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RETARDATION OF URANIUM AND NEPTUNIUM IN YUCCA MOUNTAIN SATURATED ALLUVIUM

Presented to:
Geological Society of America
Rocky Mountain Section Meeting

Presented by:
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EMPORIA STATE UNIVERSITY

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Site Evaluation

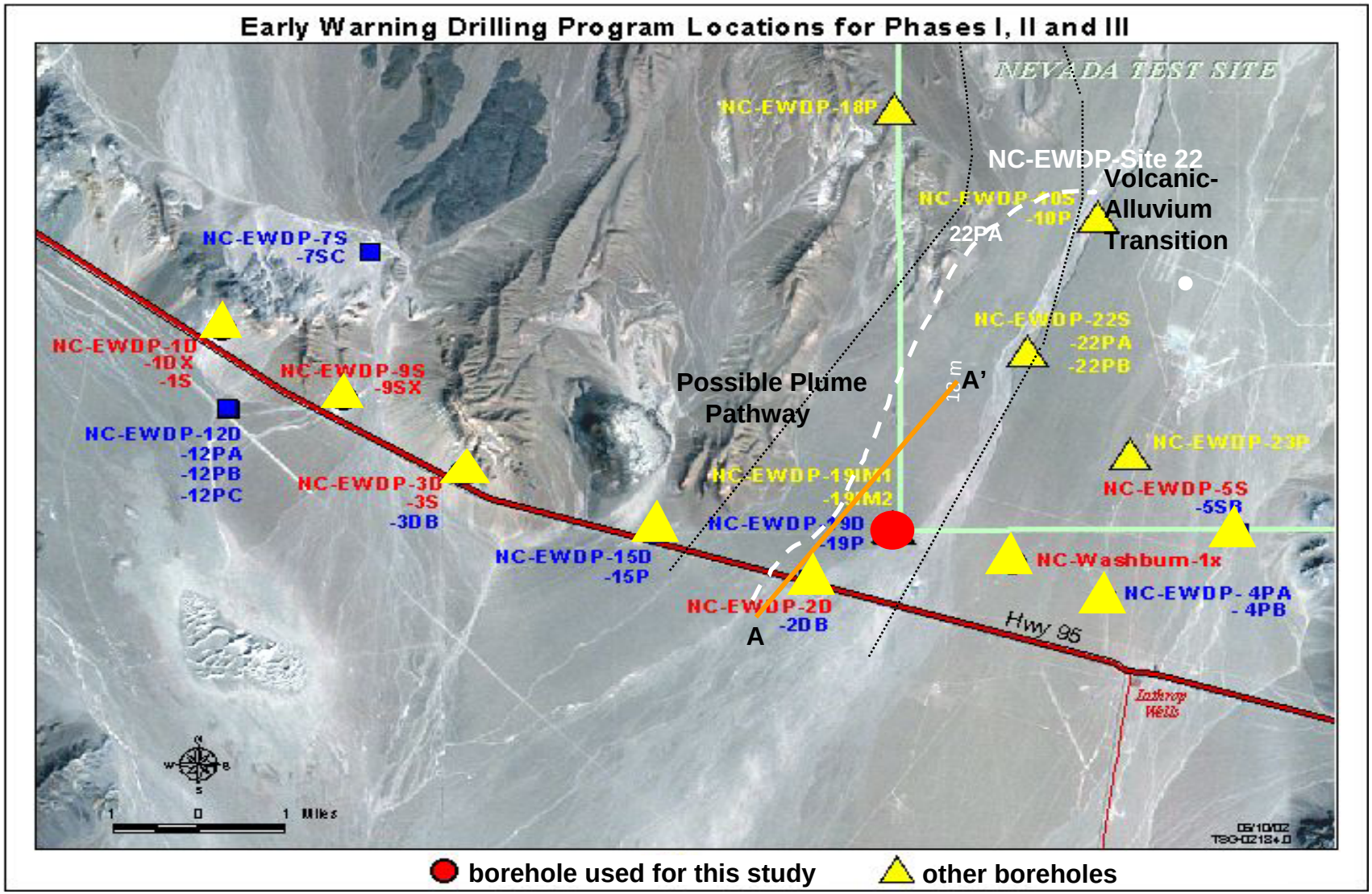
- We are working to evaluate the retardation of radionuclides in saturated alluvium to support the continuing work on evaluating the long-term behavior of the proposed Yucca Mountain spent nuclear fuel and high-level radioactive waste repository. These materials are a result of nuclear power generation and national defense programs and will remain highly radioactive for thousands of years.
  - **If man-made containment fails, how well will natural barriers work to contain radioactivity?**
    - **After moving vertically through the unsaturated zone, waste will be transported horizontally in the saturated zone**
      - **How fast will this transport be?**

Objectives

To determine if ^{233}U and ^{237}Np sorption properties differ in sedimentary layers characterized by a range of hydraulic conductivities (selection of tracers based on U and Np isotopes being predicted as significant contributors to radiation dose)

Investigate the potential impact of desorption behavior in these materials on radionuclide transport

Nye County Early Warning Drilling Program



Section A-A’

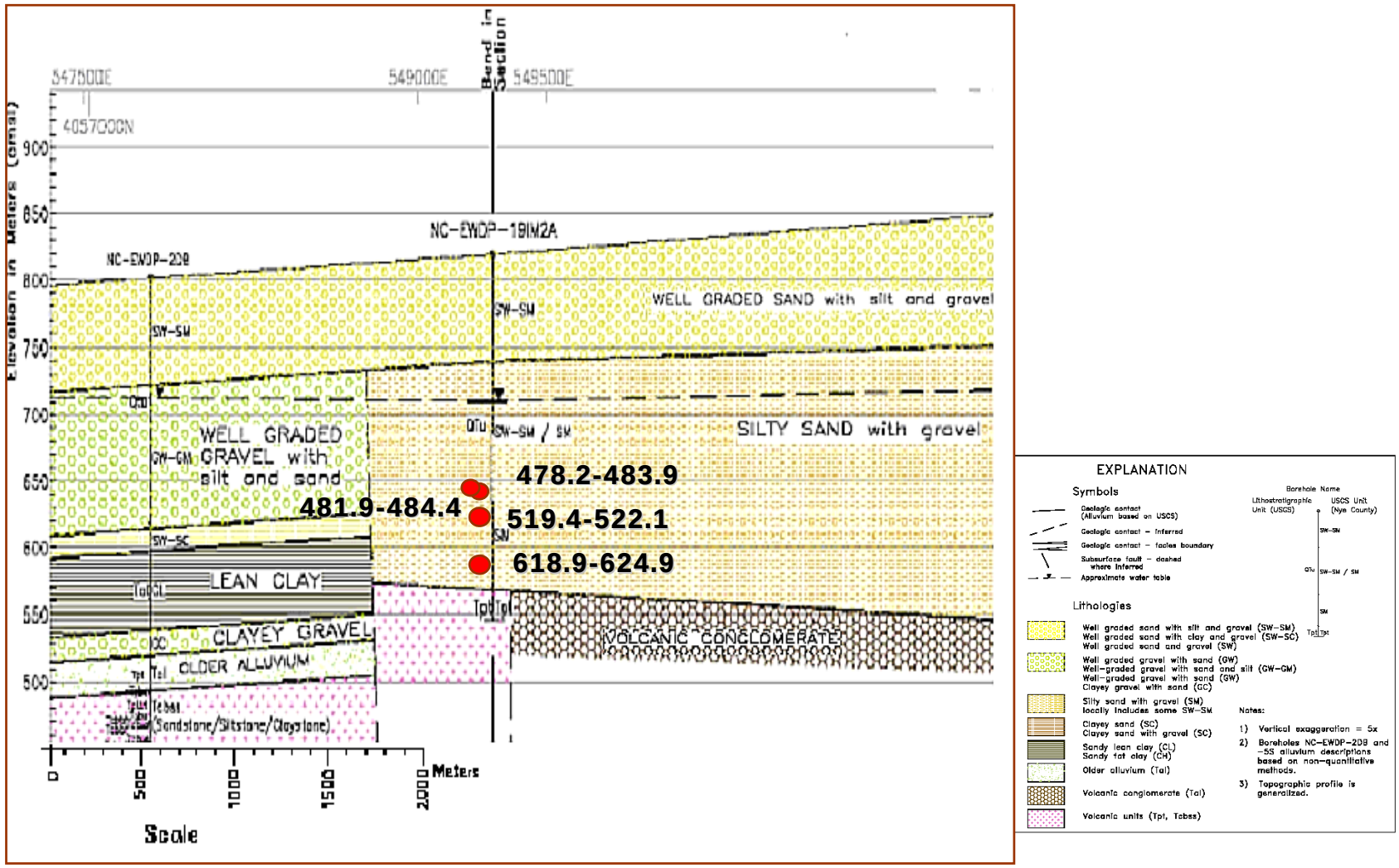
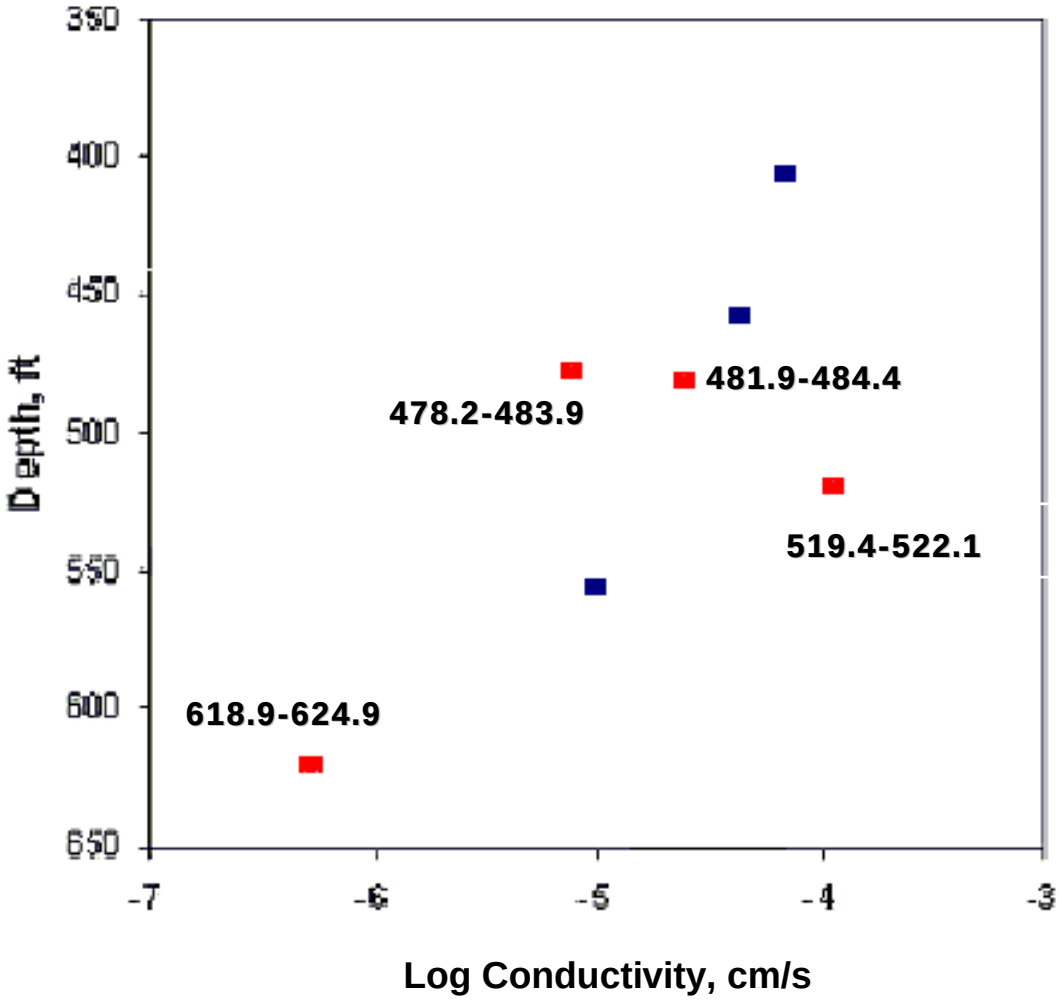


Image courtesy of Nye County Nuclear Waste Repository Project Office

Hydraulic Conductivity

- In situ hydraulic conductivity measurements vary over two orders of magnitude in the stratified alluvium
- Red points indicate samples that were studied in this experiment



Materials and Methods

- Four samples obtained from saturated Nye County alluvium from 478 to 625 feet below the land surface.
- Three size fractions (2 mm-500 μm, 500 μm-75 μm, and <75 μm) were examined
- Groundwater used in experiments was taken from depths of 413 to 431 feet below the surface.

Three size intervals of sample **481.9-484.4**

Alluvial Characteristics

Depth (ft BLS)	BET Surface Area (m^2/g)*	% Smectite and Clinoptilolite ** (by XRD)	% particles <75 μm
478.2-483.9	14.6	27.2	8
481.9-484.4	25.1	37.9	5
519.4-522.1	15.0	23.4	8
618.9-624.9	13.1	22.6	10

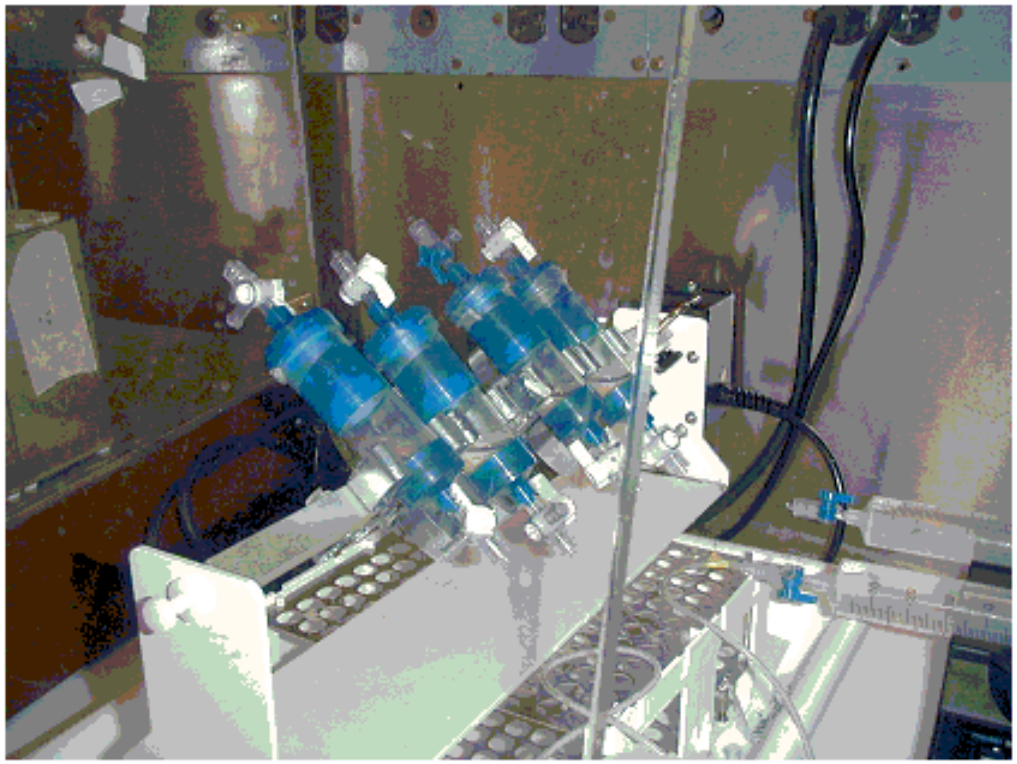
BET surface area obtained by N_2 gas adsorption to sample surface. XRD analysis obtained from sample x-ray by diffraction pattern.

*** BET analysis performed by Mei Ding, Los Alamos National Laboratory**

****XRD analysis performed by Steve Chipera, Los Alamos National Laboratory**

Phase I: Sorption

- Each sample was composed of a representative fraction of the grain sizes present in bulk.
- ~4 g of this alluvium placed in reaction vessels with 30 ml of ^{233}U or ^{237}Np tracer solution for three days.
- ^{233}U concentration 1.01×10^{-6} M
- ^{237}Np concentration 7.62×10^{-7} M



K_d value

- Radioactivity of solution after contact with alluvium analyzed by liquid scintillation counting (LSC) and compared with that of tracer solution before experiment (control experiments indicate that sorption to the column walls is negligible).
- The ratio of activity sorbed to activity remaining in solution is the K_d value (ml/g) or sorption coefficient.
- A higher K_d value indicates greater sorption capacity of a sample.

Sorption Experiment Results

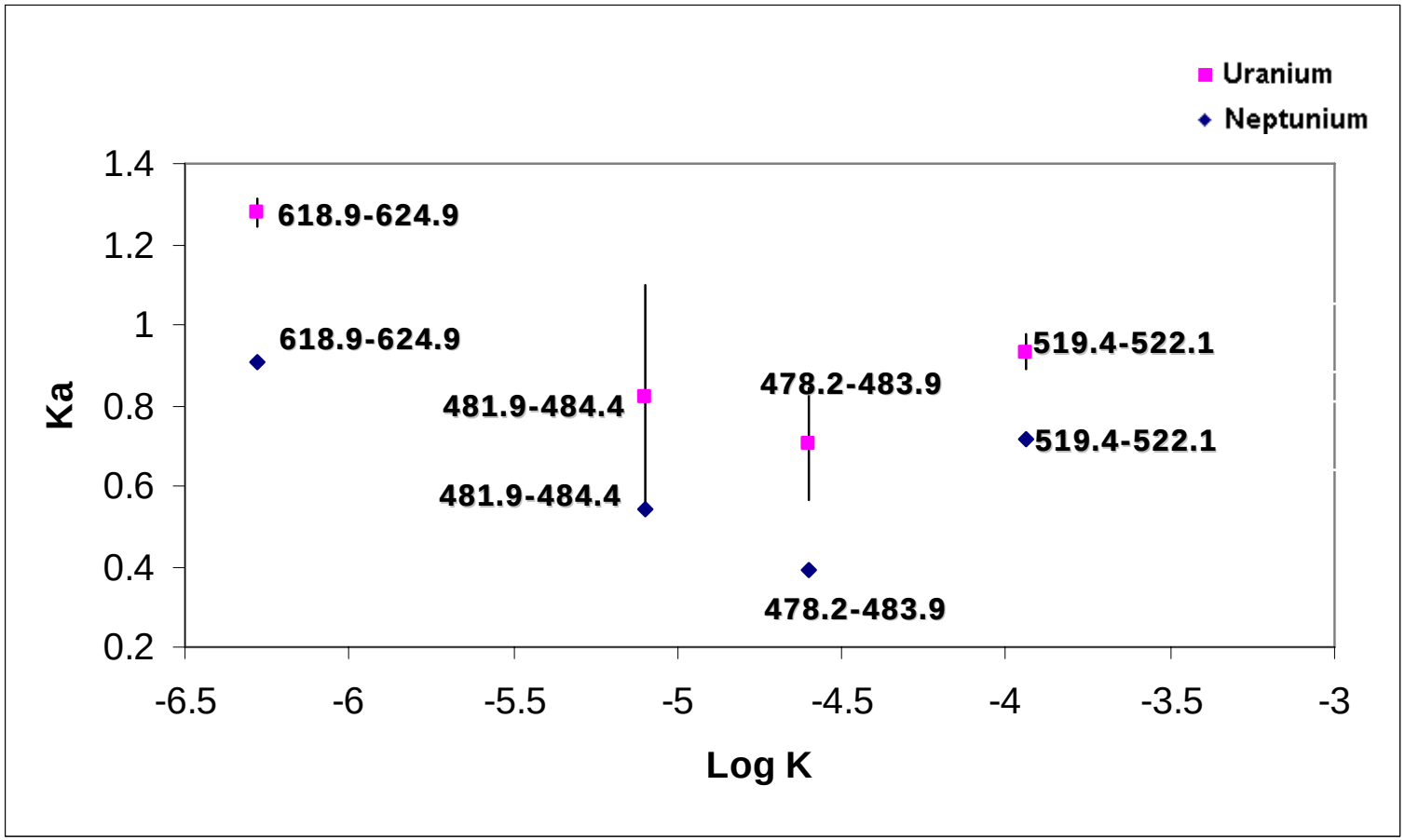
Depth (ft BLS)*	U K_d (ml/g)	Np K_d (ml/g)
478.2-483.9	14.4	8.1
481.9-484.4	16.0	9.8
519.4-522.1	13.9	12.3
618.9-624.9	16.5	11.9

*** Depth below land surface**

K_d value and the Gravel Issue

- Does K_d adequately represent sorption?
- Samples are composed of alluvium <2 mm
- Could overestimate K_d values, because larger fragments are present *in situ.* Also, larger fragments may be composed of different minerals than smaller ones.
- One problem can be resolved by normalizing K_d values for surface area, obtaining a K_a value. However, the mineralogy problem remains.

K_a vs. log hydraulic conductivity



Error bars represent uncertainty obtained from 3 batch tests

Phase II: Desorption

- Columns were attached to latex tubing and syringes which pumped ground water from the site through the columns
- Eluent was collected and analyzed by LSC
- Rate constant of desorption (k_r) values were calculated using an activity-based reversible linear kinetic sorption model

$$k_r = V/S\ (dC/dt) + qC/S$$

Where:

S = CPM/g remaining on solid

C = CPM/mL in solution

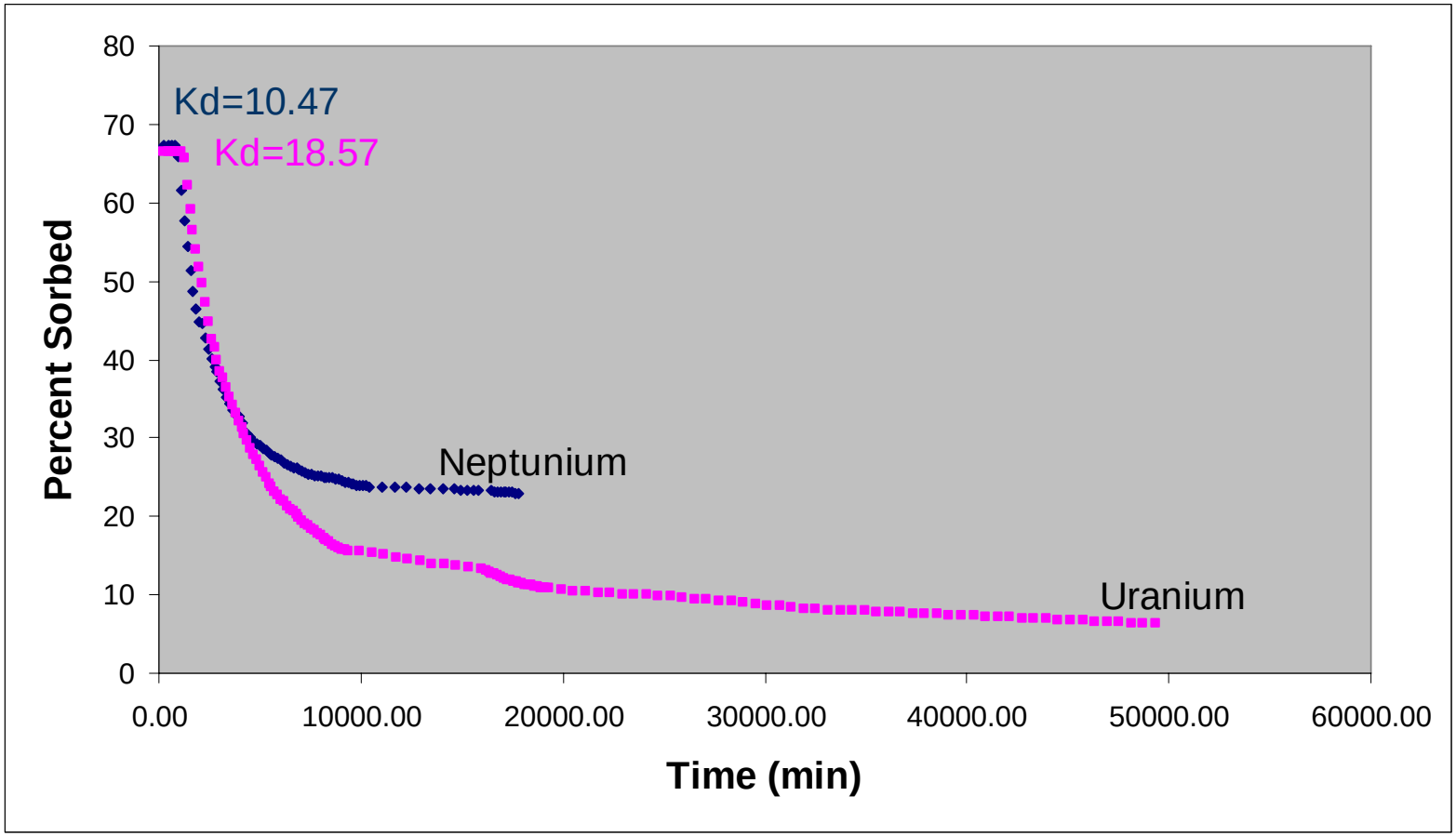
q = flow rate through column (mL/hour)

V = volume of column (30 mL)

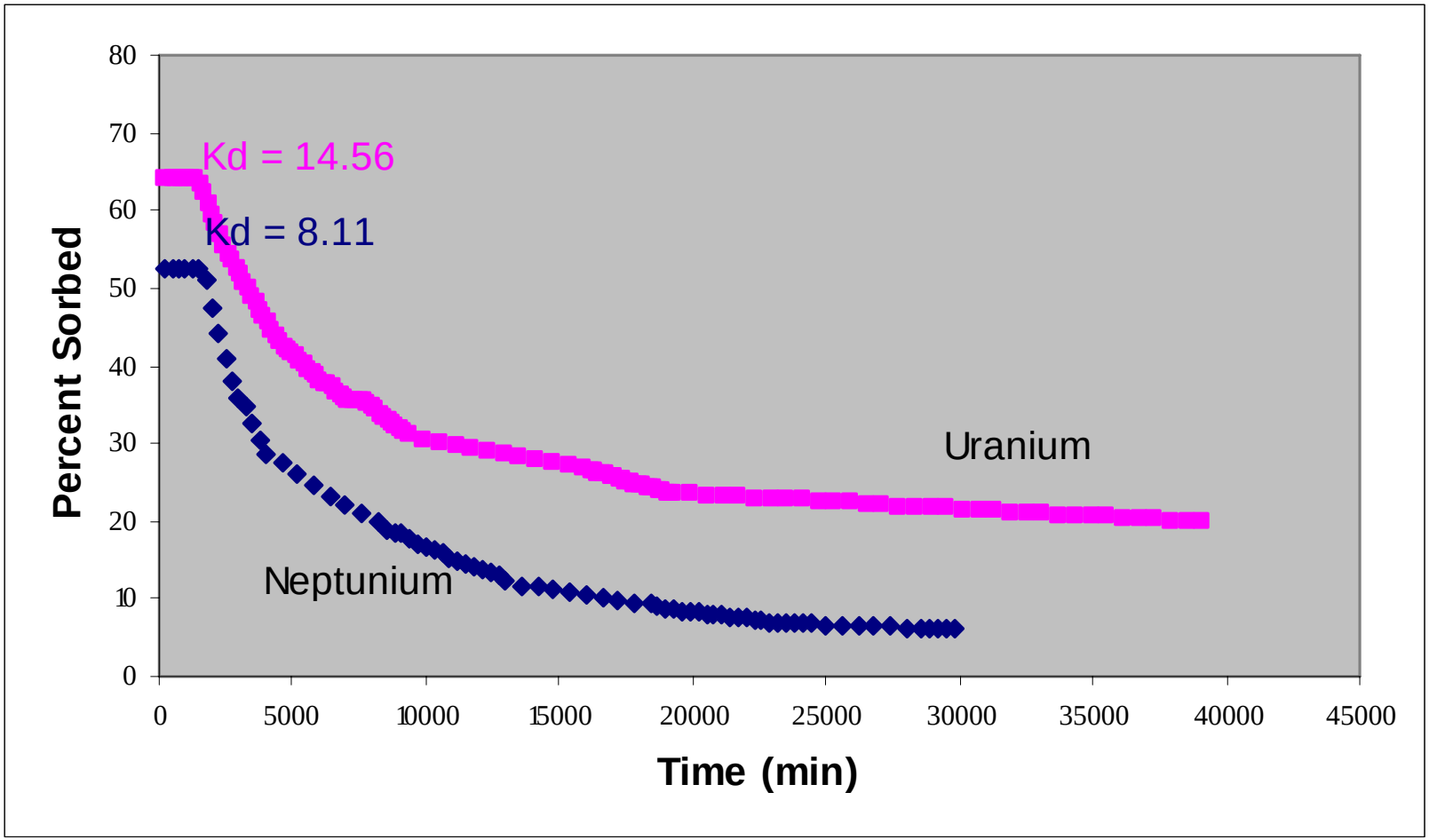
k_r = reverse rate constant (g/hr)

t = time

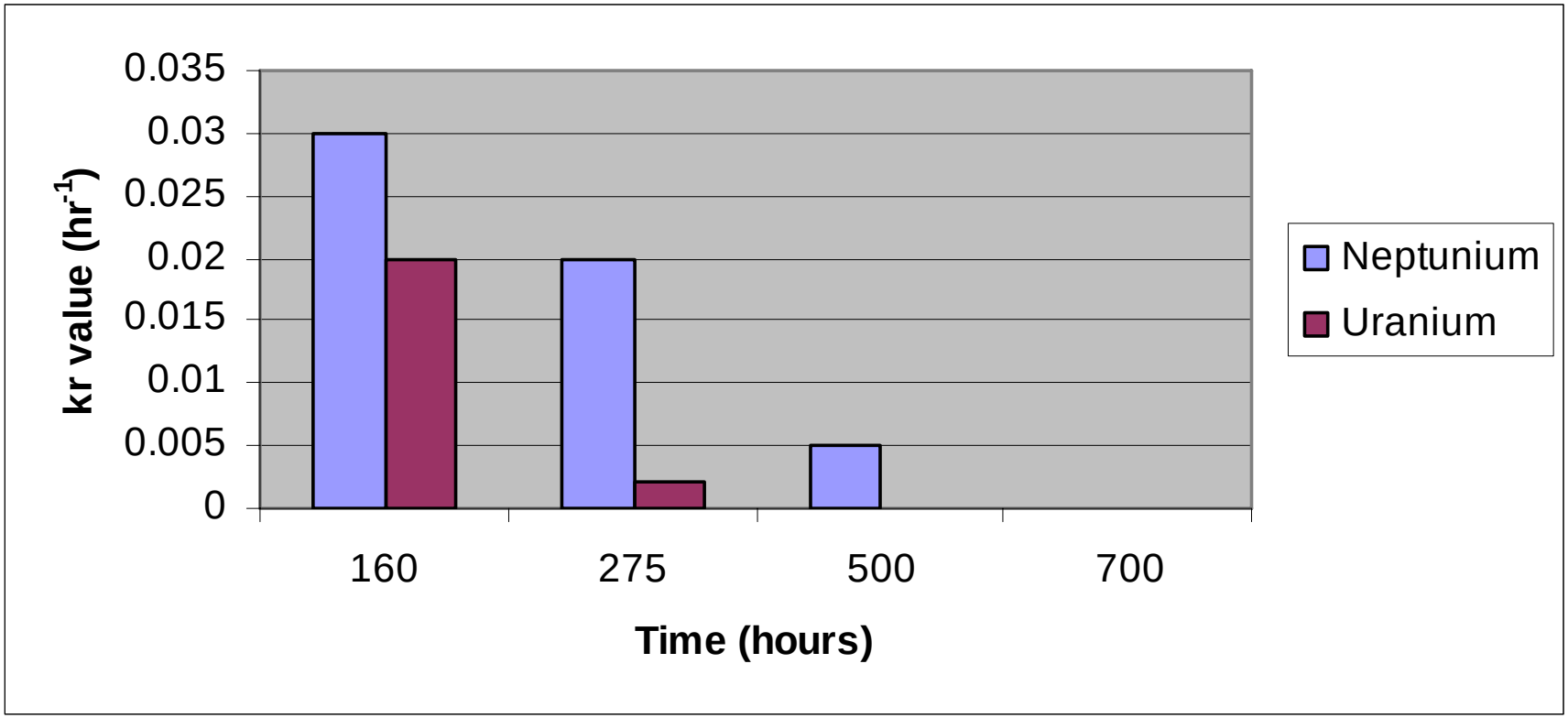
519.4 –522.1 BLS Percent sorbed vs. time



478.2-483.9 BLS Percent sorbed vs. time



478.2-483.9 BLS Desorption



Desorption Results

Depth (ft BLS)	% U Desorbed	% Np Desorbed
478.2-483.9	69.1	88.8
481.9-484.4	85.4	79.8
519.4-522.1	90.6	65.9
618.9-624.9	81.8	90.0

Carbonate Complexation

- The uranyl ion (UO_2^{2+}) is the most commonly encountered uranium species in oxidizing aqueous environments. It complexes readily with carbonate to form uranyl carbonate complexes, which reduces adsorption and increases solubility.
- Calculations show that at pH 8.5, 31 percent of Np(V) is present as the neptunyl ion NpO_2^+. The remaining fraction is complexed with either carbonate or hydroxide.
- Higher pH values result in more carbonate and hence greater carbonate complexation.

Sorption pH Values

	Uranium	Neptunium
Tracer Solution	7.6	9.0
478.2-483.9 *	7.5	8.5
481.9-484.4 *	7.3	8.6
519.4-522.1 *	7.6	8.9
618.9-624.9 *	7.8	8.3

***Value after 3 days of sorption**

Desorption pH Values

	Uranium	Neptunium
Groundwater	7.9	8.4
478.2-483.9	8.1	8.8
481.9-484.4	8.0	8.9
519.4-522.1	7.9	8.9
618.9-624.9	8.3	8.9

Concluding Remarks

- Weak negative correlation between hydraulic conductivity and sorption was observed. If the results of additional experiments confirm a negative correlation between radionuclide sorption parameters and hydraulic conductivity, this should be built into Yucca Mountain models. Incorporation of such correlations could have a significant impact on performance assessments.
- Decrease in k_r values over time indicate multiple sorption surfaces are involved - alluvium has multiple types of active sorption sites with different affinities for U-233 and Np-237.
- The observation of very slow desorption or irreversible sorption of a fraction of the radionuclides suggests that radionuclide retardation in the alluvium could be significantly greater than sorption studies or short-term desorption studies indicate.

Acknowledgement

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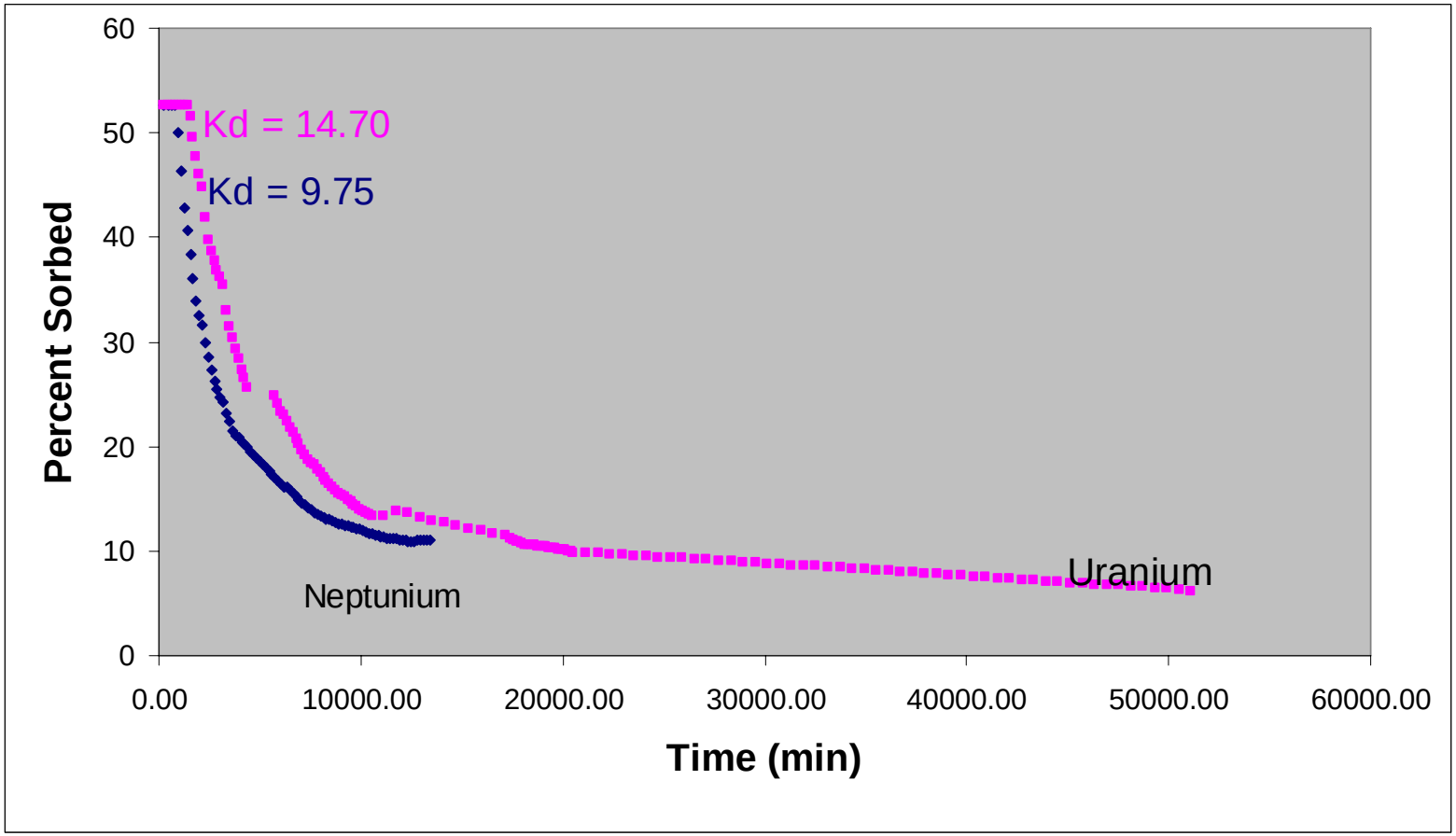
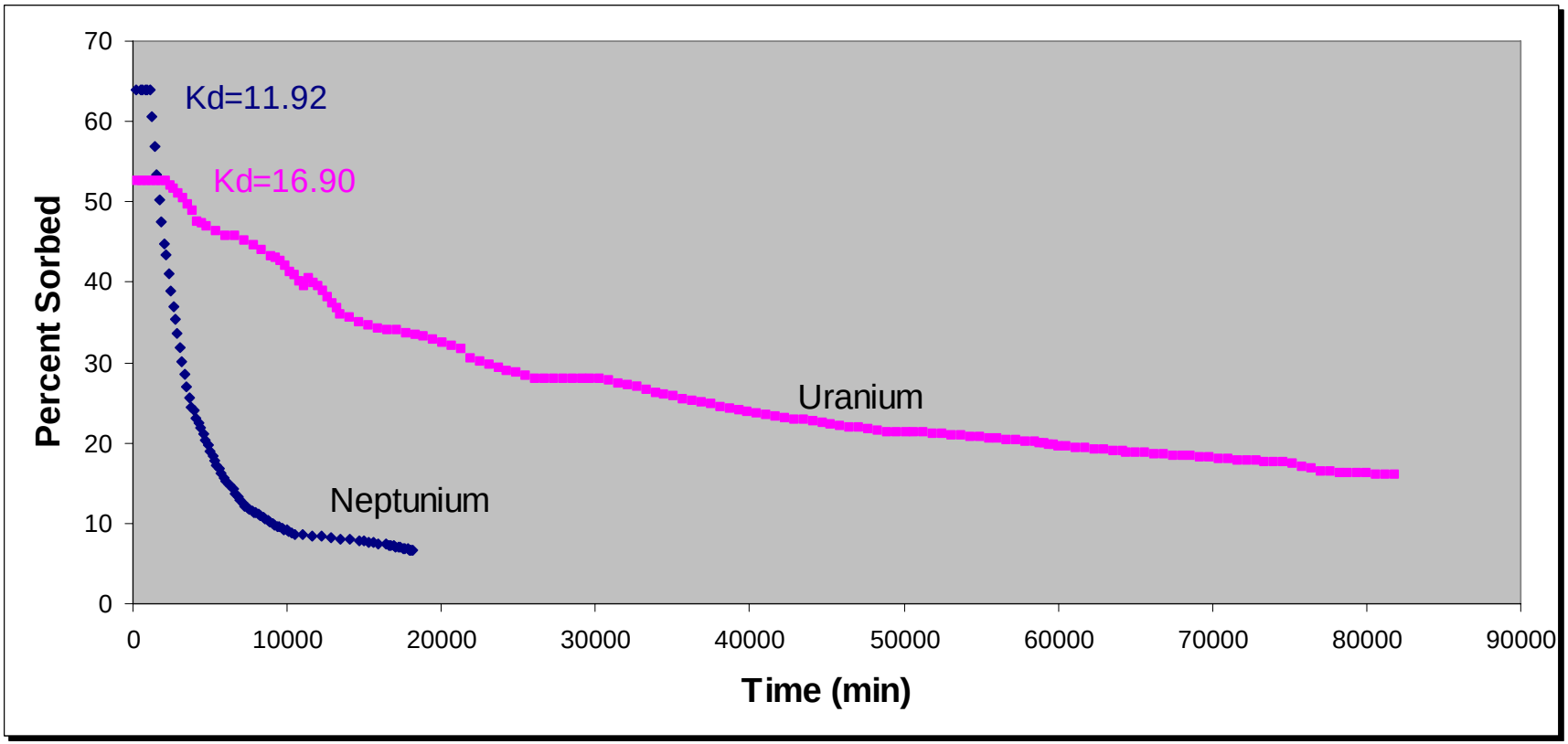
Thanks!

Questions?

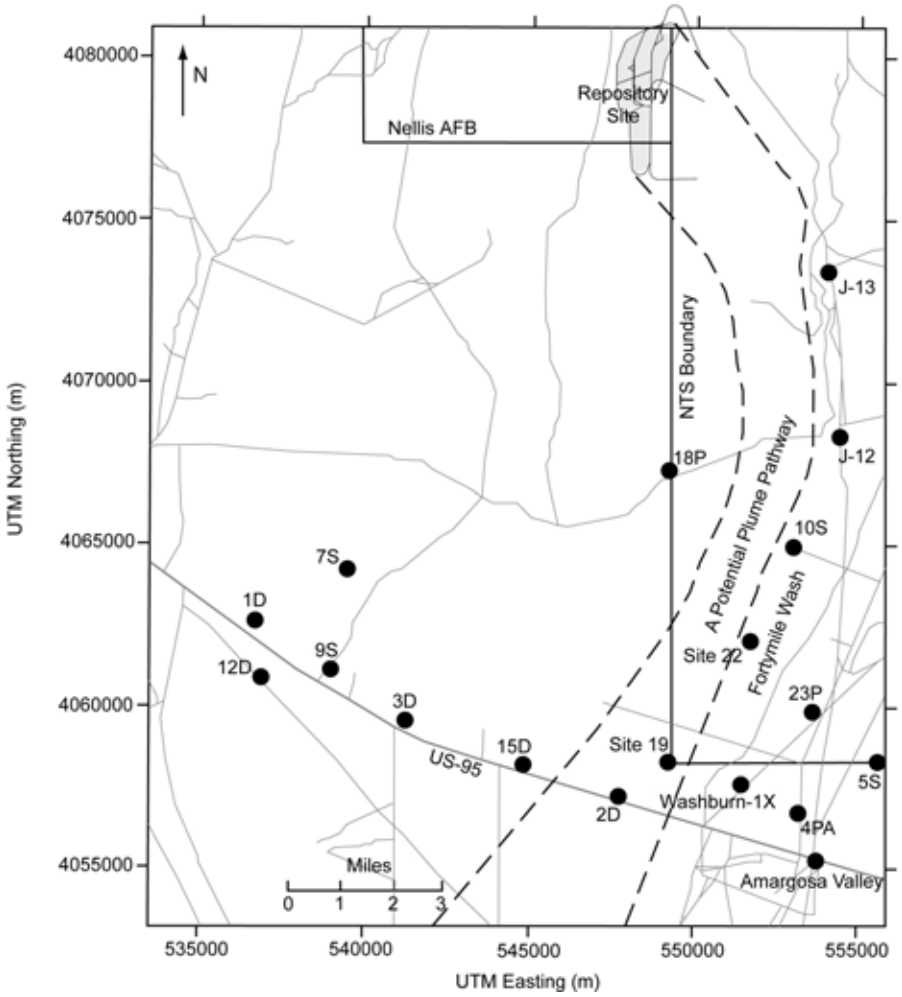
481.9-484.4 BLS Percent sorbed vs. time



618.9-624.9 BLS Percent sorbed vs. time



Additional Information



Example of dC/dt calculation