAR FUEL URANYL ALTERATION PHASES ON RADIONUCLIDE DISSOLVED CONCENTRATION LIMITS

Prepared for

U.S. Nuclear Regulatory Commission
Contract NRC–02–02–012

Prepared by

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December 2005

ABSTRACT

In a geologic repository for high-level waste, incorporation of radionuclides in secondary phases as spent nuclear fuel dissolves and corrodes is a mechanism for potentially limiting released radionuclide concentrations and, thus, doses from groundwater exposure. In particular, understanding the processes that control Np-237 release is important for dose assessments of the potential repository at Yucca Mountain, Nevada. The U.S. Department of Energy (DOE) is not including the potential for reduction in the neptunium concentration limit as a result of incorporation in secondary uranyl phases in its performance assessments. DOE has, however, proposed this process as an alternative model and may employ it in future assessments or in support of the conservatism of its adopted concentration limit abstraction. This report summarizes available information—including theoretical considerations, natural analogs, and observed solution characteristics in coprecipitation experiments and spent nuclear fuel corrosion studies—that bear on the technical basis for including this process in performance assessments.

Coprecipitation experiments, in which neptunium is added to solutions from which uranyl minerals are synthesized, suggest that solid solution may be a viable mechanism for neptunium incorporation in uranyl phases in the presence of charge-balancing cations. However, the lack of observation of coprecipitation with uranyl oxyhydroxides has not yet been satisfactorily explained, and peroxide phases do not appear to be viable long-term hosts for neptunium. There is a lack of direct observation of neptunium incorporation in uranyl phases during spent nuclear fuel corrosion experiments. The understanding of this potential process may improve as measurement techniques become more sensitive and as the oxidation/reduction behavior of neptunium in the presence of corroding uranium solids is characterized better.

This review suggests that neptunium concentration limit control by incorporation into uranyl phases does not have a strong enough technical basis to be included in performance assessment abstractions. More data would be needed, using more sensitive techniques. These techniques could provide a means for constraining the oxidation state behavior of neptunium, likely secondary uranyl phase evolution in the repository setting, and kinetic and thermodynamic controls on Np/U solid solution.

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: Sources of data are referenced at the end of the report. These sources should be consulted for determining levels of quality assurance. No unpublished CNWRA-generated data are contained in this report.

ANALYSES AND CODES: No codes were used in the analyses contained in this report.

1 INTRODUCTION

In a geologic repository for nuclear waste, radionuclides will be released into solution when the wasteform interacts with water. The aqueous concentration of a released radionuclide is important because the concentration directly affects dose at the end of the transport pathway. The aqueous concentration of a given radioelement is determined by many factors, including its concentration in the solid wasteform, the mass of wasteform exposed to water, and the amount of water in contact with the wasteform. The radioelement aqueous concentration, however, may be limited by other processes such as sorption and precipitation.

For many radioelements, the aqueous concentration is limited to a maximum value by solubility constraints, based on equilibrium between the water and a thermodynamically stable radioelement-bearing solid phase. If the radioelement concentration increases such that the solution becomes over-saturated with respect to the solid phase, the solid precipitates to restore the solution to its equilibrium condition. This concentration limit applies to the total mass of isotopes (radionuclides) of the given radioelement.

In current performance assessments for the potential repository for high-level nuclear waste at Yucca Mountain, Nevada, the concentration limit for most radioelements is based on the solubility of the pure end-member solid phase that most limits the concentration of that radioelement (Bechtel SAIC Company, LLC, 2004, 2003; Mohanty, et al., 2003). For any given water chemistry, the solubility limit is theoretically an upper bound on radioelement concentration, but other factors can and, typically, would be expected to result in a lower concentration. For example, the rate at which the radionuclide is being released from the wasteform may be insufficient to saturate the solution. The inventory may be so small, or the solubility limit so high, that the limit would never be reached. Alternatively, the concentration of dissolved radionuclides may be limited by other processes that prevent the concentration from reaching the solubility limit of the pure solid phase. These processes potentially include sorption onto the surfaces of other solids or coprecipitation by substitution into a secondary phase in which the radioelement is a trace component. A concentration limit arising from coprecipitation is analogous to the solubility limit, except that the radioelement behaves as a minor constituent of the solid. For example, under the oxidizing conditions likely in the potential Yucca Mountain repository, uranyl phases (i.e, those containing hexavalent uranium) are likely to precipitate as spent nuclear fuel dissolves. Neptunium, a trace constituent of the wasteform that is simultaneously released to solution, may substitute for uranium in a secondary uranyl phase such as schoepite (Burns, et al., 1997a). If schoepite precipitates while the aqueous neptunium concentration is still very low, the solid solution of neptunium in schoepite could limit aqueous neptunium to well below the solubility limit of a pure neptunium solid phase such as Np_2O_5.

Sorption processes have long been represented formally by model abstractions in performance assessments, but our knowledge of coprecipitation processes is not as advanced. This report, based on review of the U.S. Department of Energy (DOE) reports and the open literature, describes the status of efforts to better understand how coprecipitation in wasteform alteration phases may limit the aqueous concentrations of radionuclides. For the reasons outlined in Section 1.1, this report focuses on neptunium and the solid alteration products associated with spent nuclear fuel corrosion. While coprecipitation is the specific process most often hypothesized to limit radionuclide concentrations below solubility limits, the non-genetic term "incorporation" is most conveniently used when the chemical process for inclusion of a trace

radionuclide has not been specified. In this report, we will use the phrase "uranyl phase incorporation" to denote this general process.

1.1 Importance to Repository Performance

In recent performance assessment calculations for the potential Yucca Mountain repository, the groundwater pathway dose was dominated by neptunium (Np)-237 at times beyond 15,000 to 60,000 years (CRWMS M&O, 2000a; Mohanty, et al., 2002; DOE, 2002). This result is due to a combination of Np-237 radiological and geochemical characteristics as modeled in the DOE performance assessment—chiefly its relatively high dose conversion factor, low sorption coefficients, and high concentration limit. The concentration limit abstraction for neptunium, modeled as controlled by Np_2O_5 solubility as a function of pH and CO_2 fugacity, can allow quite high Np-237 aqueous concentrations at the wasteform to be calculated (Bechtel SAIC Company, LLC, 2004). DOE has noted (Bechtel SAIC Company, LLC, 2004, 2003; CRWMS M&O, 2000b) that aqueous neptunium concentration during spent nuclear fuel corrosion under Yucca Mountain conditions may not be controlled by pure phase solubility. DOE supports this possibility by citing spent nuclear fuel corrosion experiments that showed neptunium concentrations well below pure phase solubility limits (e.g., Wilson, 1990a,b; Werme and Spahiu, 1998; CRWMS M&O, 2000c,d; see discussions in Bechtel SAIC Company, LLC, 2003; CRWMS M&O, 2000b; Friese, et al., 2003). (It should be noted that spent nuclear fuel leaching studies should not be expected to necessarily yield radionuclide concentrations at solubility limits; rather, a well-defined solubility limit should bound the test concentrations at their upper limit.) DOE, therefore, has discussed alternative concentration limit models that rely on coprecipitation or retention of Np-237 in secondary uranyl phases that form during the oxidative alteration of spent nuclear fuel (Bechtel SAIC Company, LLC, 2003; Buck, et al., 2003). Because coprecipitation as a solid solution limits concentration to below the pure phase solubility limit, this approach would lead to lower predicted Np-237 aqueous concentrations in water in contact with the wasteform. Because the modeled groundwater dose from Np-237 depends directly on the source concentration, implementation in the performance assessment of coprecipitation with secondary uranyl phases would result in lower calculated dose. DOE continues to consider such a model for possible inclusion in their total-system performance assessment (TSPA) model; therefore, review of the technical basis for incorporation is warranted.

As discussed elsewhere in this report, uranyl phase incorporation can potentially affect other radioelements—most notably plutonium—released from corroding spent nuclear fuel. Because plutonium solubility limits are relatively low, dissolved plutonium isotopes do not strongly affect estimated groundwater doses in performance assessments for the potential Yucca Mountain repository. Therefore, DOE has not made an effort to justify even lower plutonium concentration limits imposed by uranyl phase incorporation—the same may be said for other actinides. A strong technical basis is lacking for incorporating other radioelements such as technetium (e.g., Chen, et al., 2000). In addition, DOE has not argued for concentration limits based on incorporating radionuclides within other waste package materials such as altered glass. For these reasons, this report will focus on neptunium associated with spent nuclear fuel alteration phases.

1.2 Relevant Abstractions in Total System Performance Assessment

At the time this report was prepared, DOE was not planning to implement uranyl phase incorporation in abstracting the neptunium concentration limit for TSPA. Rather, the neptunium concentration limit is based on the solubility of the pure phase Np_2O_5 (Bechtel SAIC Company, LLC, 2004, 2003). The TSPA abstraction consists of a lookup table that provides neptunium concentration limits as a function of carbon dioxide fugacity and solution pH; the latter two parameters are extracted from other abstractions in TSPA. Over the applicable range of pH (3.0 to 11.0) and Log f_{CO2} (−1.5 to −5.0), the abstracted solubility limit ranges from 3.0×10^{-2} to 3.1×10^{4} mg/L [1.3×10^{-7} to 1.3×10^{-1} M] (Bechtel SAIC Company, LLC, 2003, Table 6.6-2, Figure 6.6-1).

As an alternative to the basecase solubility model for neptunium, DOE has proposed an empirically-based coprecipitation model for neptunium in secondary uranyl minerals that form as spent nuclear fuel corrodes (Bechtel SAIC Company, LLC, 2003; Chen, et al., 2002). This abstraction is based on a number of cited studies; effects on calculated dose have not been reported. A corroborating mechanistic process model has also been developed by DOE (Chen, 2003; Chen, et al., 1999). In an independent analysis using the NRC performance assessment code, a model assuming that radionuclide release (including Np-237) is controlled by the dissolution rate of the secondary uranyl mineral schoepite was used as an alternative case (Murphy, 2000; Murphy and Codell, 1999). This analysis resulted in groundwater doses lower than the NRC basecase.

Because radionuclide incorporation in secondary uranyl phases has not been implemented in DOE performance assessment basecases, evaluating these model abstractions is beyond the scope of this report. DOE has concluded that the technical basis is insufficient for inclusion in the basecase (Bechtel SAIC Company, LLC, 2004, 2003), but studies have continued.

1.3 Approach of This Report

As discussed in Section 1.1, risk considerations suggest that, in reviewing any license application for a potential Yucca Mountain repository, the NRC staff are unlikely to have to consider uranyl phase incorporation for any radioelement other than neptunium. Section 1.2 showed that, because DOE has not yet implemented an abstraction in TSPA, detailed evaluation of DOE incorporation models would be premature. This report, therefore, will focus on the available data, from both DOE-sponsored studies and the wider literature, that would be relevant to the technical basis for any Np-237 concentration limit abstraction DOE may choose in the future. Even without a DOE abstraction for uranyl phase incorporation, the data are relevant because DOE may use observations of neptunium incorporation as corroborating information to support the conservatism of their solubility-based neptunium concentration limit abstraction. Table 1-1 contains a list of nominal formulae for the uranium minerals mentioned in this report.

Table 1-1. Nominal Uranium Mineral Formulae*	
Becquerelite	$Ca(UO_2)_6O_4(OH)_6 \bullet 8H_2O$
Curite	$Pb_2U_5O_{17} \bullet 4H_2O$
Ianthinite	$UO_2 \bullet 5UO_3 \bullet 10H_2O$
Metaschoepite	$UO_3 \bullet nH_2O$ (n<2)
Metastudtite	$UO_4 \bullet 2H_2O$
Na-compreignacite	$(Na,K)_2(UO_2)_6O_4(OH)_6 \bullet 8H_2O$
Schoepite	$UO_3 \bullet 2H_2O$
Sklodowskite	$(H_3O)_2Mg(UO_2)_2(SiO_4)_2 \bullet 2H_2O$
Soddyite	$(UO_2)_2SiO_4 \bullet 2H_2O$
Sodium Boltwoodite	$(H_3O)(Na,K)(UO_2)SiO_4 \bullet H_2O$
Studtite	$UO_4 \bullet 4H_2O$
Uraninite	UO_2
Uranophane	$(H_3O)_2Ca(UO_2)_2(SiO_4)_2 \bullet 3H_2O$

*Fleischer, M. *Glossary of Mineral Species*. 5th Edition. Tucson, Arizona: The Mineralogical Record, Inc. 1987.

2 AVAILABLE INFORMATION

2.1 Theoretical and Interpretive Studies

There is widespread recognition of the potential importance of coprecipitation in limiting ion concentrations in natural aqueous systems (e.g., Langmuir, 1997). Efforts to model coprecipitation in high-level waste repository systems have been based on interpretations of laboratory and natural system observations and include considerations of secondary uranium, iron, and carbonate minerals (e.g., Bruno and Sandino, 1988; Bruno, et al., 1998, 1995; Curti, 1997). Based on ideal solid-solution thermodynamics, a conditional solubility constant that relates dissolved concentration and mole product of the minor component in the major phase has been used successfully in some cases (Bruno, et al., 1998). A similar approach was used in a DOE model proposed for the dissolved concentration limit of neptunium on the basis of the uranium concentration limit and a theoretical maximum solid phase Np/U ratio based on schoepite (Finch and Cunnane, 2001). In contrast, the DOE model of Chen, et al. (1999) used the spent nuclear fuel Np/U ratio and an empirical neptunium concentrating factor. As mentioned in Section 1.2, these models will not be evaluated in this report.

The potentially important role of secondary uranyl phases in controlling radionuclide release in the oxidizing Yucca Mountain environment is well established (Finch and Ewing, 1992; Wronkiewicz, et al., 1992; Pearcy, et al., 1994). The theoretical crystal-chemical basis for incorporating actinides into uranyl phases in the context of Yucca Mountain was developed by Burns, et al. (1997a,b), Burns (1997), and Miller, et al. (1997). These studies concluded that viable mechanisms exist for the substitution of plutonium and neptunium into uranyl mineral structures. Pentavalent neptunium, the state expected in oxidizing waters, can be accommodated in uranyl structures as long as compensating local charge balance and bond-valence substitutions take place (Burns, et al., 1997a).

2.2 Natural Analogs

The fate of trace metals and radionuclides associated with natural uranium minerals can provide useful information on spent nuclear fuel release mechanisms (e.g., Curtis, 1986; Curtis, et al., 1989; Brookins, 1990; Fabryka-Martin and Curtis, 1992; Bros, et al., 1993; Jensen, et al., 2000; Horie and Hidaka, 2004; Hidaka, et al., 2005). As expected, these behaviors are variable and site-specific. Direct, detailed studies of element redistributions resulting from oxidation of natural uranium minerals are not common. Horie and Hidaka (2004) reported that the rare earth elements were depleted and differentially mobilized on the oxidation of uraninite to curite and sklodowskite. In contrast, Zhao and Ewing (2000) concluded that secondary uranyl phases from the Colorado Plateau tend to concentrate trace metals such as thorium and the rare earth elements relative to primary uraninite. There is currently a lack of natural analog data bearing directly on the potential for incorporation of other actinides in uranyl minerals.

2.3 Laboratory Studies on Spent Nuclear Fuel Alteration Phases

Virtually any laboratory study on spent nuclear fuel corrosion or leaching can be thought of as addressing the question of secondary uranyl phase incorporation. Measured solution radionuclide concentrations can be compared with those expected on the basis of solubility and wasteform dissolution rate, and implications for the possible role of incorporation can be

discussed. However, only through more direct observation can a stronger, more quantitative basis be obtained for including such a process in performance assessment. Therefore, this review of laboratory studies will emphasize those in which direct observation of radionuclide incorporation in secondary phases was attempted, or those otherwise designed to simulate the process (e.g., coprecipitation during mineral synthesis) more directly.

2.3.1 Coprecipitation Studies Not Involving Neptunium

One approach to understanding incorporation behavior is through coprecipitation experiments, in which mineralogical control and characterization is likely to be more straightforward than in spent nuclear fuel corrosion experiments. In a series of studies, Quiñones, et al. (2001, 2000, 1996) precipitated radionuclides in solutions produced by dissolution of spent nuclear fuel and SIMFUEL. The solutions were diluted in groundwater or in synthetic NaCl solutions, and precipitation was effected by pH adjustment. By measuring solution compositions during precipitation, Quiñones, et al. (2001, 2000, 1996) concluded that the trivalent actinides americium and curium and the trivalent rare earth element europium have concentrations controlled not by pure phase solubility, but by coprecipitation with either sodium polyuranate or as an actinide/lanthanide hydroxide solid solution. Plutonium, however, had aqueous concentrations consistent with the pure phase amorphous $Pu(OH)_2$. In a related coprecipitation study, Diaz Arocas, et al. (1996) also concluded that trivalent rare earth elements were controlled by sodium polyuranate coprecipitation, but that tetravalent thorium concentrations were consistent with a pure hydroxide phase.

Kim, et al. (2002, 2000) conducted coprecipitation experiments under oxidizing conditions by adding tetravalent cerium (Ce) and trivalent neodymium (Nd) as actinide surrogates to solutions from which ianthinite, becquerelite, and an unspecified uranyl hydroxide were precipitated. Cerium and neodymium coprecipitation was strongest for the mixed U(IV)/U(VI) phase ianthinite, but both also coprecipitated with the uranyl phase becquerelite (Kim, et al., 2000). Coprecipitation was also observed with uranyl hydroxide (Kim, et al., 2002), but temporal trends showed a decrease in incorporation over time that pointed to the possible kinetic significance of surface area and growth rates.

Rousseau, et al. (2002) coprecipitated thorium with UO_{2+x} under reducing conditions. At pH greater than four, aqueous Th(IV) was controlled by pure thorium phase solubility. At lower pH, a non-equilibrium solid solution with UO_{2+x} was formed. The authors emphasized the importance of kinetic control of the solid phase Th/U ratio.

While these studies are not directly applicable to the effort to quantify neptunium uranyl phase incorporation, they are useful in demonstrating the potential success of coprecipitation experiments in predicting radionuclide release behavior. The results also point to the need to consider kinetic processes that can complicate simple thermodynamic interpretations and to the importance of solution characteristics such as pH.

2.3.2 Neptunium Coprecipitation Studies

The coprecipitation experiments of Quiñones, et al. (2000) discussed in Section 2.3.1 also produced data on neptunium uranyl phase incorporation based indirectly on solution composition. Neptunium aqueous concentrations on precipitation of spent nuclear fuel solutions (saline and groundwater) were at least two orders of magnitude below pure phase solubility

limits calculated by the authors. The pattern of variation in neptunium concentration with pH, however, was not consistent with a model of ideal solid solution with the observed sodium polyuranate secondary phase.

Rai, et al. (2004) reported carefully controlled Np(IV)/U(IV) coprecipitation experiments that produced an amorphous oxide solid solution. A thermodynamic analysis suggested that measured solubilities agreed well with an ideal solid solution model. These results are not likely to be directly applicable to expected Yucca Mountain conditions because of the reduced oxidation states of uranium and neptunium.

Recent neptunium coprecipitation studies directly relevant to the potential Yucca Mountain repository have been conducted by synthesizing candidate uranyl alteration phases in the presence of dissolved Np(V) under oxidizing conditions. The earliest such report published was by Buck, et al. (2003), which, in part, summarized the characterization of neptunium-doped synthesized studtite and uranophane at Pacific Northwest National Laboratory. Studtite, a uranyl peroxide phase, was precipitated by reacting uranyl nitrate with H_2O_2; conditions for uranophane synthesis were not detailed. Electron energy-loss spectroscopy on a transmission electron microscope was used to identify neptunium as a trace structural component of the uranyl phases. Quantification was not possible.

Later published reports from Pacific Northwest National Laboratory, with contributions from Washington State University and the University of Michigan, expanded on these earlier results (Buck, et al., 2004; Douglas, et al., 2005a,b; Friese, et al., 2004a,b). Buck, et al. (2004) was essentially a short summary of the Buck, et al. (2003) report and reached the same conclusions. Friese, et al. (2004a) focused on neptunium coprecipitation results for metaschoepite synthesized at room temperature. Virtually no neptunium was associated with the solid phase at pH 4.5 and 5.5, but the amount of neptunium in the solid increased to 100 percent of the total neptunium as pH was increased to 10.4 (experimental details may be found in Friese, et al., 2004b). The authors were unable to confirm that neptunium had formed a solid solution with metaschoepite rather than a pure solid phase.

Douglas, et al. (2005a) examined the fate of neptunium when synthesized metaschoepite was transformed to studtite by adding H_2O_2. Neptunium concentration measured by gamma spectrometry was negligible in the starting metaschoepite, but was 6,500 ppm in the solid after studtite was formed. No firm conclusion could be reached concerning the neptunium incorporation mechanism. After long-term storage in the laboratory, the studtite dehydrated to metastudtite and dissolution studies were carried out. Neptunium was released during metastudtite dissolution at a rate far exceeding what would be congruent with bulk dissolution. Douglas, et al. (2005a) concluded, therefore, that neither metaschoepite nor metastudtite would act at a significant level to incorporate neptunium during spent nuclear fuel corrosion in a repository setting.

Hydrothermal coprecipitation experiments (at pH 8 and 10) with the uranyl silicate minerals uranophane and sodium boltwoodite were discussed by Douglas, et al. (2005b). On the basis of bulk solid and solution analyses and electron energy-loss spectra, the authors concluded that neptunium was incorporated into the uranyl phases and did not form a discrete pure phase. Neptunium mass concentrations in the bulk solid ranged up to 1.6 percent.

In a separate series of studies, Burns, et al. (2004) have also examined the coprecipitation of neptunium with hydrothermally synthesized uranyl phases at pH 4.2 to 5.7. Neptunium was analyzed in the bulk solid by inductively coupled plasma mass spectrometry, but microanalyzing solid phases was not attempted. In most cases, solids were subjected to acetic acid wash to remove sorbed, non-precipitated neptunium. Burns, et al. (2004) found that the uranyl oxyhydroxide phases metaschoepite and β-$(UO_2)(OH)_2$ incorporated little to no neptunium, whereas the sodium uranyl oxyhydroxide phase Na-compreignacite and the calcium uranyl silicate phase uranophane did incorporate neptunium in direct proportion to its solution concentration. The authors argue that true incorporation in the latter two phases is supported by the linear relationship between neptunium concentration in solid and solution and the lack of X-ray evidence for discrete neptunium solids. The contrast in results for Na-compreignacite and uranophane versus metaschoepite and β-$(UO_2)(OH)_2$ was attributed to the lack of charge-balancing cations in synthesis solutions for the latter two. Such a mechanism may be required for true substitution of Np(V) into U(VI) phases (Burns, et al., 1997a). Preliminary results from the same University of Notre Dame group also suggest significant neptunium incorporation into the uranyl minerals soddyite and becquerelite (Klingensmith and Burns, 2005).

The wasteform group at Argonne National Laboratory has recently initiated Np/U coprecipitation experiments which, like those of Quiñones, et al. (2001, 2000, 1996), involve precipitation of neptunium and uranium from oxide solutions by pH adjustment (Ebert, et al., 2005). The experimental solutions include appreciable amounts of nickel, which is expected at high concentrations in waters that have reacted with waste package internal components. In some experiments, sodium was also added for pH adjustment as hydroxide and to provide a potential charge-balancing cation. Results, which are preliminary and do not include solids characterization, show retention of at least 10 percent of neptunium in the solids at pH 4.4 to 8.2, with the percentage in solids increasing up to 94 percent with increasing pH and sodium concentration. Ebert, et al. (2005) speculate that these observations are related to the availability of sodium for charge balance in the unidentified solids, facilitating Np(V)/U(VI) substitution.

In summary, the available coprecipitation studies to date for Yucca Mountain-relevant conditions suggest the following conclusions:

- Retention of neptunium in uranyl peroxides studtite and metastudtite is unlikely to be important in the long term even if, as some suggest, these phases could persist over long time scales in a repository environment (Hughes Kubatko, et al., 2003; Hanson, et al., 2005).

- Evidence is lacking for significant neptunium incorporation in uranyl oxyhydroxide phases, such as metaschoepite and β-$(UO_2)(OH)_2$, in the absence of potential counter-ions that would accommodate Np(V)/U(VI) substitution by charge balance. Definitive coprecipitation data do not yet exist on the behavior of these systems in the presence of charge-balancing cations such as potassium and calcium. Solids characterization by the Argonne National Laboratory group (Ebert, et al., 2005) and continued studies by the groups at Pacific Northwest National Laboratory and the University of Notre Dame may provide relevant information.

- Calcium and sodium uranyl silicate phases, as well as the sodium uranyl oxyhydroxide Na-compreignacite, appear to have a capacity for appreciable neptunium coprecipitation. Notably, these systems all contain potential charge-balancing cations.

2.3.3 Neptunium in Spent Nuclear Fuel Corrosion Tests

While coprecipitation experiments (Section 2.3.2) provide focused, potentially more mechanistic information on incorporation processes, tests on spent nuclear fuel and surrogates may yield more realistic results for understanding radionuclide behavior during oxidative corrosion. The first report of neptunium incorporation into a secondary uranyl phase during spent nuclear fuel corrosion was by Buck, et al. (1998). Electron energy-loss spectroscopic analysis of products of water vapor corrosion suggested neptunium coprecipitation in dehydrated schoepite, but not in uranyl silicate from drip corrosion tests. The lack of incorporation in uranyl silicates, or in any solids in drip tests, was confirmed by Finch, et al. (1999) and CRWMS M&O (2000b). The positive metaschoepite results of Buck, et al. (1998) were evaluated by Fortner, et al. (2004, 2003), who concluded that apparent identification of neptunium in the electron energy-loss spectrum was a spurious artifact of the uranium spectrum. Fortner, et al. (2004, 2003) used X-ray absorption analysis of vapor test uranyl corrosion products to demonstrate little or no neptunium incorporation. As pointed out by Ebert, et al. (2005), there is now agreement among research groups that the Buck, et al. (1998) report of incorporation cannot be supported and that no reliable detection of neptunium coprecipitation in any uranyl phase has been positively identified from spent nuclear fuel vapor and drip corrosion tests (Buck, et al., 2004; Douglas, et al., 2005b). The same conclusion applies to the Finch, et al. (2002) preliminary identification of neptunium incorporation in dehydrated schoepite in corrosion tests of unirradiated, neptunium-doped U_3O_8, based on electron energy-loss spectroscopy.

Ebert, et al. (2005, Section 2) conducted a detailed study of the uranyl phases in corroded spent nuclear fuel from the discontinued Argonne National Laboratory drip tests, employing X-ray absorption spectroscopy in an attempt to identify neptunium incorporation. As stated in Ebert, et al. (2005), "Uranyl alteration products are found to be devoid of, or at least relatively depleted in, neptunium (relative to the original fuel)." This conclusion is consistent with previous studies and with the re-evaluation of Buck, et al. (1998). As Ebert, et al. (2005) discuss, however, the accumulated evidence for this lack of neptunium incorporation is not consistent with the coprecipitation experimental results demonstrating incorporation into uranyl silicates (see Section 2.3.2 of this report). It is possible that the absence of neptunium in uranyl silicates in corrosion tests is due to the release of neptunium during the earlier stages of corrosion when uranyl oxyhydroxide phases—which coprecipitation experiments suggest incorporate little neptunium—are favored (e.g., Wronkiewicz, et al., 1992; Pearcy, et al., 1994). There is therefore little neptunium available for uranyl silicates as they later replace oxyhydroxides.

Ebert, et al. (2005, Section 2) conclude that a more likely explanation for the lack of neptunium incorporation in uranyl phases is that neptunium in spent nuclear fuel is maintained at the reduced Np(IV) state. Tetravalent neptunium at the surface of corroded spent nuclear fuel in the drip tests is consistent with X-ray absorption spectra, as well as spatial patterns of relative uranium and neptunium intensities. On an X-ray absorption spectroscopic map of corroded spent nuclear fuel, the Np/U ratio was highest on unaltered fuel grains and lowest on uranyl phases, consistent with Np(IV) retention on the unoxidized fuel surface (Ebert, et al., 2005, Figure 2-19). This oxidation state of neptunium would imply lower aqueous concentrations [due to the lower solubility, in general, of Np(IV) solids compared with Np(V) solids] and preclude

significant substitution in U(VI) phases, and would support a model of solubility control by NpO_2. This hypothesis, not yet fully tested, is consistent with observations of the formation of NpO_2 under oxidizing conditions during corrosion of neptunium-doped U_3O_8 (Finch, 2002), as well as reduction of dissolved Np(V) at UO_2 surfaces during sorption experiments (Albinsson, et al., 2001). In contrast, in the synthesis/coprecipitation experiments (Section 2.3.2), dissolved Np(V) may coprecipitate with uranyl phases prior to undergoing any reduction to Np(IV).

From a separate series of spent nuclear fuel corrosion experiments, McNamara, et al. (2005, 2004) have reported association of neptunium with a uranyl peroxide phase. In these tests, small volumes of initially deionized water remained in contact with spent nuclear fuel samples for two years. This configuration led to a build-up of radiolytic peroxide in solution and precipitation of a floating aggregate dominated by metastudtite that was relatively rich in neptunium and plutonium, but not enriched relative to uranium. The incorporation mechanism and the neptunium-bearing solid phase were not positively identified. While it cannot be ruled out that the conditions that led to the formation of peroxides could be present in a repository setting (Hanson, et al., 2005; Hughes Kubatko, et al., 2003), these phases have not been observed in any other corrosion studies, including tests involving low water volumes. Furthermore, the coprecipitation experiments of Douglas, et al. (2005a) suggest that metastudtite will not sequester neptunium on long time scales. Confirmation of the potential for neptunium incorporation in uranyl peroxides awaits further study.

The collective implication of spent nuclear fuel corrosion experiments is that neptunium incorporation in secondary uranyl phases is not yet quantifiable and has not yet been demonstrated to be viable for the long term in a repository setting.

3 SUMMARY

Understanding the processes that control Np-237 release from a high-level waste repository is important for dose assessments. DOE has not included the potential reduction in the neptunium concentration limit as a result of retention in secondary uranyl phases in its performance assessments. DOE has, however, proposed this process as an alternative model and may employ it in future assessments or in support of the conservatism of its adopted concentration limit abstraction. Theoretical considerations, natural analogs, and observed solution characteristics in spent nuclear fuel corrosion studies suggest that neptunium uranyl incorporation is a hypothesis worth testing.

Experiments involving neptunium coprecipitation on the synthesis of uranyl phases suggest that solid solution may be a viable mechanism for neptunium incorporation in the presence of charge-balancing cations. However, lack of observation of coprecipitation with uranyl oxyhydroxides has not yet been satisfactorily explained and is likely to continue to be a subject of study. Peroxide phases do not appear to be viable long-term hosts for neptunium.

The coprecipitation test results stand in contrast to the lack of direct observation of neptunium incorporation in uranyl phases during spent nuclear fuel corrosion. The understanding of this potential process will improve as measurement techniques become more sensitive and as the oxidation/reduction behavior of neptunium in the presence of corroding uranium solids is better characterized.

This review suggests that neptunium concentration limit control by incorporation into uranyl phases does not have a strong enough technical basis for inclusion in performance assessment abstractions, particularly in light of the negative spent nuclear fuel corrosion test results. More data would be needed, using more sensitive techniques, that would provide a means for constraining (i) the oxidation state behavior of neptunium, (ii) likely secondary uranyl phase evolution in the repository setting, and (iii) the kinetic and thermodynamic controls on Np/U solid solution.

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