

Uranium and Neptunium Desorption from Yucca Mountain Alluvium

Presented to:
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Radioactive Waste Management
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Presented by:
**Cynthia D. Scism
Los Alamos National Laboratory**

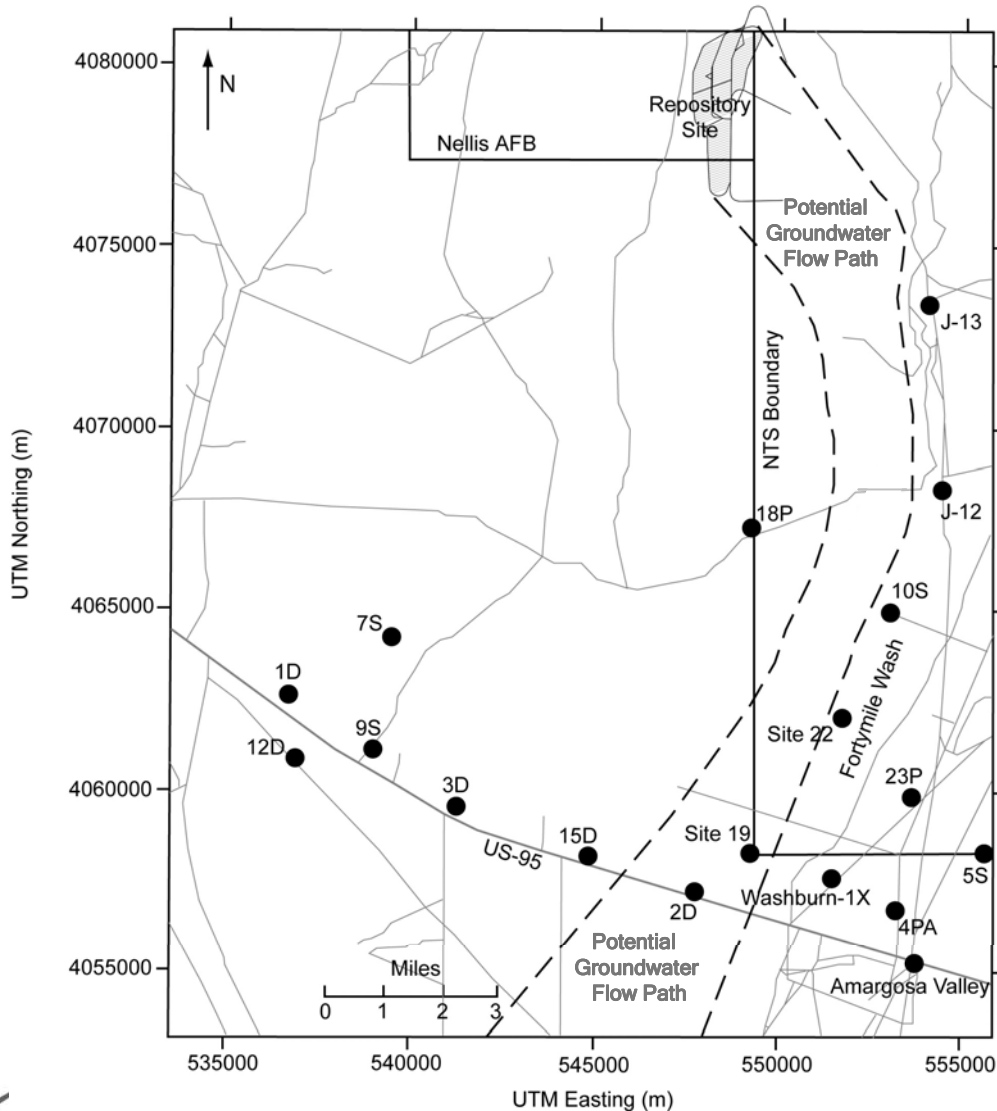
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Contributors: Paul W. Reimus, Mei Ding and
Steve J. Chipera

Uranium and Neptunium Desorption from Yucca Mountain Alluvium

- The saturated alluvium south of the proposed repository represents the final feature of the Lower Natural Barrier with characteristics and processes that can substantially reduce radionuclide migration before reaching the regulatory compliance boundary.
- Overall objectives:
 - demonstrate that radionuclide retardation in the saturated alluvium is likely to be significantly higher than is currently assumed in YMP models.
 - Emphasis on U and Np because of their high solubility, relatively weak sorption, and high contributions to potential dose in Yucca Mountain performance assessments. Also, emphasis on alluvium because of lack of existing data.
 - Focus on desorption measurements rather than classic emphasis on sorption measurements.
- Secondary objectives:
 - Vary the radionuclide contact time with alluvium during sorption to study the effects of residence time on long-term desorption.
 - Study effects of water chemistry and mineralogy on sorption and desorption behavior.
 - Develop modeling approach compatible with SZ process models.

Locations of Alluvium Wells



Alluvium and water from NC-EWDP wells:

- 19IM1, 740-745 ft bgs;
19D zones 1 and 4
water

- 22S, 557.5-560 ft bgs;
19D zones 1 and 4
water

- 10S, 680-685 ft bgs;
10S water

Alluvium-Quantitative X-Ray Diffraction

Mineral Phase	Well NC-EWDP-191M1A (wt %)	Well NC-EWDP-22SA (wt %)	Well NC-EWDP-10SA (wt %)
Quartz	15.3	10.1	8.7
Plagioclase	23.0	28.4	26.0
K-Feldspar	24.4	17.5	30.6
Clinoptilolite	7.6	12.0	11.6
Mica	1.3	1.0	1.8
Kaolinite	0.5	0.2	0.4
Cristobalite	5.8	5.9	8.1
Tridymite	4.1	4.3	1.6
Opal-CT	13.6	---	---
Hematite	0.4	0.6	0.5
Smectite	4.6	19.4	8.0
Total	100.6	99.4	97.4
Surface Area (m²/g):	6.32	16.64	5.87

22SA alluvium QXRD sample contains a higher weight percent of smectite and results in greater partitioning of the radionuclide to the solid phase of this alluvium sample in the initial sorption phase of the experiment.

Alluvium Column Desorption Experiments

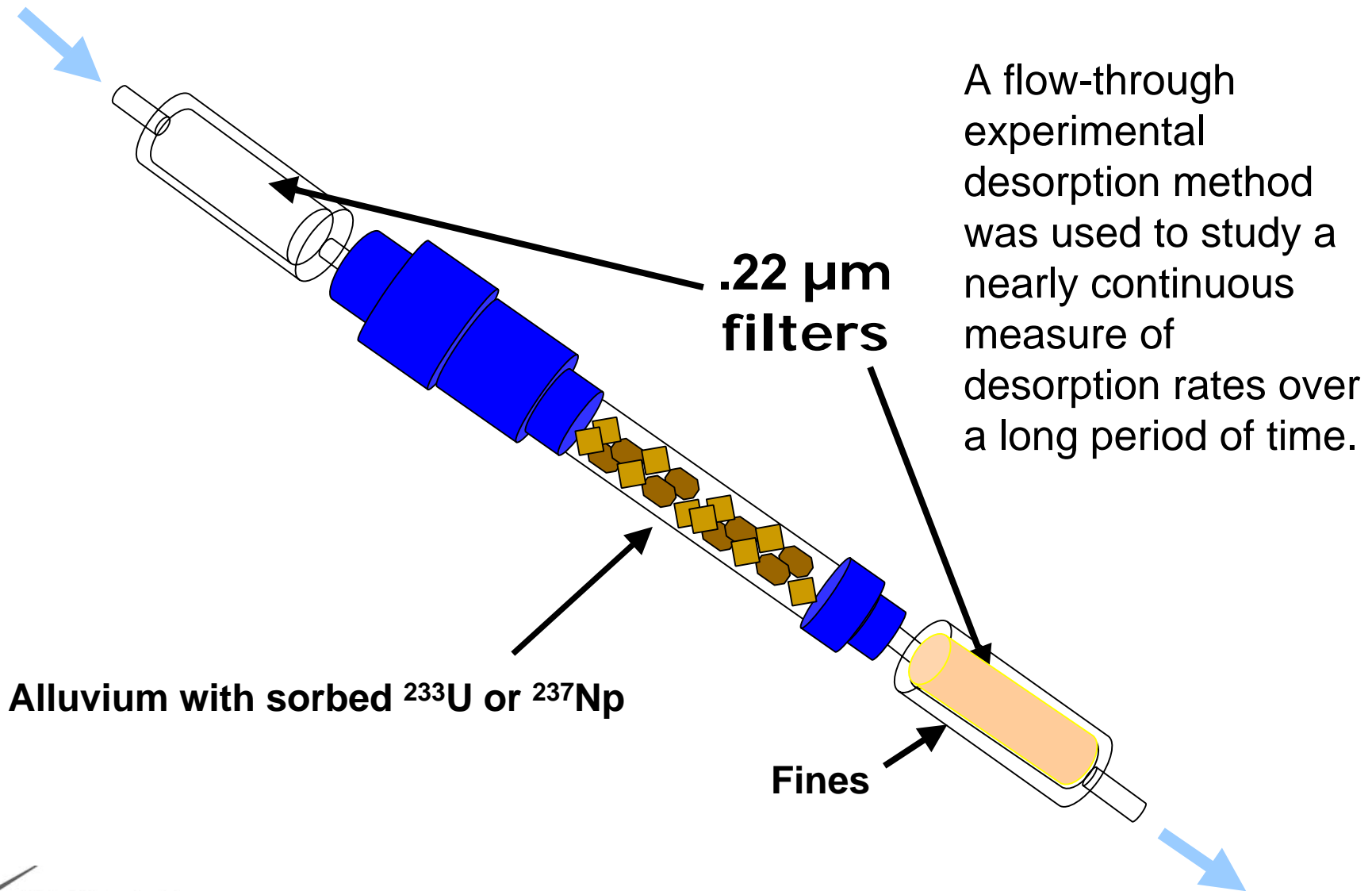
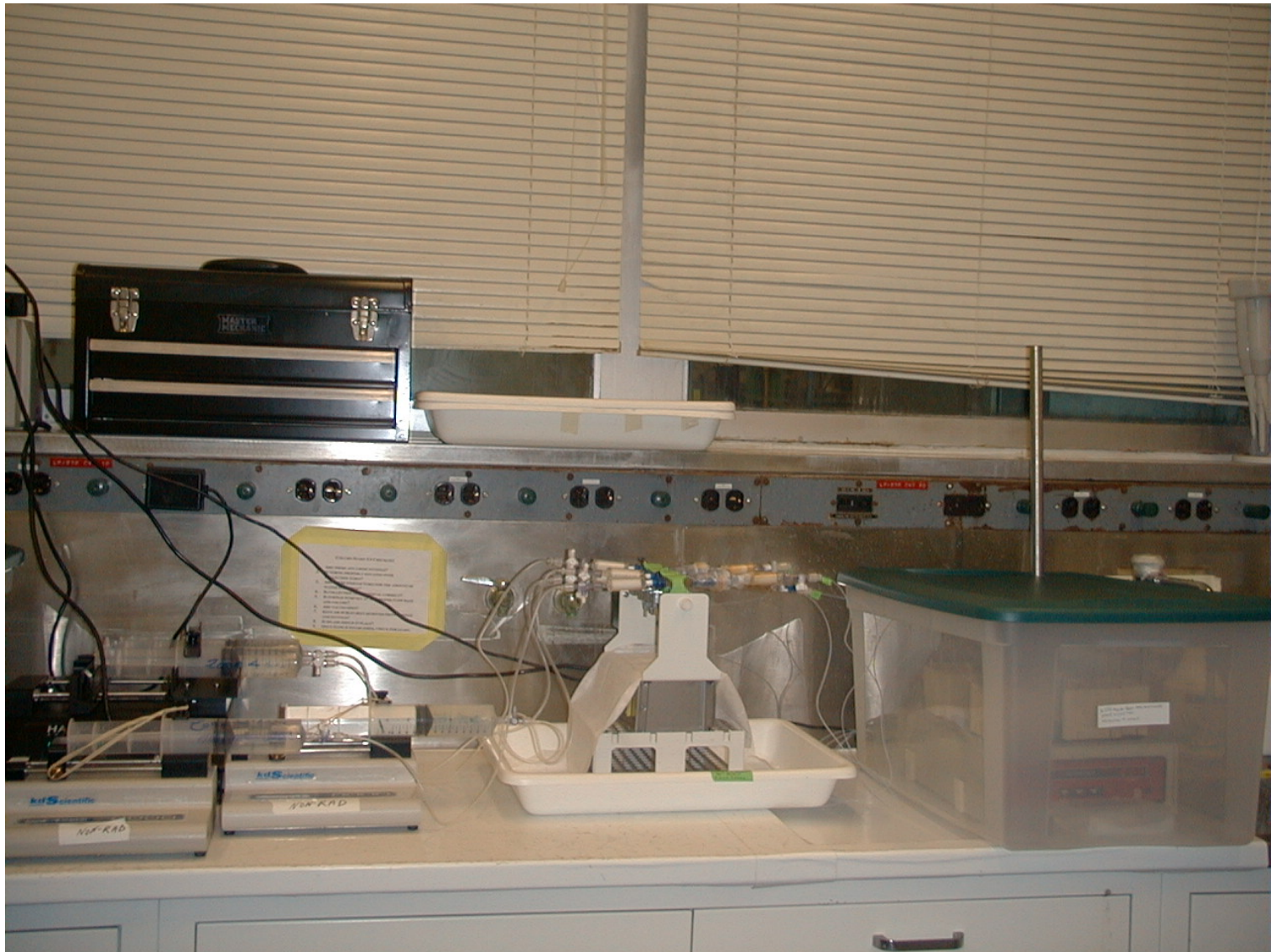
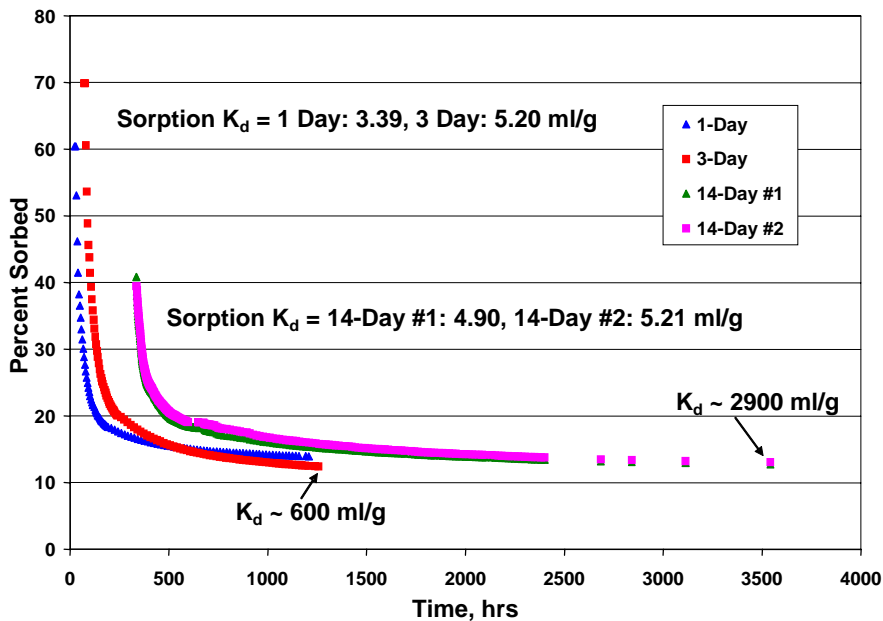


Photo of Four Alluvium Desorption Experiments

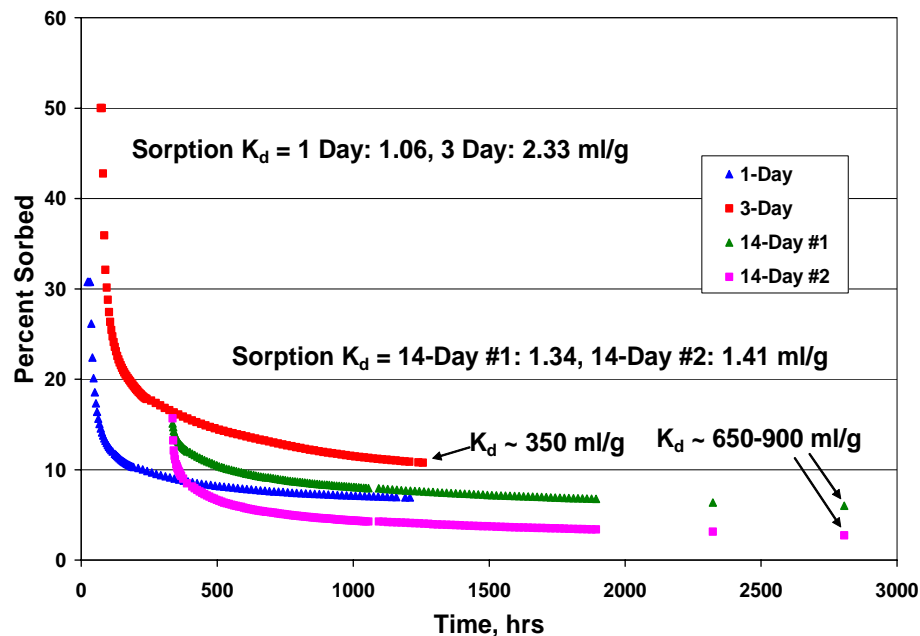


Uranium Sorption/Desorption to Alluvium – 19IM1

Lower pH, Lower Bicarbonate Water



Higher pH, Higher Bicarbonate Water



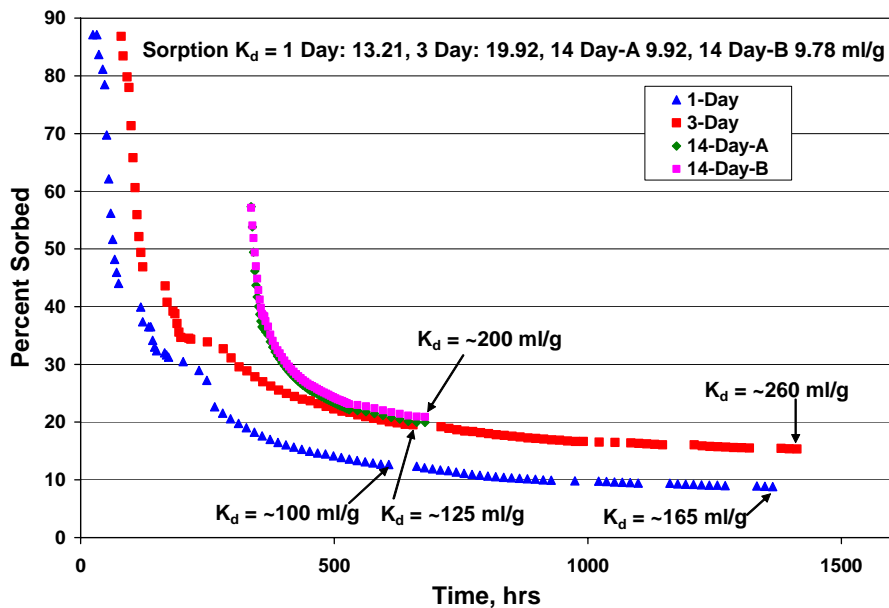
1-day and 3-day experiments: 3×10^{-6} M Tracer Solution

14-day experiments: 1×10^{-6} M Tracer Solution

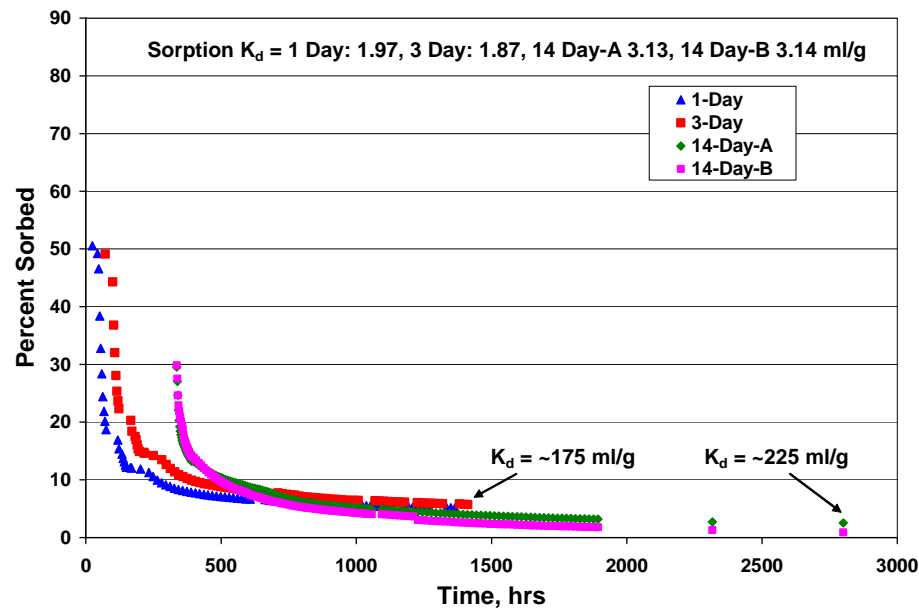
Alluvium Wt% from XRD: 7.6% Clinoptilolite, 4.6% Smectite, Opal-CT 13.6%

Uranium Sorption/Desorption to Alluvium – 22SA

Lower pH, Lower Bicarbonate Water



Higher pH, Higher Bicarbonate Water



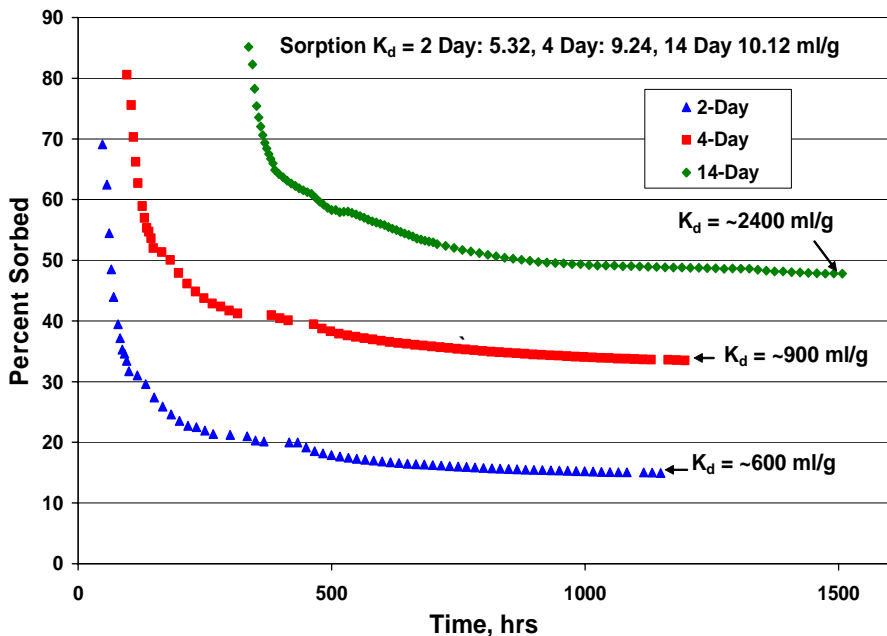
1-day and 3-day experiments: 3×10^{-6} M Tracer Solution

14-day experiments: 1×10^{-6} M Tracer Solution

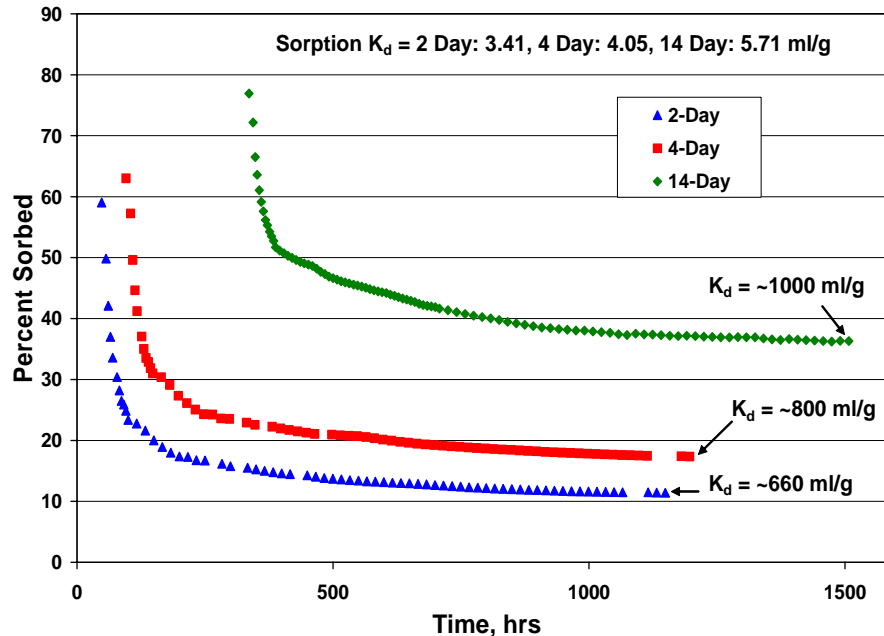
Alluvium Wt% from XRD: 12.0% Clinoptilolite, 19.4% Smectite

Neptunium Sorption/Desorption to Alluvium - 19IM1

Lower pH, Lower Bicarbonate Water



Higher pH, Higher Bicarbonate Water

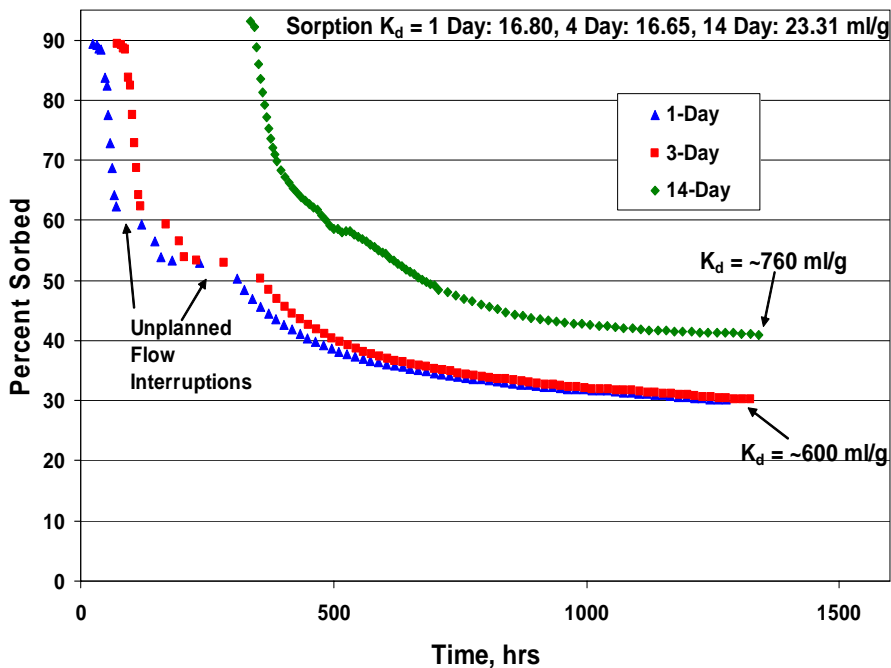


All experiments: 3×10^{-6} M Tracer Solution

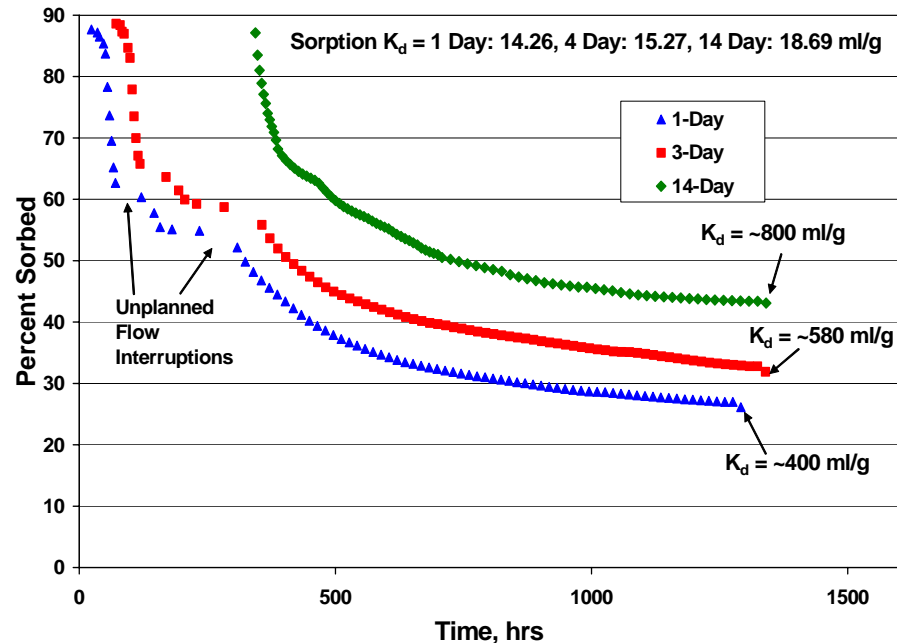
Alluvium Wt% from XRD: 7.6% Clinoptilolite, 4.6% Smectite, Opal-CT 13.6%

Neptunium Sorption/Desorption to Alluvium – 22SA

Lower pH, Lower Bicarbonate Water



Higher pH, Higher Bicarbonate Water



All experiments: $3 \times 10^{-6} \text{ M}$ Tracer Solution

Alluvium Wt% from XRD: 12.0% Clinoptilolite, 19.4% Smectite

Fitting Desorption Curve with a multi-site Reaction Model

$$\frac{dc}{dt} = \frac{1}{V} \left\{ Q(C_{in} - C) - \left[k_i \left(1 - \frac{S_i}{S_{i\max}} \right) \right] C + k_{ri} S_i \right\}$$

$$\frac{dS_i}{dt} = \left[\frac{k_i \left(1 - \frac{S_i}{S_{i\max}} \right) C - k_{ri} S_i}{M} \right]$$

where,

C = concentration out of column, CPM/mL

C_{in} = conc. in solution flowing into column, CPM/mL

S_i = amount sorbed to site i , CPM/g

$S_{i\max}$ = maximum sorption capacity of site i , CPM/g

V = volume of solution in column, mL

Q = flow rate through column, mL/hr

M = mass of solid, g

k_i = sorption rate constant for site i , mL/hr

k_{ri} = desorption rate constant for site i , g/hr

CPM = counts per minute.

t = time, hr

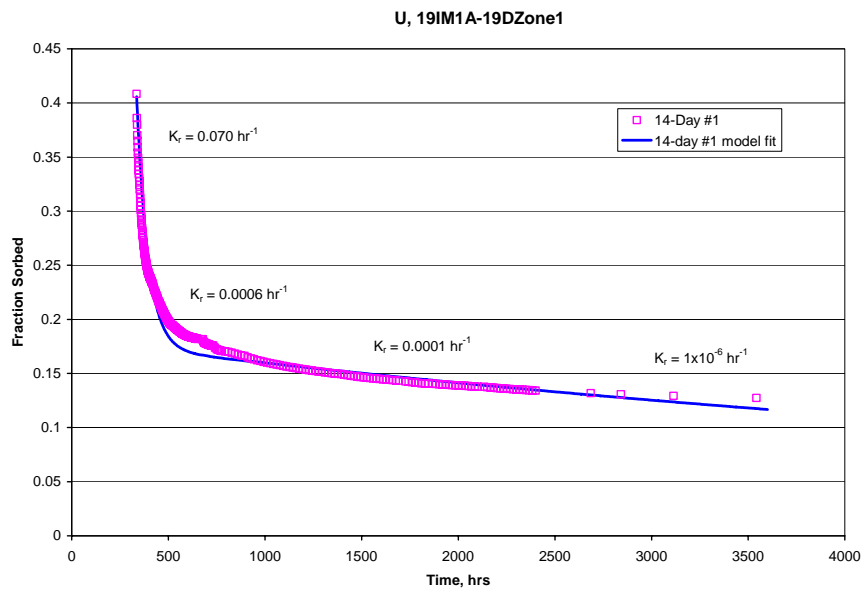
- Fit experimental data as closely as possible using one type of site.

- Add site types as necessary to improve fit.

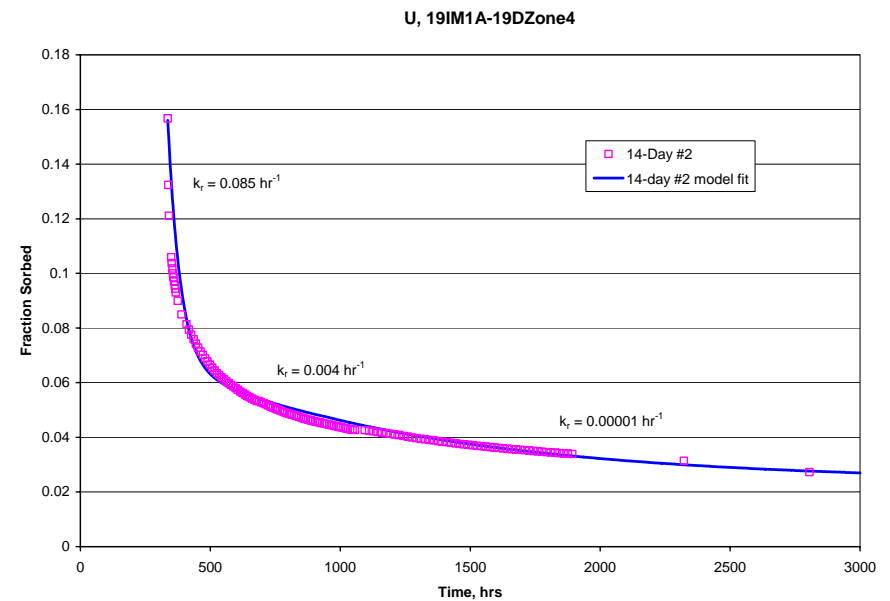
- The model has been adapted to fit the fraction of radionuclide remaining sorbed to the solid phase as a function of time.

Fitting Desorption Curve with a multi-Site/Reaction Model

Lower pH, Lower Bicarbonate Water



Higher pH, Higher Bicarbonate Water



Conceptual Model

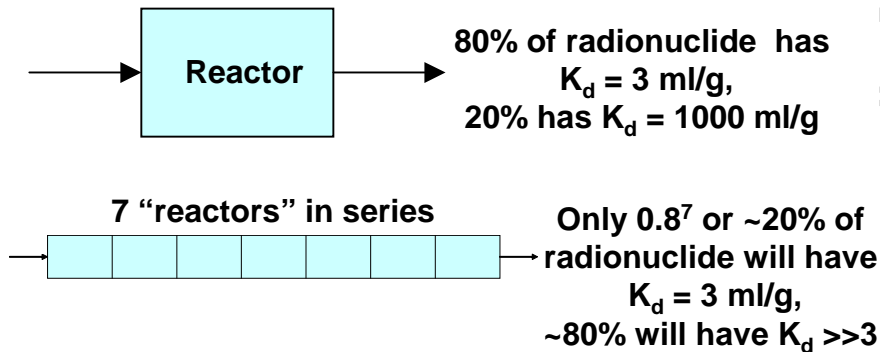
Consider a simple two-site, two-rate system:

80% of sites are "fast" with $K_d = 3 \text{ ml/g}$

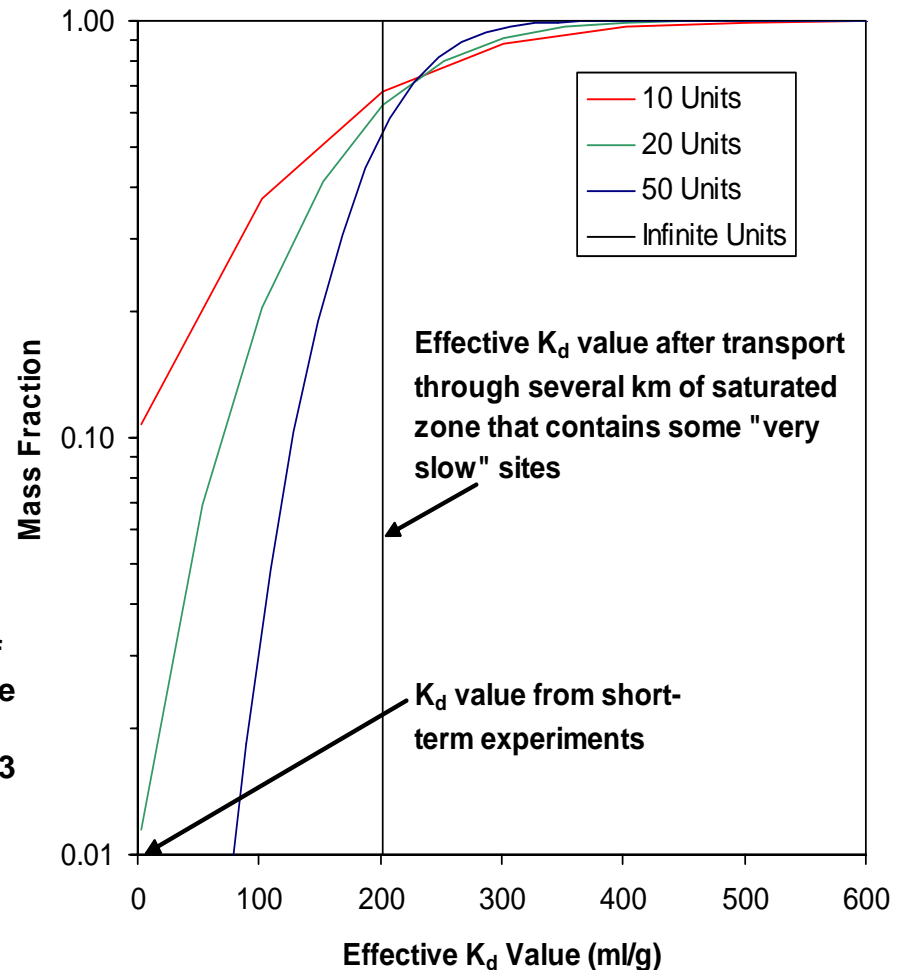
20% of sites are "very slow" with $K_d = 1000 \text{ ml/g}$
(approximates observed behavior)

In a short-term batch experiment, the APPARENT K_d for ALL of the Uranium will be $\sim 3 \text{ ml/g}$, so this is the value used in YMP TSPA

Now consider the saturated zone to be numerous small reactors in series, each of which contains an 80:20 split between fast and slow sites
(similar to that observed in small-scale experiments)



Fraction of radionuclide mass experiencing different K_d values as a function of number of distance units through which transport occurs.



Conclusions

- A wide range of desorption rate constants exist for uranium and neptunium due to many different reaction sites in the heterogeneous alluvium.
- An increase in radionuclide contact time with alluvium results in higher partitioning of uranium and neptunium to the solid phase during sorption and a greater percent of radionuclide remaining sorbed to the solid phase at the end of long-term desorption.
- Increased smectite content in alluvium increases initial sorption of uranium and neptunium, but has less of an effect on the long-term desorption results when compared to the experiments using the alluvium with a lower weight percent of smectite.
- Higher carbonate water results in lower sorption and lower radionuclide remaining sorbed after long-term desorption most likely due to uranyl and neptunyl carbonate complex formation.
- Effective K_d values will be much larger over long time and distance scales if these results are considered rather than the results of batch sorption and short-duration desorption experiments.

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