DT# 47664 QA:NA 5/8/06 CB

Solubility Enhanced Immobility of Neptunium in the Unsaturated Zone at Yucca Mountain, Nevada

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Prepared for
TOUGH2 Symposium 2006
May 15, 2006

Acknowledgment

Yvonne Tsang
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YMP Reviewers

Outlines

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1. Objectives

- Existing studies account for advection, diffusion and sorption in nuclide transport.
- This work tries to include precipitation mechanism for potential enhanced immobility of Np nuclide in the UZ of Yucca Mountain.

2 UZ Pore Water Chemistry

UZ Pore Waters: Slightly alkaline and increased pHs from TSw to CHn

Other compositions: K^+ 3.0 ~ 10.6 mg/L
 SO_4^{-2} 9.0 ~ 240 mg/L

Pore water data compiled from various DTNs summarizing measurement data mainly from Yang et al. (USGS Report, 1996) THC data (BSC, 2005)

3. Neptunium Solubility and Conceptual Model

Neptunium Minerals: $\text{Np(IV)O}_{2(s)}$ inside waste package
 $\text{Np(V)}_2\text{O}_{5(s)}$ originally does not exist in natural environments, to be precipitated from the leachate

Np Mineral Dissolution and Precipitation in Natural Waters:

in Pure Water: pH, and (reduction and oxidation potential) Eh

in Natural Waters: pH, and Eh, and complexations with major negative ions

Np valence states: IV, V, and VI

Solubility Calculation: Considering total carbonate, SO_4^{-2} , pH, Eh, etc.

Data Base: Data0.ymp.R2

Neptunium Solubility in Natural Waters

Neptunium Solubility Calculated with $\text{Np}_2\text{O}_{5(s)}$
(25°C Eh = 400 mVolts).

(Note: Transport modeling uses fixed CO_2 partial pressure $1.32\text{E-}3$ bar).

Conceptual Model:

- (1) Slightly alkaline pore water accommodates less dissolved Np than in lower pH case (pH driven precipitation).
- (2) Controlling solid $\text{NpO}_{2(s)}$ was specified as Np source and
- (3) $\text{Np}_2\text{O}_{5(s)}$ can either precipitate and/or dissolve in the UZ.

4. Model Development and Results

Flow Model

(1) Model discretization: quasi 1-D

Total of 74 gridblocks

Gridblocks as small as 0.2 m spacing near the source

(2) The source volume is represented as unit-length volumetric value ($\sim 2 \text{ m}^3$) of waste package and horizontal area ($\sim 1.5 \text{ m}^2$) for connection area with neighboring blocks.

(3) Infiltration Rate: 5.9 mm/year, 100% of which flowing through the source and

(4) Transverse Mixing: Extra seepage added to the downstream of the source to account for lateral mixing, by the amount of 4 times the water flowing through the source.

Reactive Transport Model

TOUGHREACT 3.0 (Xu et al., 2005)

Pore water measurement data (Yang et al., 1996) were used in our model.

pH in pore water: Surface complexation for pH adjustment to average field value 8.2

(In addition: source at fixed pH throughout the simulation)

Np Minerals:

(1) Np Source: Mineral $\text{NpO}_{2(s)}$

Dissolved and released, assuming equilibrated with seepage water flowing through, and under oxidized environment

pH range: 4.5~8.5 (BSC, “Dissolved Concentration Limits of Radioactive Elements” AMR, 2005)

(2) $\text{Np}_2\text{O}_{5(s)}$ allowed to precipitate and/or dissolve in the UZ according to field conditions,

Rock Minerals and Pore waters

Minerals in the Rocks (Tuffs) (Mineral surface area and grain diameter not listed here)

Zones	Minerals	Volume fractions	Kinetic rate constants ($\text{mol m}^{-2} \text{s}^{-1}$)
Np source	$\text{NpO}_{2(s)}$	0.0005	6.8400e-07
Np (in the UZ)	$\text{Np}_2\text{O}_{5(s)}$	(to be precipitated in UZ)	variable
UZ Rock	calcite	0.0095	equilibrium
	tridymite	0.0919	3.4491e-13
	cristoba-a	0.1516	3.4491e-13
	quartz	0.0079	4.5206e-14
	glass	0.0152	7.7233e-15

Modeling Results

$\text{Np}_2\text{O}_{5(s)}$ precipitation in the UZ was kinetically dependent on pH and $[\text{NpO}_2^+]$. The precipitation was set at relatively low rate, equivalent to half-life of several years to tens of years

Note: The volume fraction at the source location marks the amount of $\text{NpO}_2(s)$ dissolved. A relatively fast precipitation rate for $\text{Np}_2\text{O}_{5(s)}$ in the UZ will shrink the precipitation zone in the above figures dramatically.

Concentration Profiles

NpO_2^+ along the flow path in the UZ varied with pH at the source

5 Summary and Conclusions

- (1) This study investigates the transport of neptunium under the conditions at Yucca Mountain UZ through chemical reactive transport.**
- (2) Conceptually there are two predominant mechanisms for the removal of Np from pore waters:**
 - A. pH driven (by a significantly higher pH in the UZ pore water); and**
 - B. Concentration driven.**
- (3) Modeling results show that there are potentially conditions for the Neptunium precipitation along the flow path in the UZ and**
- (4) There are uncertainties associated with the models, such as infiltration rates, pH at the source, and kinetic rates, which need to be further addressed.**