



# A Comparison of NH<sub>4</sub>OH and NaOH Treatments for Uranium Immobilization in the Presence of Kaolinite

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## Background

The DOE Hanford Site in Washington State has deposited over 200,000 kg of uranium (U) in the vadose zone. This is legacy contamination from the production of plutonium during the Cold War. In addition, U is a major risk driver at the site due to the large release and its high mobility in the groundwater. Its increased mobility is due to the site's oxidizing conditions and the presence of carbonate creating mobile species [ $K_d$  at pH 8 (0.11 – 4 L/kg)] (Zachara *et al.*, 2007).

However, the remediation of U is further complicated by the deep vadose zone. This zone is ~270 feet deep, consisting largely of quartz and aluminosilicate clays. Remediation approach requires a method that would reduce uranium mobility and its downward migration to the groundwater without addition of liquid amendments.

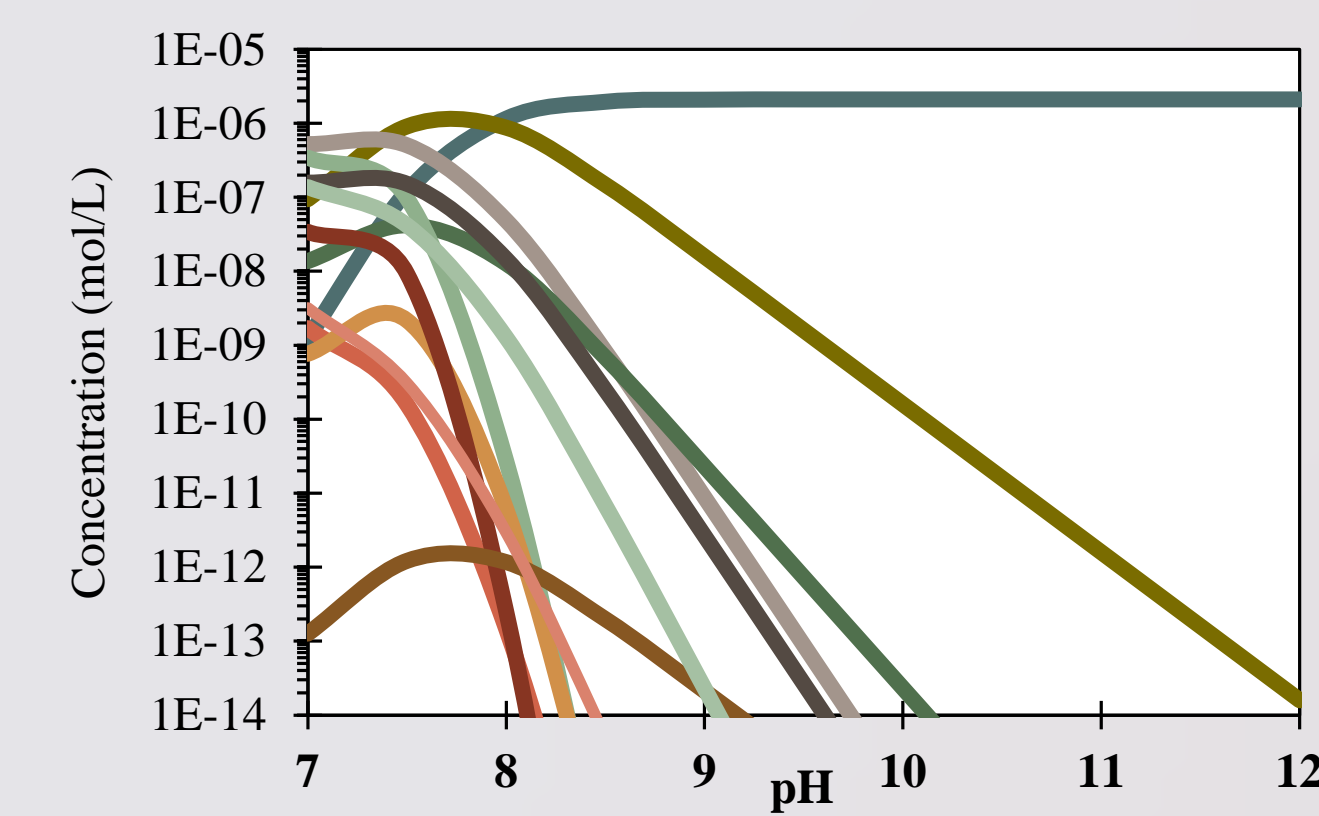


Figure 1. Aqueous speciation for 500 ppb U in 0.007 M NaCl and 0.00038 atm CO<sub>2</sub>

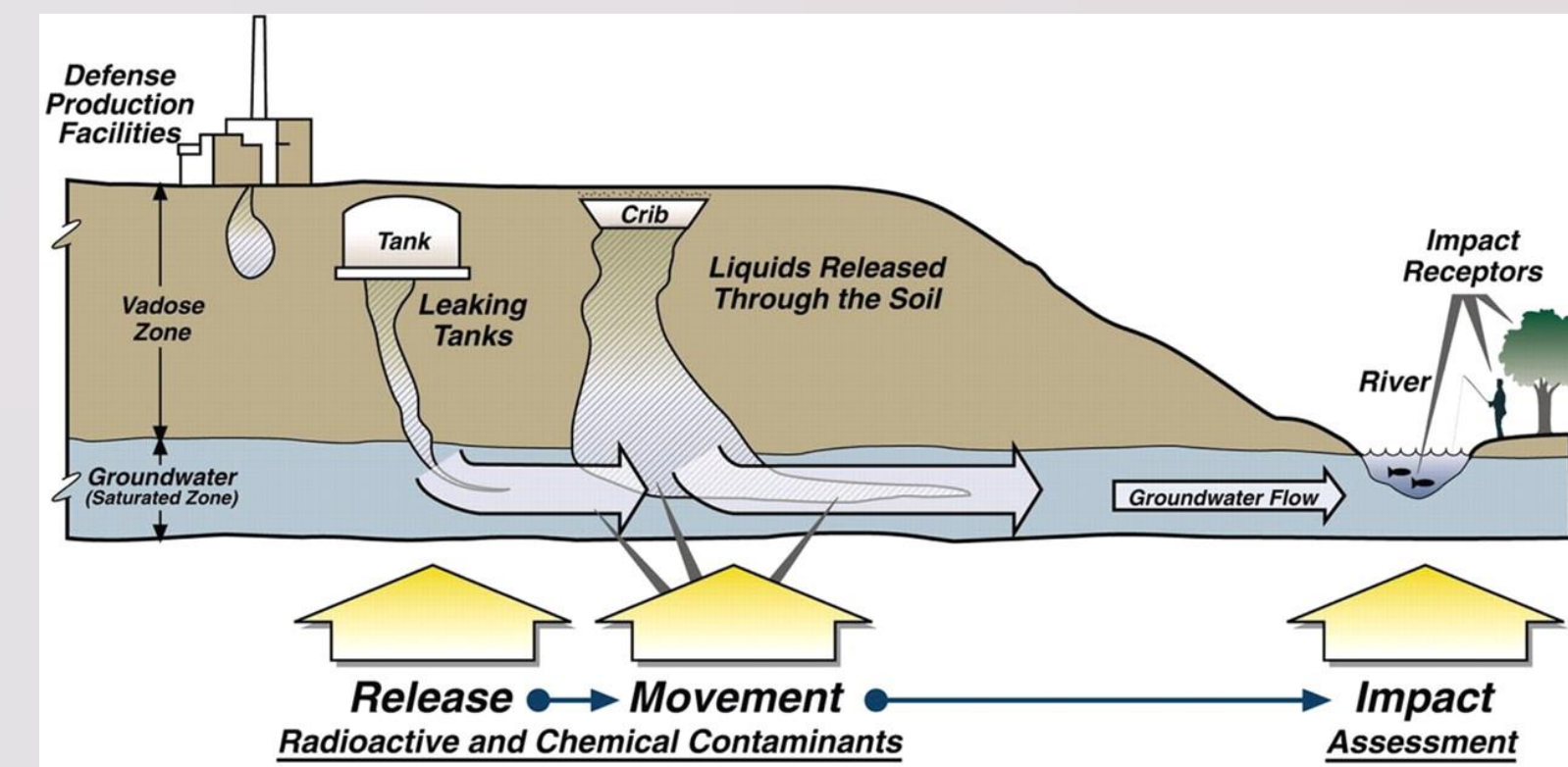


Figure 2. Schematic diagram of waste discharges to the Hanford Site vadose zone (Gee *et al.*, 2007)

## Ammonia Gas Injection Technique

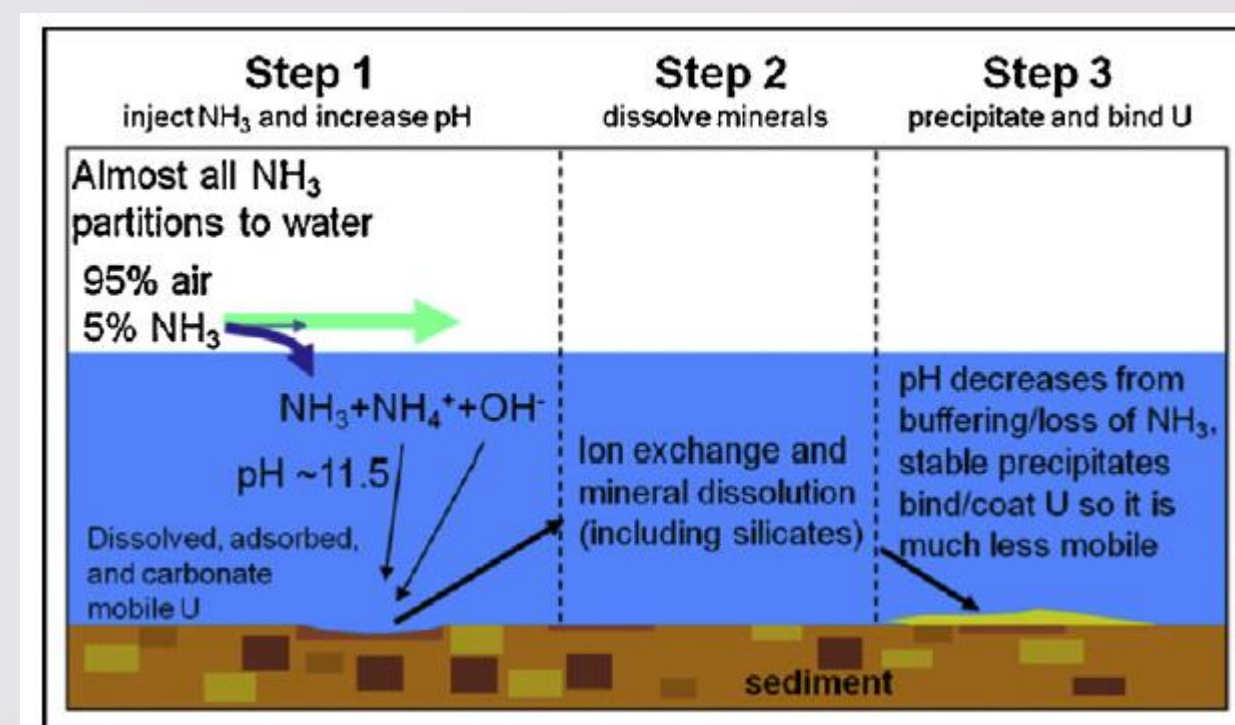
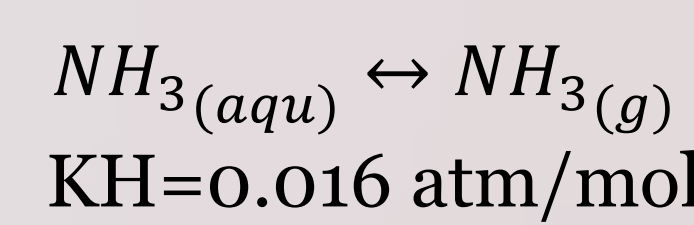
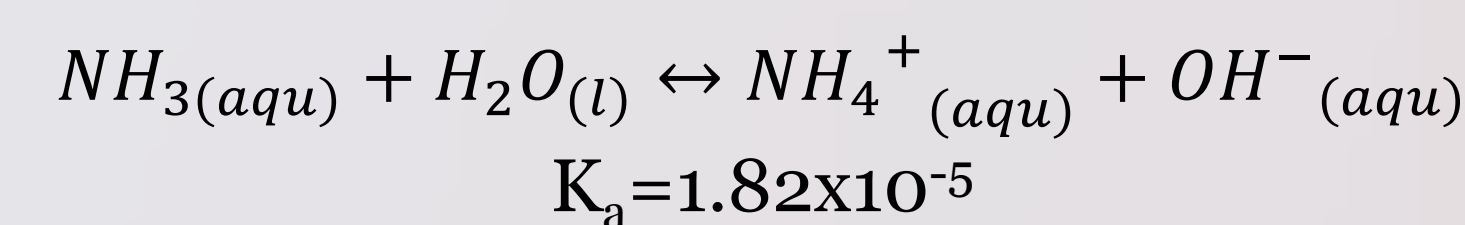


Figure 3. Process that occurs with injection of ammonia vapor into unsaturated sediments (Zhong *et al.*, 2015)

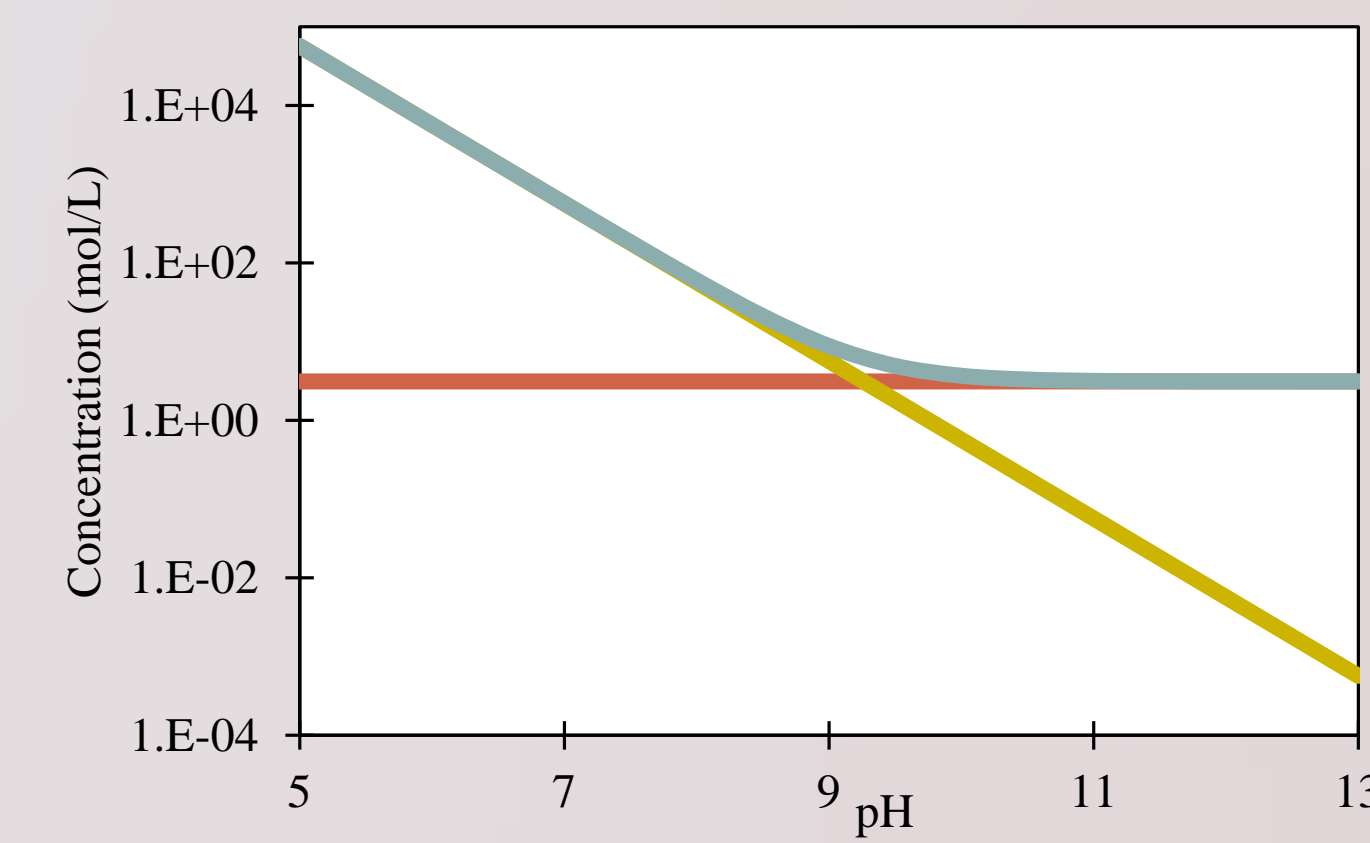


Figure 4. Ammonia solubility in 5% NH<sub>3</sub> gas

## Project Objective

To understand NH<sub>3</sub> gas injection for remediation of uranium in the vadose zone at the Hanford Site. To establish a baseline, this technology is being compared to NaOH injection.

- To understand equilibrium U removal from the aqueous phase [adsorption and (co)precipitation]
- To determine the fate of NH<sub>3</sub> gas in the vadose zone

## Batch Experimental Protocol

### Initial Equilibrium Partitioning of U

- Six initial samples prepared at pH ~7.5, ionic strength solution (3.2 mM NaCl or synthetic porewater) and mineral (kaolinite - 5 g/L) with 40 mL total volume
- Adjusted to pH prior to addition of U(VI)O<sub>2</sub><sup>2+</sup> at 500 ppb [Ricca Chemical]
- Monitored for ~3 days to ensure that equilibrium was reached
- Aliquot was then centrifuged and spun to remove solids > 120 nm
- Aqueous phase analyzed by KPA (U), ICP-OES (Al and Si), ammonia gas-sensing electrode (total NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>)



Figure 5. Shaker rotator equilibrating samples at 120 rpm



Figure 6. Kaolinite mineral [Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>]



Figure 7. Centrifugation step with ThermoScientific centrifuge to remove particles >120 nm, 5000 rpm for 30 min

### Equilibrium Partitioning of U following injection of NH<sub>3</sub> or NaOH

- Samples adjusted to pH ~11.5
  - Samples 1-3 adjusted by 2.5 M NaCl + 0.025 M NaOH
  - Samples 4-6 adjusted by 2.5 M NH<sub>4</sub>OH
- Monitored for ~3 days to ensure that equilibrium was reached
- Aliquot centrifuged and spun to remove solids >120 nm
- Aqueous phase analyzed by KPA (U), ICP-OES (Al and Si), ammonia gas-sensing electrode (total NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup>)

Table 1. Synthetic Porewater Constituents

Salts	Conc (mmol/L)	Ionic Strength (mmol/L)
KHCO <sub>3</sub>	0.22	0.22
NaHCO <sub>3</sub>	1.10	1.10
CaCl <sub>2</sub>	1.40	4.19
MgCl <sub>2</sub>	0.57	1.70
total	3.28	7.20

Data is presented below as a  $K_d$  (mL/g):

$$K_d = \text{partitioning coefficient} = \frac{\text{solid conc.}}{\text{aqueous conc.}}$$

$K_d \gg$  will be immobile,  $K_d \ll$  will be mobile

Note: In this system, we are using an "apparent"  $K_d$  as it represents multiple processes (i.e., precipitation, sorption and complexation).

## Results and Discussion

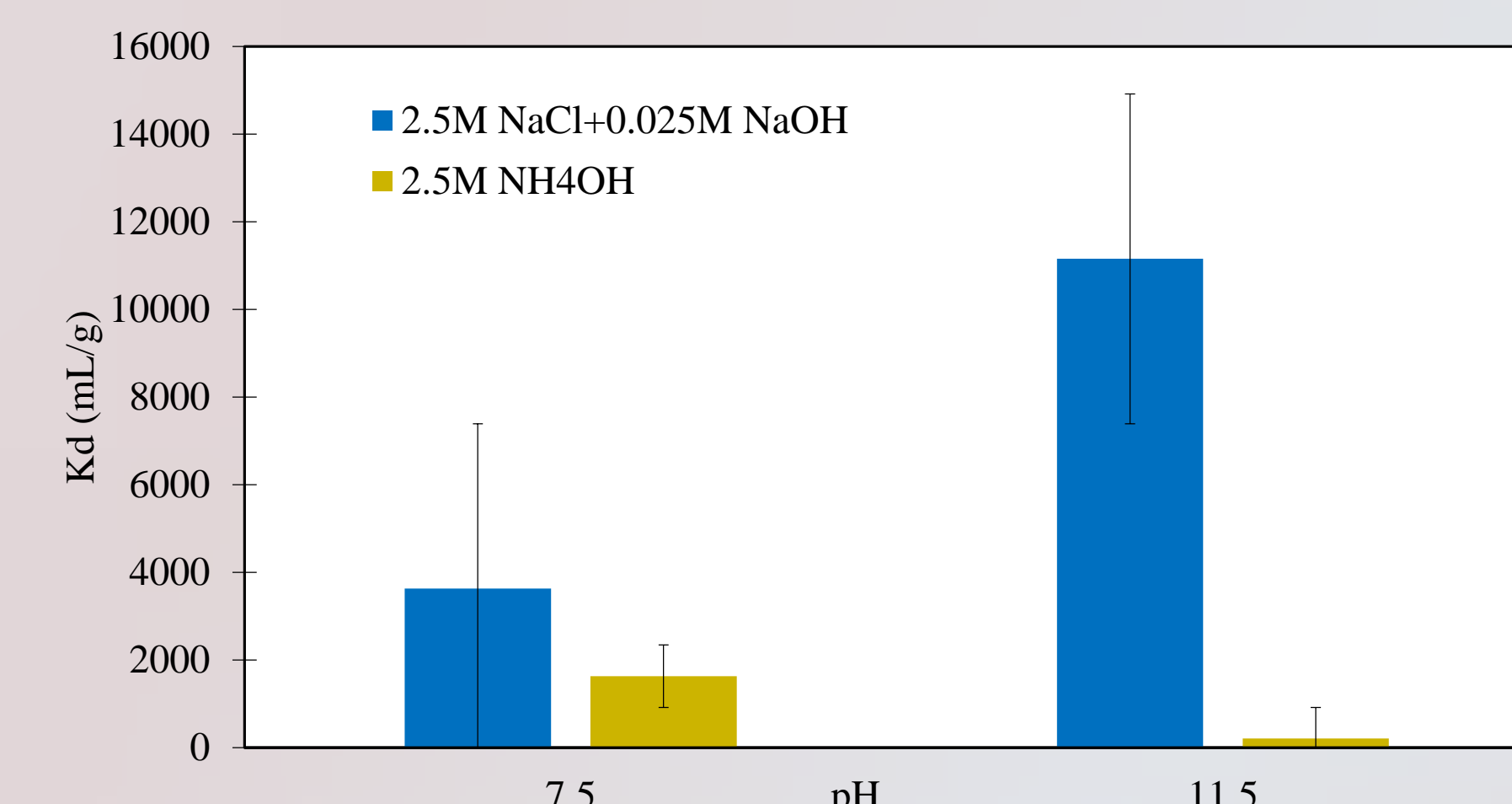


Figure 8.  $K_d$  (mL/g) for U (500 ppb) sorption to kaolinite (5 g/L) in 0.007 M NaCl solution using either 2.5 M NH<sub>4</sub>OH (yellow) or 0.025 M NaOH + 2.5 M NaCl (blue)

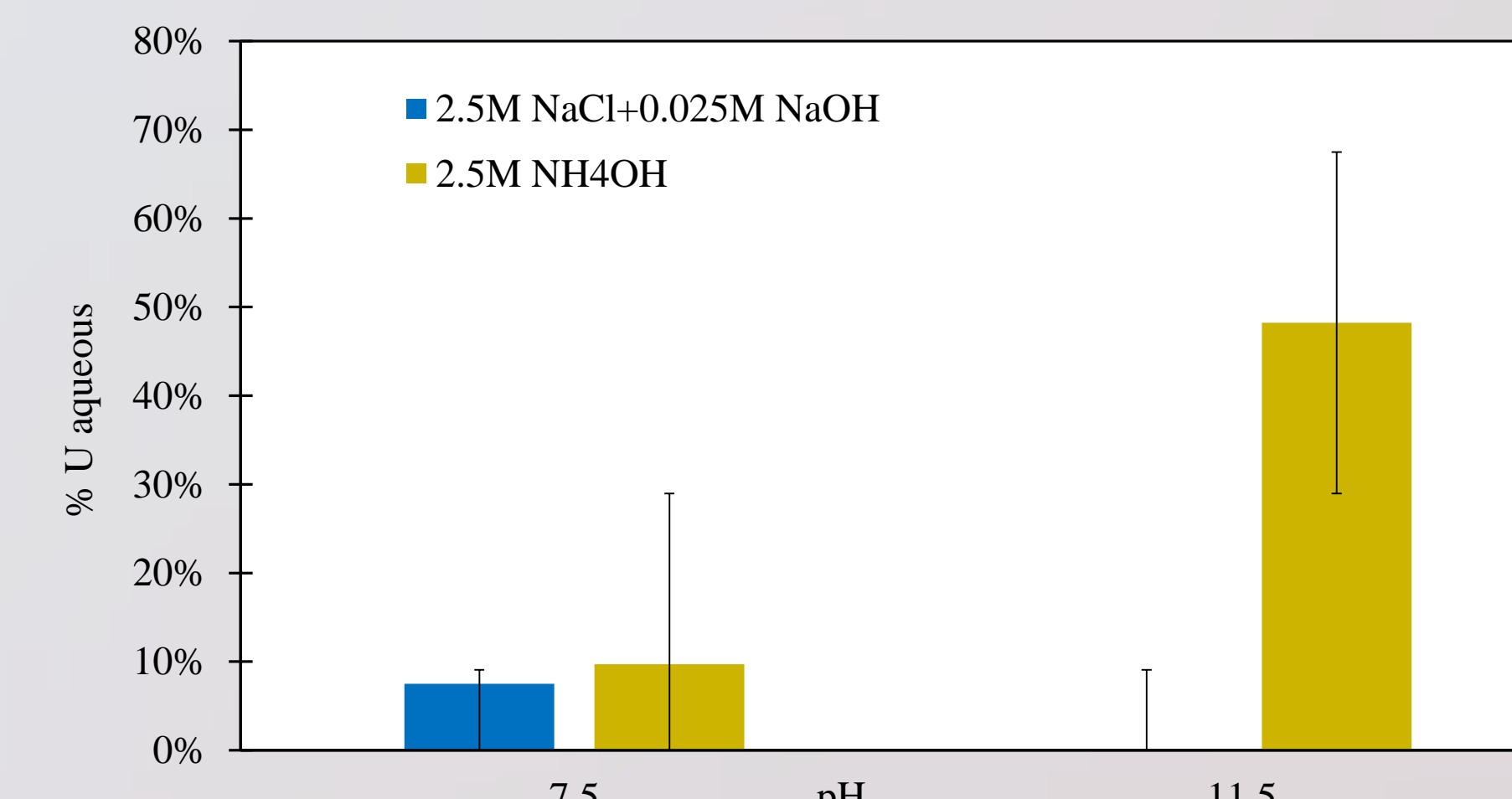


Figure 9. Aqueous fraction of U (500 ppb) with respect to pH for kaolinite (5 g/L) suspensions in NaCl solution with pH adjusted up with either 2.5 M NH<sub>4</sub>OH (yellow) or 0.025 M NaOH + 2.5 M NaCl (blue)

A significant increase occurs in the partitioning coefficient when adjusting pH using NaOH + NaCl versus NH<sub>4</sub>OH in NaCl background electrolyte.

The aqueous fraction of U increases as pH increases due to repulsive forces with kaolinite's negative surface and negative/neutral U species in NaCl background electrolyte.

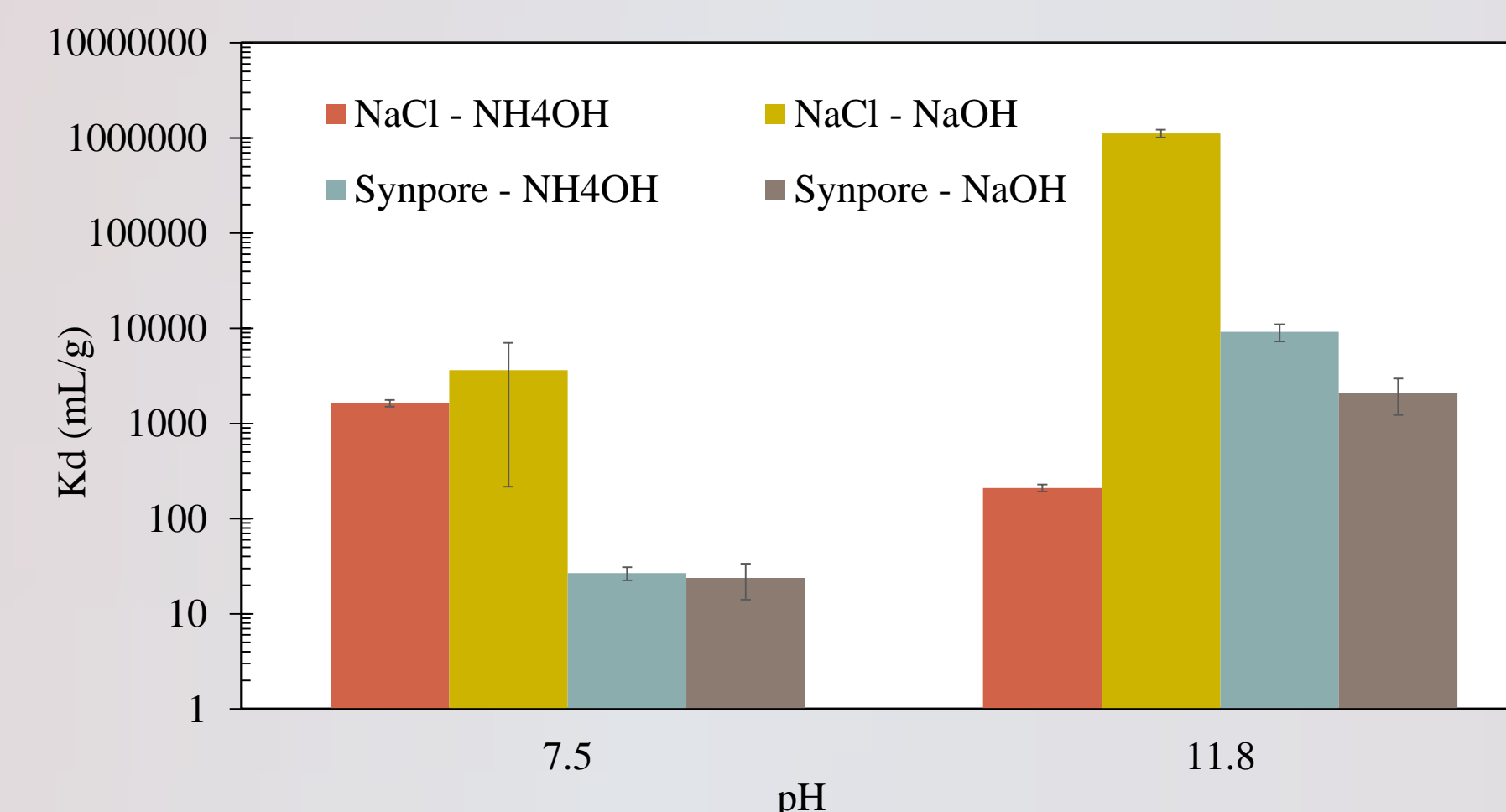


Figure 10. Comparison of U partitioning between NaCl and synthetic porewater background electrolyte at similar total ionic strength

In synthetic porewater, removal of U from the aqueous phase increases with pH as shown by the increased partitioning coefficient.

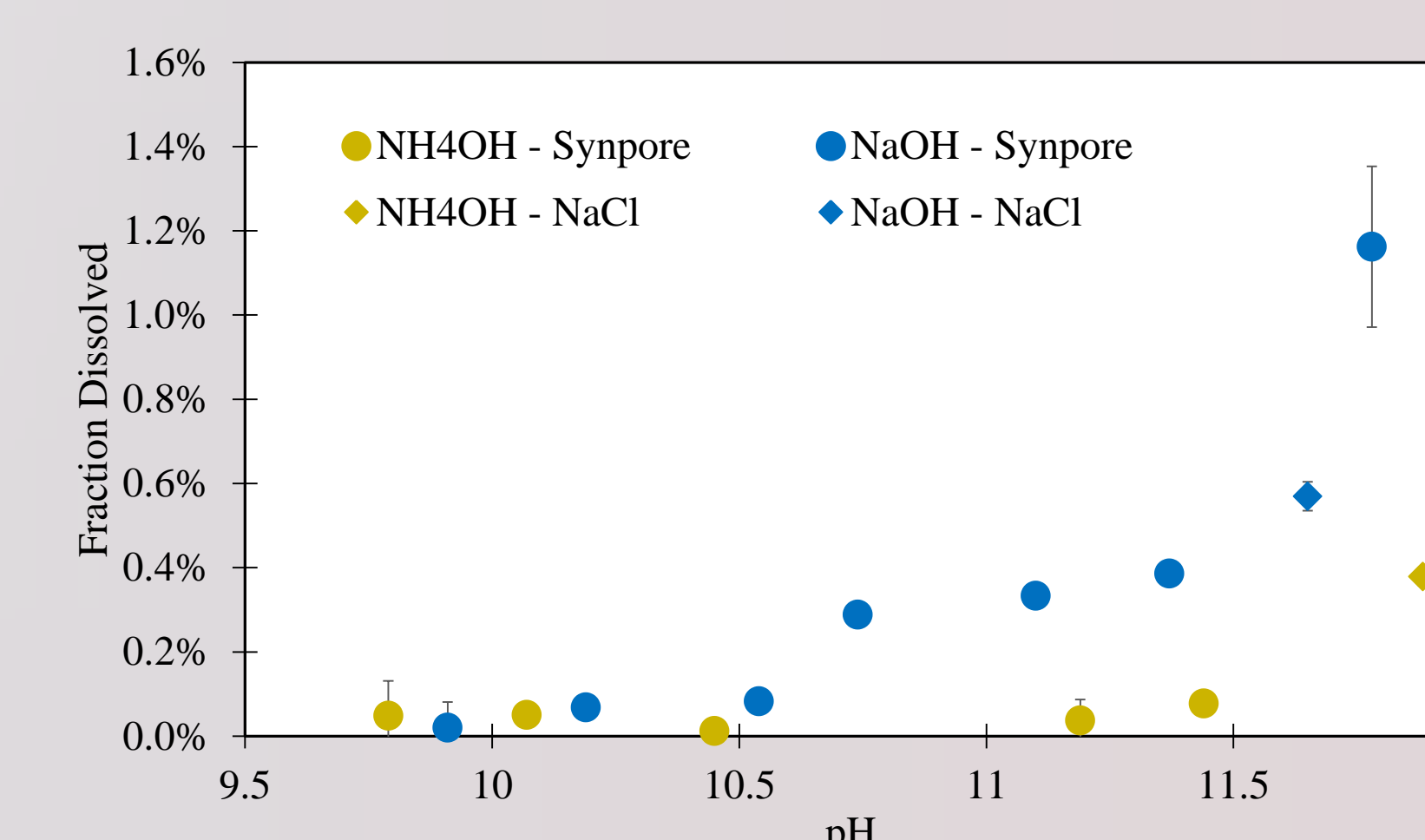


Figure 11. Comparison of Si dissolution from kaolinite (5 g/L) in either synthetic porewater or NaCl with pH adjustment by either NaOH (blue) or NH<sub>4</sub>OH (yellow)

Dissolution of Al & Si containing minerals at high pH can potentially allow for U to co-precipitate.

## Conclusions

- At pH ~7.5 significantly greater sorption occurs for NaCl as compared to synthetic porewater due to greater formation of U-carbonate species in synthetic porewater
- At pH ~11.5 in NaCl, aqueous U in NH<sub>4</sub>OH solution increases due to desorption from kaolinite as neutral or negative U-carbonate species form [Figure 9]
- At pH ~11.5 in synthetic porewater, significant removal of U occurs with both treatments but is higher of NH<sub>4</sub>OH possibly due to a decrease in solubility due effect of molecular species on solubility (i.e. NH<sub>3</sub>) [Figure 10]
- Significant dissolution of kaolinite occurs at elevated pH and Si and Al may co-precipitate with U species [Figure 11]. It is likely that co-precipitation occurs at elevated pH for synthetic porewater but is also expected to occur as pH decreases as NH<sub>4</sub>OH evaporates in NaCl system leading to oversaturation of Al/Si.

### Significance for Remediation:

- Ammonia gas injection may be an effective remediation technique for U in the Hanford vadose zone due to its significant removal of U from the aqueous phase (~10<sup>4</sup> mL/g compared to 10<sup>-1</sup> to 10<sup>0</sup> mL/g in natural conditions)
- As ammonia evaporates, pH returns to neutral allowing for U-aluminosilicate complexes precipitates. If (co)precipitation occurs, then U mobility decreases
- Ammonia gas will not increase the liquid flux to the groundwater

## Future Work

- Batch experiments for additional minerals and sediments (illite, montmorillonite, quartz, muscovite and natural sediments relevant to Hanford 200 Area)
- Sequential extractions to understand the lability of sorbed and co-precipitated U species
- Speciation modeling of the aqueous U
- Mineral and sediments characterization (XRD, BET, SEM + EDS)
- Kinetic batch experiments

## Acknowledgements

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