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Title: Impact of the Formation of NpO2 and Np2O5 on the Np Soluability in YM Waters

Author(s): Wolfgang Runde, CST-7
David Janecky, CST-7
John Kaszuba, CST-7
C. Drew Tiat, CST-7

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Yucca Mountain Project

Los Alamos National Laboratory
Los Alamos, NM 87545

# Impact of the Formation of $NpO_2$ and $Np_2O_5$ on the Np solubility in YM Waters

Deliverable No. SPU33M4

W. Runde, D. Janecky, J. Kaszuba, C.D. Tait

**Summary:** The objective of this activity is to evaluate the impact of different Np solids on the solubility of neptunium in YM waters. Special interest is on the impact of $Np_2O_5$ found in solubility experiments as the Np solid phase. The formation and stability of $Np_2O_5$ is discussed and its stability calculated in J-13 based upon new solubility data. Clearly, the results show that $Np_2O_5$ is the most stable Np(V) solid phase that determined the solubility of neptunium under aerobic conditions. Both solubility experiments and geochemical modeling show a decrease of the neptunium solubility in J-13 of about two orders of magnitude (compared to previously reported results) based on the new solubility data. Under anaerobic conditions $NpO_2$ is the most stable Np bearing solid phase. Its formation would decrease the Np solubility by several orders of magnitude. This work was supported by the Yucca Mountain Site Characterization Project Office of Los Alamos National Laboratory as part of the Civilian Radioactive Waste Management Program of the US Department of Energy.

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## Table of Contents

## Impact of the Formation of $NpO_2$ and $Np_2O_5$ on the Np solubility in YM Waters

W. Runde, D. Janecky, J. Kaszuba, C.D. Tait.
Los Alamos National Laboratory, Chemical and Science Technology Division, Los Alamos, NM 87545.

### 1. Introduction

TSPA results have shown that the inventory of Np from stored nuclear waste under current scenarios would be sufficient to consider Np a potential problem contaminant, with $^{237}Np$ being the largest contributor to the radioactivity of a nuclear waste repository at times between $10^4$ to $10^7$ years (Andrews et al., 1994; Wilson et al., 1994; Rechard et al., 1995; Langmuir, 1997). Neptunium is considered to be the most hazardous radionuclide for repository times beyond $10^4$y in the most recent TSPA for the Yucca Mountain site (Rechard et al., 1995). Neptunium may exist as Np(IV) or as Np(V) in natural waters. In groundwater with low Eh Np(IV) dominates and reflects high immobility due to the formation of very insoluble Np(IV) solid phases. Low ionic strength and carbonate concentrations up to the millimolar range characterize waters from the Yucca Mountain site support the formation of oxide and hydroxide solids.

Under YM conditions, the final oxidation state of Np is yet not known, and the solubility limiting solid is predicted to be either Np(IV) or Np(V) depending on the redox of the infiltrating water and on the source of the database (Wilson and Bruton, 1990; Hakanen and Lindberg, 1991; Janecky et al., 1994, 1995). While Np(IV) is expected to be the dominant oxidation state under reducing conditions in natural groundwater, Np(V) is the most common oxidation state in oxygen-rich natural waters (Katz et al, 1986; Lieser and Mohlenweg, 1988; Hobart, 1990). For Np(IV), solubility-controlling solids include $Np(OH)_4$(am) and, especially, $NpO_2$(c). Under conditions for the Np(IV) redox state, the solubility in water to at least a total carbonate concentration of up to $10^{-2}$ M is expected to be lower than $10^{-8}$ M (Langmuir, 1997). Np(V) is reported to form carbonate and oxide solids in YM waters with solubilities orders of magnitude higher that those predicted for Np(IV). However, Np(IV) has not been observed to form in laboratory experiments with YM waters. So far, the impact of the reduction of Np(V) to Np(IV) can only be estimated

from modeling results. In this report we discuss the role of the solid phase and the oxidation state on the solubility of neptunium to be expected in YM waters.

This letter report deliverable has been designed to support the following level 3 reports: Summary Report of Geochemistry/Transport Lab Test, UZ Site Transport Model, and the SZ Transport Model. This letter report documents the impact of the Np solid NpO2 and Np2O5 on the neptunium solubility in YM waters to be expected and will be considered complete upon acceptance by the SPO technical lead for geochemistry.

## 2. Stability of Np(V) Carbonates versus Np(V) Hydroxides/Oxides

Carbonate complexation is one of the most important geochemical reactions of actinides in the environment. Stability constants are orders of magnitude higher than those of other potential ligands in natural aquifer systems, such as chloride, fluoride, or nitrate. Carbonate complexation of Np(V) in solution has been shown to occur in YM waters and soluble Np(V) carbonate complexes participate significantly in the Np(V) species distribution with about 40 to 60% of the total dissolved Np(V) concentration in the neutral pH range. However, Np(V) carbonate solids require a charge balance by alkali cations, in specific $Na^+$ or $K^+$. $NaNpO_2(CO_3)\cdot nH_2O$ and $Na_3NpO_2(CO_3)_2\cdot nH_2O$ have been determined as the predominant solid phases governing the Np(V) solubility in carbonate containing solutions. A clear stability dependence on the sodium carbonate concentration in solution has been found.(Neck et al., 1995; Runde et al., 1996) High sodium carbonate concentration support the formation of $Na_3NpO_2(CO_3)_2\cdot nH_2O$, while $NaNpO_2(CO_3)\cdot nH_2O$ is stable at low sodium carbonate concentrations. However, at low ionic strength and thus low sodium concentrations the formation Np(V) carbonates is suppressed and the formation of $NpO_2OH$ favoured. Figure 1 illustrate the stability of Np carbonates versus Np oxides/hydroxides. Of course, the stability of carbonate solids increases with the $CO_2$ partial pressure. However, in contrast to previously reported studies Np(V) carbonate solids have not been found in solubility experiment from both over- and undersaturation under J-13 conditions and pH $\leq$ 7. Increasing the pH from 7 to 8.5 raises the carbonate concentration by three orders of magnitude according to the known $CO_2$ dissociation equilibrium:

$$CO_2(g) \xrightleftharpoons{K_H} CO_2(aq) \xrightleftharpoons{K_1} H^+ + HCO_3^- \xrightleftharpoons{K_2} H^+ + CO_3^{2-} \qquad (1)$$

and the correlation between $[CO_3^{2-}]$ and measured $[H^+]$:

$$\log [CO_3^{2-}] = \log(K_H K_1^* K_2) + \log PCO_2 - 2\log[H^+] \quad (2)$$

At this high pH the formation of a Np(V) carbonate solid may occur due to the higher concentration of carbonate. However, we have not seen any formation of Np(V) carbonate solid phases in J-13 and calculations show that pH values higher than 9 are required to form Np(V) carbonate solids in J-13 water.

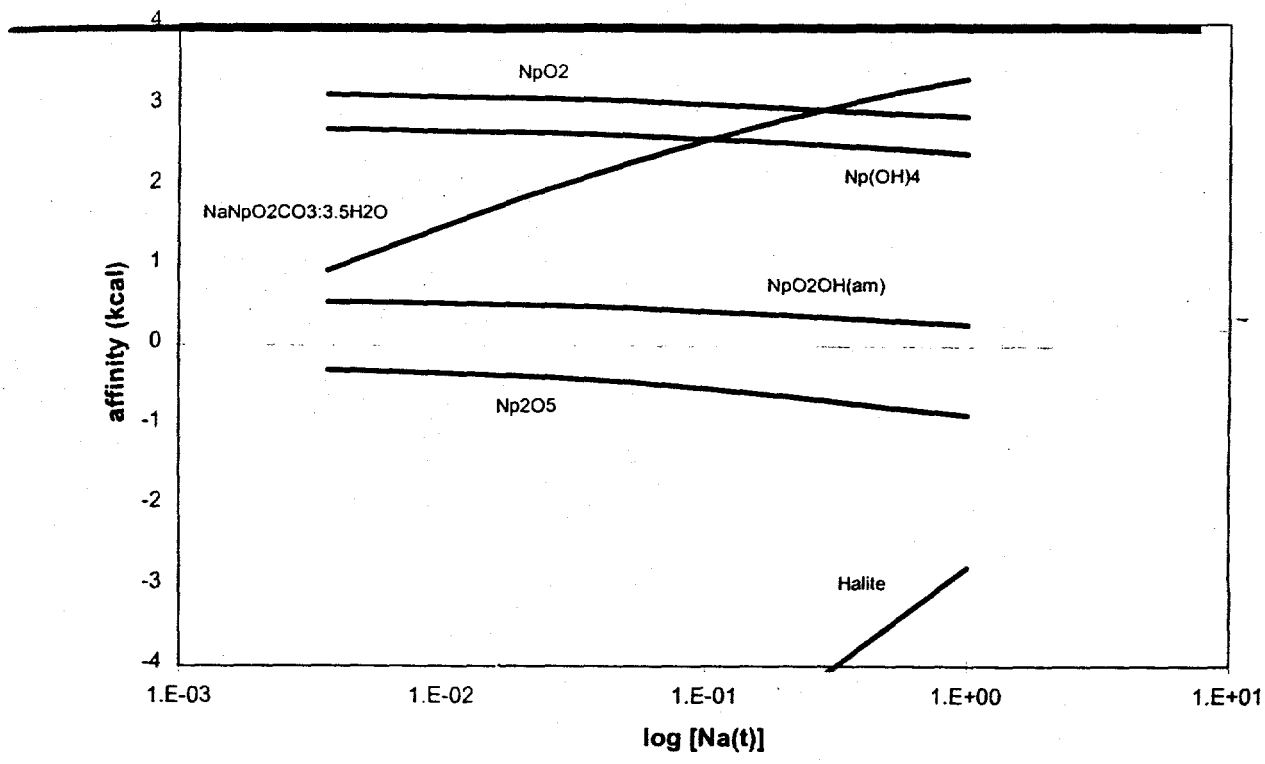


**Figure 1:** Stability of Np(IV) and Np(V) solids as a function of sodium concentration.

## 3. Redox Stability of Np(IV) and Np(V)

Under YM conditions, the final oxidation state of Np is not known, but the solubility limiting solid is predicted to be either Np(IV) or Np(V) depending on the redox of the infiltrating water and on the source of the database (Wilson and Bruton, 1990; Hakanen and Lindberg, 1991;

Janecky et al., 1994, 1995). The solubility of the two oxidation states is quite different, with Np(IV) having a solubility several orders of magnitude less than Np(V). While Np(IV) is expected to be the dominant oxidation state under reducing conditions in natural groundwater, Np(V) is the most common oxidation state in oxygen-rich natural waters (Katz et al, 1986; Lieser and Mohlenweg, 1988; Hobart, 1990). For Np(IV), solubility-controlling solids include $Np(OH)_4$(am) and, especially, $NpO_2$(c). Important solution species include $Np(OH)_4^0$ in low carbonate solutions (for pH>3) and $Np(OH)_3CO_3^-$ in higher carbonate solutions (e.g. total carbonate = $10^{-2}$ M, similar to UE25 water, pH range from 5 to 11). Under conditions for the Np(IV) redox state, the solubility in water to at least a total carbonate concentration of up to $10^{-2}$ M is expected to be lower than $10^{-8}$ M (Langmuir, 1997).

The predominance regions of Np(IV) and Np(V) solutions can be estimated in the $E_h$/pH diagrams shown in Figs. 2 and 3. In these diagrams, the top and bottom lines represent the limits of the stability field of water; above the top line, water is oxidized, while below the bottom line, it is reduced.(Pourbaix, 1966) The approximate Np(IV)/Np(V) solution boundary has been estimated for ambient temperatures by Hobart (1990) and Langmuir (1997), with the Np(IV) region shown in the shaded area. For Np(V), the solution area is dominated by the $NpO_2^+$ species, while for the Np(IV) area, it is dominated by the $Np(OH)_4^0$(aq) and, for carbonate-containing solutions, the $Np(OH)_3CO_3^-$ species. For the solid phase, $NpO_2$(c) is calculated to be the dominant solid phase even up to +0.5 to +0.6 volts (Langmuir, 1997). So far, YMP solubility experiments have only identified Np(V) solids (e.g. $NpO_2OH$ and $Np_2O_5$; Efurd et al., 1996, 1997, 1998), contrary to thermodynamic expectations. The Np(V) solids may therefore be metastable, with a large activation barrier of interconversion due to the large stability of the dioxo (yl) unit in the Np(V) solids. Two possible ways to overcome the metastable state may be (1) heat the sample to higher temperatures relevant to the near-field or (2) convert Np(V) to Np(IV) in the solution phase in contact with the solid(s).

The second possibility leads to the consideration of solution redox reactions with common mineral assemblages at YM. Superimposed on top of the Np $E_h$/pH diagram is the similar diagram for Fe(II)/Fe(III) and Mn(II)/Mn(IV) in environmental conditions (Stumm and Morgan, 1981). From Figures x and y, it is not certain that Mn(II) will be reducing enough to reduce Np(V), or whether Fe(II) will reduce Np(V) solutions in near-neutral to acidic conditions. On the other hand,

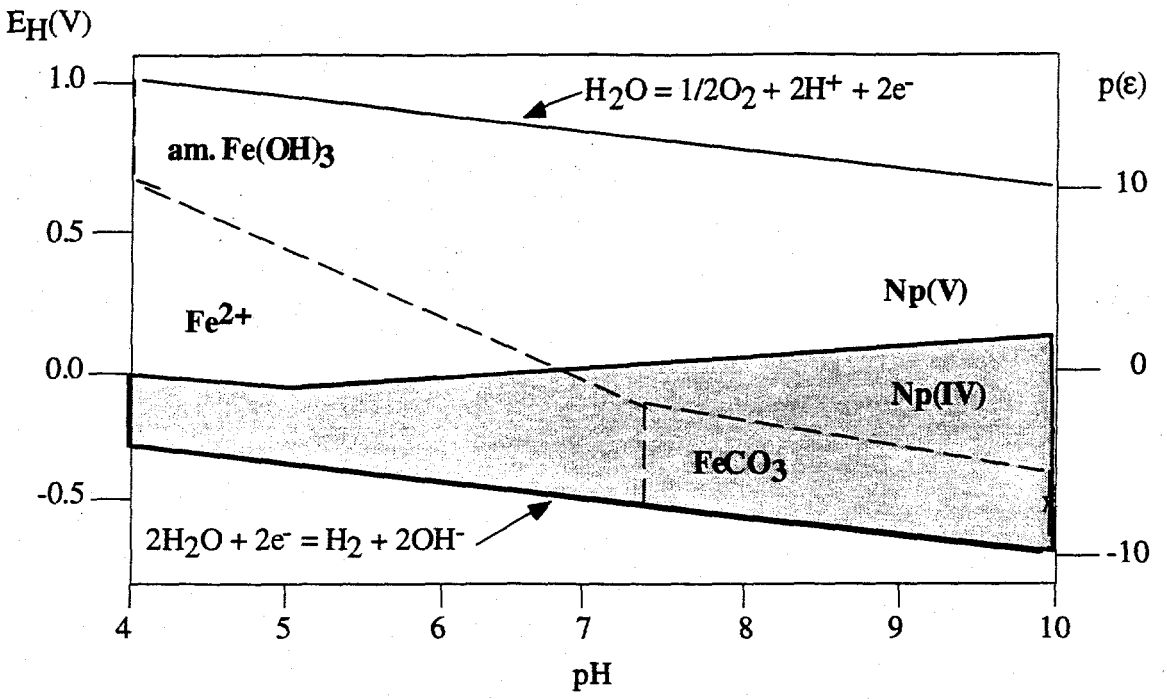


**Figure 2:** Eh/pH diagram for neptunium solution species and the Fe, $CO_2$, $H_2O$ system (25°C). Solid Fe phases considered: $Fe(OH)_3$(am), $FeCO_3$ (sidderite), $Fe(OH)_2$, Fe, $C_T = 10^{-3}$M, [Fe] = $10^{-5}$ M.

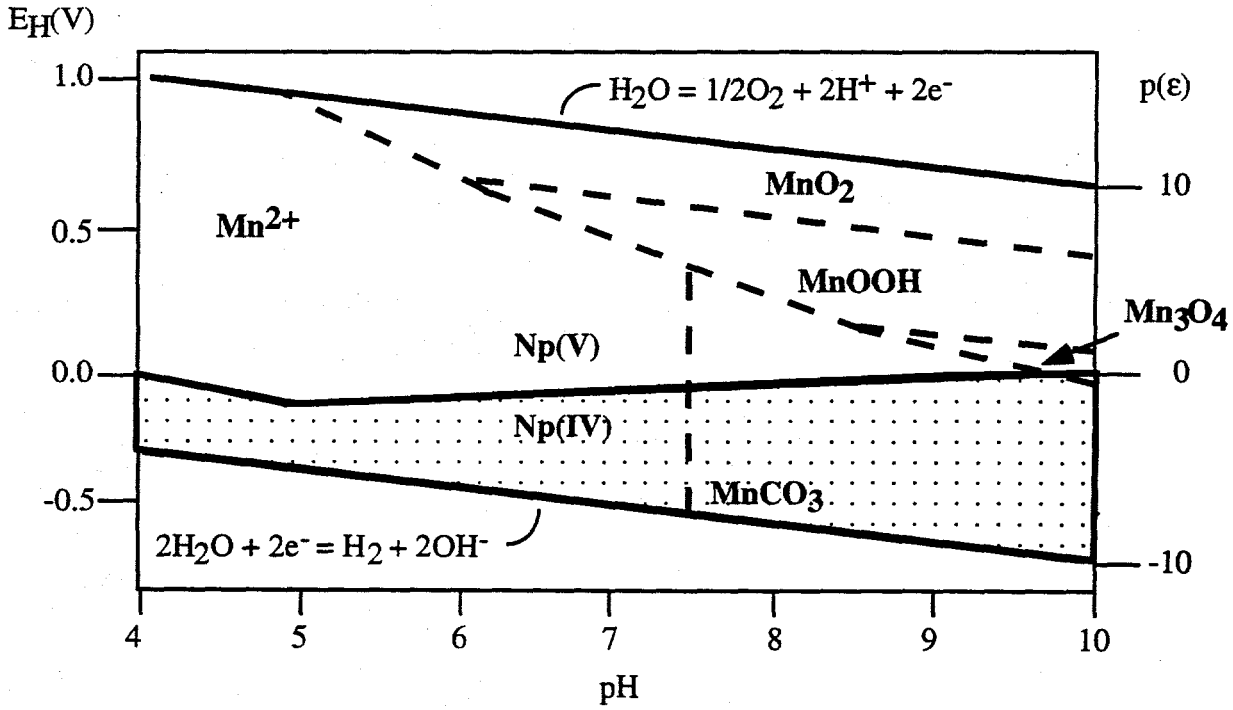


**Figure 3:** Eh vs. pH diagram for manganese/manganese minerals in contact with air and for the Np(IV/V) couple. Solid Mn phases considered : $Mn(OH)_2$ (pyrochroite), $MnCO_3$ (rhodochrosite), $Mn_3O_4$ (hausmannite), γ-MnOOH (manganite), and γ-$MnO_2$ (nsutite).

reduction with Fe(II) in basic conditions seems very plausible. We have reported on initial attempts to verify these predictions in a previous YMP Letter Report SP34FAM4 (Efurd et al., 1997). In neutral conditions, no reduction of Np(V) in J-13 like conditions was reported after 56 days at ambient temperatures or after heating the solution to 85°C for an hour (Efurd et al., 1997). However, neptunium was removed from the solution when Fe(II) was added to the solution at pH=9. The iron was definitely oxidized, but whether it was the Np(V) or contaminant $O_2$ in the system can not be proven at this point. Therefore, either Np reduction followed by precipitation (presumable as $NpO_2(c)$) or iron oxidation followed by iron precipitation and co-precipitation or sorption of Np(V) resulted in removal of Np from solution.

## 4. Formation of $NpO_2$

As for uraninite described above, the stability field for $NpO_2(c)$ may extend into the $E_h$ region in which Np(V) solution species may also exist (Langmuir, 1997). This extention depends critically upon the database used. Np(V) solubility-limiting solids include $Np_2O_5(c)$, $NpO_2OH(am)$, and, in high ionic strength carbonate media, the so-called double carbonate salts $Na_{1-2x}NpO_2(CO_3)_x$ (x=1 to 3) (Volkov et al., 1979, 1981; Neck et al., 1994, 1995). In the absence of carbonates, the solution speciation of Np(V) is dominated by the highly soluble $NpO_2^+$, which does not hydrolyze readily below a pH of 10 (Moskvin, 1971; Rosch et al., 1987; Neck et al., 1992; Tait et al., 1995). In J-13 type waters, the carbonate-complexed Np(V) species of importance includes $NpO_2CO_3^-$, where the higher carbonate complexes are not strong enough to be predominant, even at higher temperatures (Tait et al., 1995).

As for uraninite ($UO_2(c)$ ), the stability field for $NpO_2(c)$ may extend into the $E_h$ region in which Np(V) solution species may also exist (Langmuir, 1997). Different data bases for Np exist for thermodynamic modeling, but they all agree that $NpO_2(c)$ is the most stable form of neptunium solid. Using the Lemire-based data (Lemire, 1989) accepted into GEMBOCHS by the YM project, $NpO_2$ is always the most thermodynamically stable solid in J-13 from pH = 6 to 9 and T=20°C to 90°C (Janecky et al., 1994; Janecky et al., 1995; Efurd et al., 1996, 1998). This stability extends to an ionic strength of 0.1 M, at which point the sodium neptunyl carbonate becomes stabilized. Other solids of calculated importance include (in decreasing importance) $Np(OH)_4$ (the hydrated

amorphous form of $NpO_2$), $NpO_2OH$ (am), and $Np_2O_5$ (the actually observed bulk solid; see below for more details on this ordering). Although only Np(V) solids have been noted in YM pure actinide solubility experiments, the starting point for Np has always been $NpO_2^+$ and the breaking of the yl bonds have been implicated in giving metastability to the Np(V) solids. However, in the $UO_2$ matrix of spent fuel, Np might be expected to start out as a reduced Np(IV) solid, thereby mitigating the metastability concerns. In solubility experiments directly involving spent fuel (Bruton and Shaw, 1988; Wilson and Bruton, 1990; Wilson, 1990), Np concentrations did not exceed $3x10^{-9}$ M in oxidized J-13 water at 25 and 85°C after achieving steady-state within six months. It should be noted that this value is most consistent with the formation of $Np(OH)_4$(am) as the solubility-limiting solid rather than the even more stable $NpO_2$(c) (Langmuir, 1997).

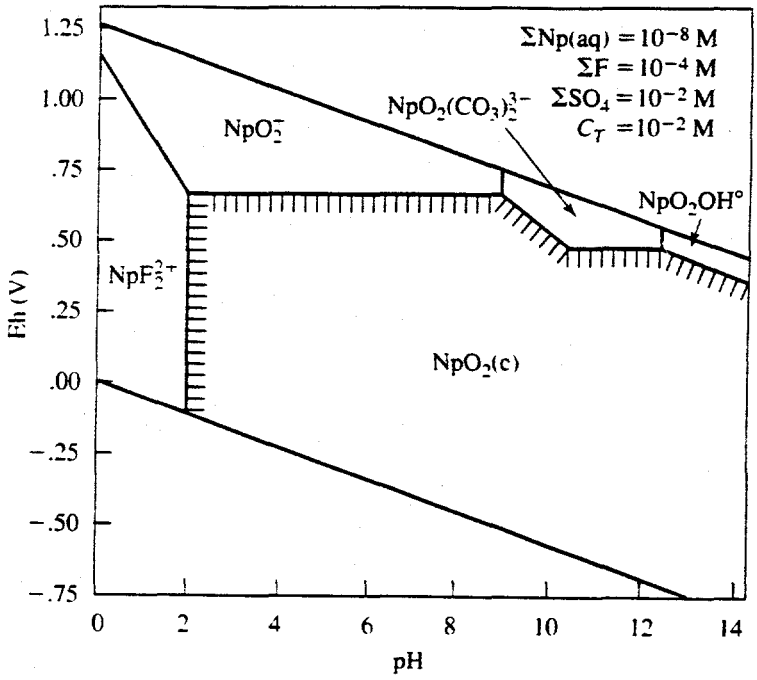


**Figure 4:** Stability field of $NpO_2$ and of predominant aqueous species (taken from Langmuir, 1997).

## 5. Formation of $Np_2O_5$

$NpO_2OH$ was the only Np(V) hydroxide reported to form in solubility experiments and thus considered as predominant Np(V) solid at low carbonate concentrations. The solubility of the Np(V) hydroxide has been studied in NaCl and $NaClO_4$ solutions at various ionic strengths.(Lierse and Kim, 1985; Neck et al. 1992; Runde et al., 1996) It is to note that a freshly precipitated amorphous $NpO_2OH$ is reported to have about 0.5 orders of magnitude higher solubility than an aged form of the Np(V) hydroxide. The aging process was observed only in 1 M $NaClO_4$. At higher electrolyte concentrations only the 'aged' Np(V) hydroxide was formed, at lower sodium perchlorate concentrations only the amorphous phase was observed. However, a solid state characterization was not performed and a conclusive evaluation of the nature of the solid phase in these solubility experiments is not possible.

$NpO_2OH$ may undergo a dehydration reaction following Eq. (3)

$$2\ NpO_2OH = Np_2O_5 + H_2O \qquad (3)$$

and form $Np_2O_5$. Original thermodynamic data were reported by Belyaev and coworkers (1979) and implemented into geochemical modeling supporting Lemire's thermodynamic database. In comparison to other Np(V) solid phases, $Np_2O_5$ is modeled to be the least stable solid Np(V) phase as shown in Figure 1. Even in waters with low ionic strength and sodium carbonate concentrations, as in J-13 water, Np(V) carbonates have been calculated to be thermodynamically more stable than $Np_2O_5$. In concurrence to these modeling results based on Belyaev's published data, Nitsche et al. (1993, 1994) and Efurd et al. (1996, 1997) found $Np_2O_5$ in solubility experiments in J-13 water. The solid phase was characterized using X-ray diffraction and the results agreed with the presence of $Np_2O_5$. Merli and Fuger (1994) reported thermodynamic data for the reaction

$$Np_2O_5 = NpO_2 + 0.5\ O_2 \qquad (4)$$

that are about eight orders of magnitude different from those reported by Belyeav et al. (1979). Thus the accurate determination of the solubility product of $Np_2O_5$ is needed to model the

solubility of neptunium in YM waters. We estimated the solubility of $Np_2O_5$ from our solubility data reported previously (Efurd et al., 1996, 1997) and modeled its stability. As shown in Figure 5, $Np_2O_5$ appears as the most stable Np(V) solid phase in J-13 water and is less soluble than the Np(V) hydroxide. This result is in agreement with the principle of the minimum free energy for the crystalline solid and less stability of the amorphous forms. While the stability of Np(V) carbonates are close to that of the amorphous Np(V) hydroxide, the new thermodynamic data result in a higher stability of $Np_2O_5$ than the Np(V) carbonates.

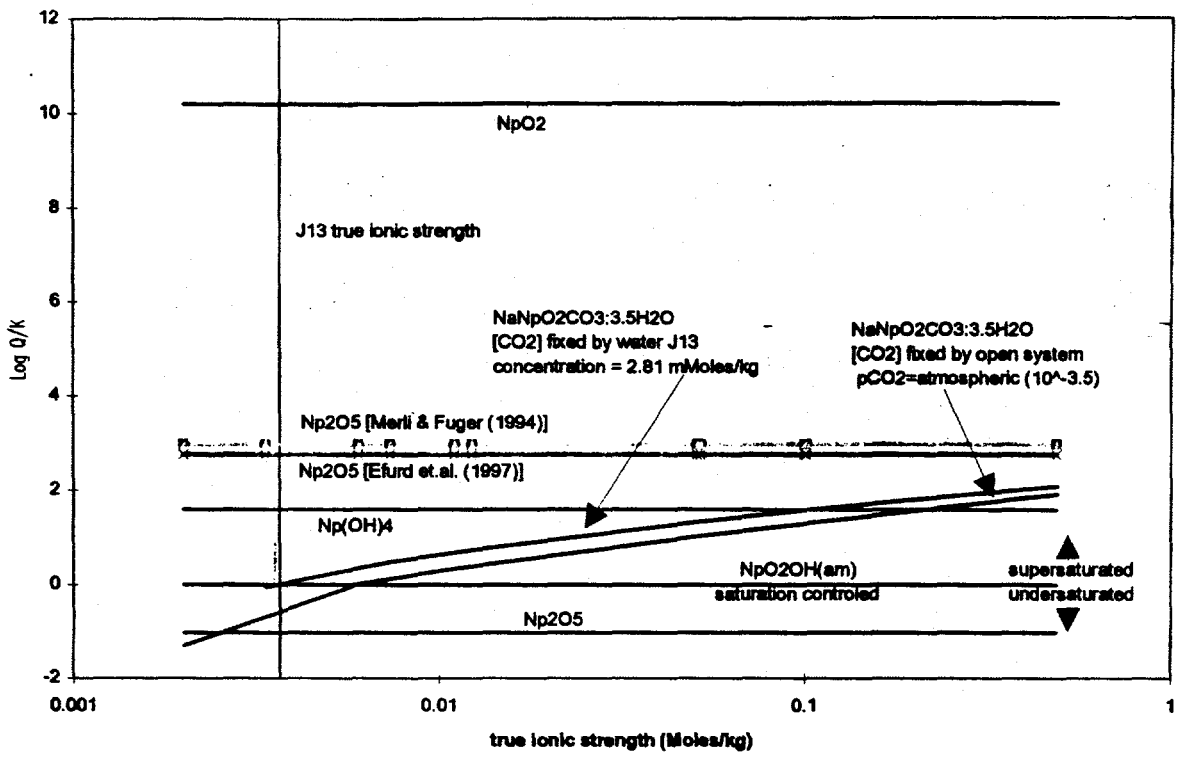


**Figure 5:** Stabilities of Np solids based on revised thermodynamic data. For the calculation of the $Np_2O_5$ stability previously reported solubility data were used (Efurd et al. 1996, 1997). Our calculated stability of $Np_2O_5$ agree well with that reported by Merli and Fuger (1994).

**6. Conclusion.** The nature and composition of the solid phase that limits the solubility of actinides in YM waters is essential for interpretation of experimental solubility data and geochemical modeling. It has been shown that in low ionic strength waters, such as J-13, $Np_2O_5$

is formed as Np bearing solid phase. Its solubility is about 1-2 orders of magnitude lower than those of Np(V) carbonates which are likely to form at higher carbonate concentration and at higher ionic strength. The results from solubility studies and the high predicted solubility of $Np_2O_5$ indicated a non-accurate thermodynamc value in the Lemire thermodynamic database. Under anaerobic conditions $NpO_2$ is the most stable Np bearing solid phase. Its formation would decrease the Np solubility by several orders of magnitude and reduce the Np mobility from a repository effectively.

This work was supported by the Yucca Mountain Site Characterization Project Office of Los Alamos National Laboratory as part of the Civilian Radioactive Waste Management Program of the US Department of Energy.

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## 8. List of Figures

**Figure 1:** Stability of Np(IV) and Np(V) solids as a function of sodium concentration.

**Figure 2:** Eh/pH diagram for neptunium solution species and the Fe, $CO_2$, $H_2O$ system (25°C). Solid Fe phases considered: $Fe(OH)_3$(am), $FeCO_3$ (sidderite), $Fe(OH)_2$, Fe, $C_T = 10^{-3}$M, [Fe] = $10^{-5}$ M.

**Figure 3:** Eh vs. pH diagram for manganese/manganese minerals in contact with air and for the Np(IV/V) couple. Solid Mn phases considered : $Mn(OH)_2$ (pyrochroite), $MnCO_3$ (rhodochrosite), $Mn_3O_4$ (hausmannite), γ-MnOOH (manganite), and γ-$MnO_2$ (nsutite).

**Figure 4:** Stability field of $NpO_2$ and of predominant aqueous species (taken from Langmuir, 1997).

**Figure 5:** Stabilities of Np solids based on revised thermodynamic data. For the calculation of the $Np_2O_5$ stability previously reported solubility data were used (Efurd et al. 1996, 1997).