The Effects of Ca Ions on the Removal of U(VI) via In-Situ NH_3 Gas Injection at the Hanford Site 200 Area

Claudia Cardona, Yelena Katsenovich, Leonel Lagos
Applied Research Center
Florida International University

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- Background
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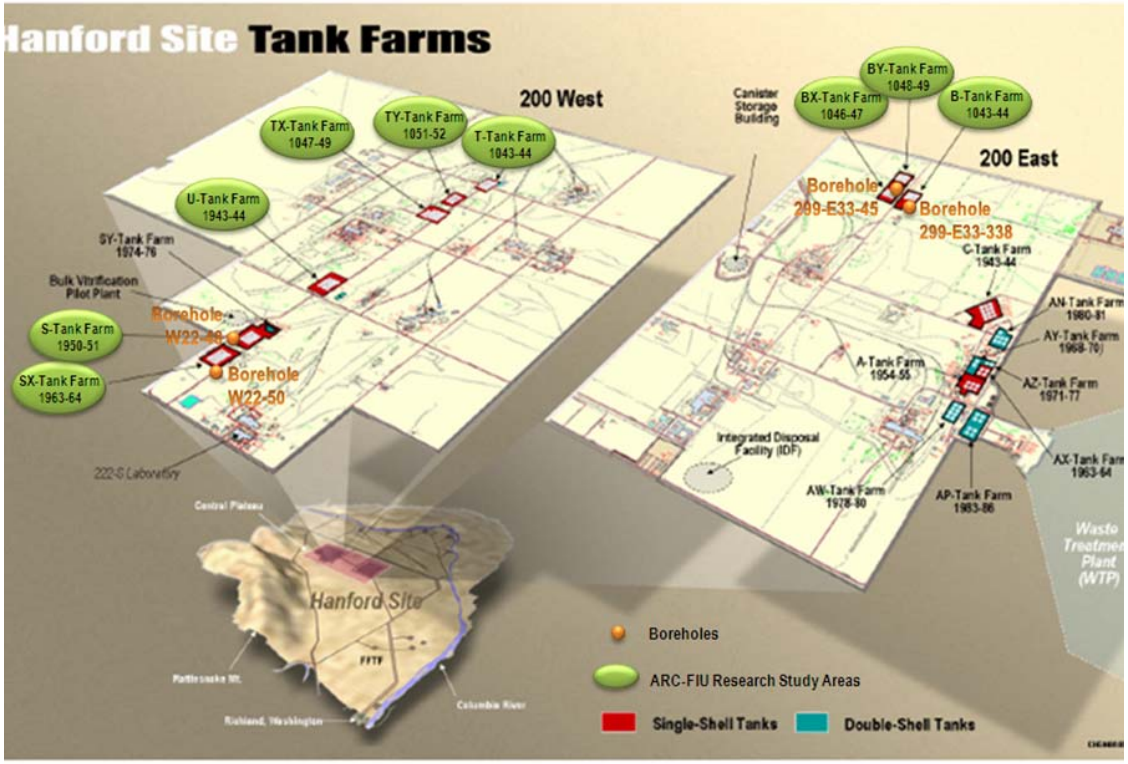
Background



Past U-Pu extraction and enrichment processes generated large amounts of radioactive waste containing uranium and other constituents at the Hanford Site 200 Area

Background

- ✓ These processes have left ≈ 200,000 kg of legacy U contamination to the ground surface
- ✓ Impacted the vadose zone (VZ)
- ✓ This U is a potential source for GW contamination
- ✓ Created a risk to receptors through water uptake from contaminated wells or discharge to surface water.

The Injection of NH_3 in the VZ

Innovative technology used to decrease uranium mobility in the subsurface contaminated with radionuclides

- NH_3 is a highly soluble gas

- The NH_3 gas rapid partition into liquid results in the reactions:

$$NH_3\ (g) \leftrightarrow NH_3\ (aq) \quad K_h = 6.58 * 10^{-4}\ N$$

$$NH_3\ (aq) + H^+ \leftrightarrow NH_4^+$$

The Injection of NH_3 in the VZ

- Formation of NH_4OH
- Increase in pH (from pH=8 to pH=11)
- Induce dissolution (release of elements such as Si, Al, Ca, Mg, Na, and K) from soil minerals to pore water
- Change the pore water chemistry
- Decrease in pH as the system stabilizes and reaches equilibrium will cause U co-precipitation

Objectives

- Evaluate the role of major pore water constituents on the removal of U(VI)
  - Formation of precipitates after NH_3 injection to the VZ.

- Examine the effect of the concentration ratios of Si/Al, in the presence of various HCO_3 and Ca^{2+} concentrations.

Materials

Five major components were used in the test solutions: silica, aluminum, calcium, uranium, and bicarbonate

Stock Solution	Salt Used	Molecular Weight of Salt (g/mol)	Stock Solution Concentration (mM)	Amount to prepare 50 mL (g)
Bicarbonate	$KHCO_3$	100.114	400.00	2.002
Metasilicate	$Na_2SiO_3 \cdot 9H_2O$	284.196	422.24	5.998
Aluminum	$Al(NO_3)_3 \cdot 9H_2O$	375.129	50.00	0.938
***Calcium**	$CaCl_2 \cdot 2H_2O$	147.01	2500 / 5000	3.675 /1.837

* 5 mM and/or 10 mM of Ca and 2 ppm of U(VI) were injected to the 5 mL samples

Experimental Method

Stock Solutions Al, Si and HCO_3^-

Mixed Samples
Al = 5 mM
Si/Al=1,10, 20, 30, 40,and 50 mM
HCO_3^-= 0, 2.9, 25, 50,75, and 100 mM

pH adjusted to 8

Injection of NH_3 Gas (5% NH_3 in 95% N_2 trough µm pores of the metal gas sparger, until pH of the solution reached 11

Tested samples, 5 mL samples were amended with Ca^{2+} (5 and 10 mM) and 2 ppm of U(VI)

Experimental Method

Shaker

Centrifuged

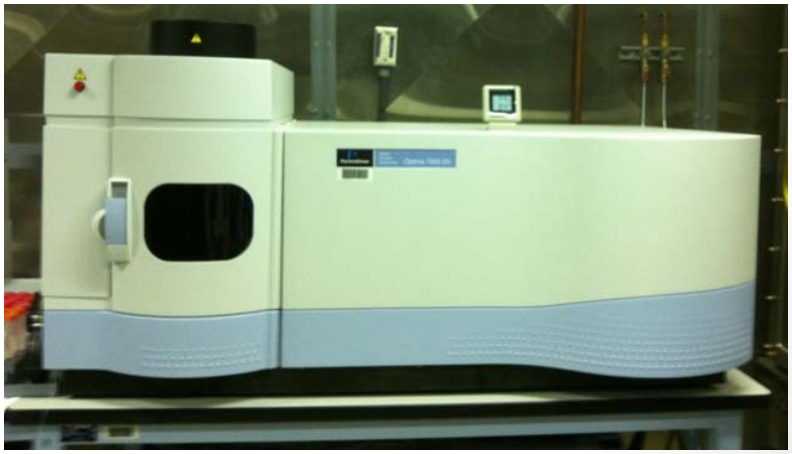
Supernatant

Analytical Procedures

- **U(VI)** was measured by Kinetic Phosphorescence Analyzer KPA-11 (Chemcheck Instruments)

- **Si, Al, and Ca** were determined using the ICP-OES (Perkin Elmer)

- All samples were diluted with 1% HNO_3

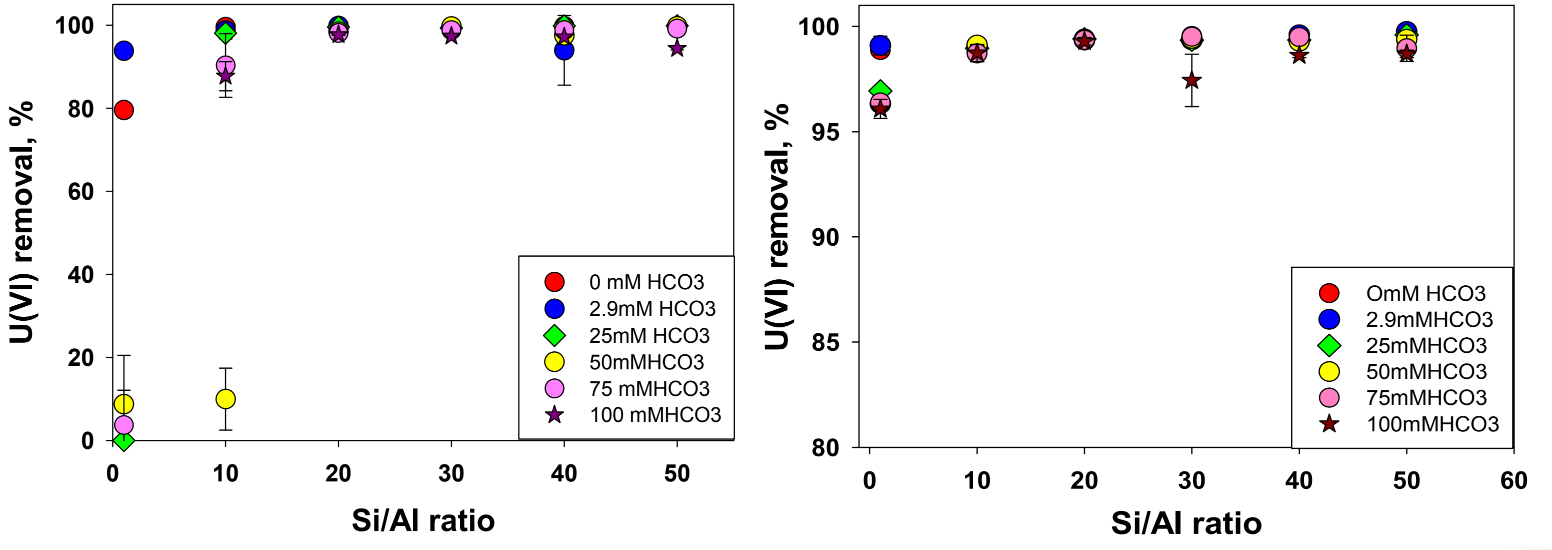


Speciation Modeling

- MINTEQ /Geochemical equilibrium modeling
- Updated with the Nuclear Energy Agency's thermodynamic database for uranium and calcium-uranyl-carbonate complexes
- T=25^{o}C and the CO_2 pressure fixed to atmospheric pressure (3.9×10^{-4} bar)
- Calculated U(VI) speciation in the elements of interest and saturation indexes (SI) for solid phases

Removal of U(VI)

- In the presence of Ca^{2+}, the removal of U(VI) yielded 98% - 99% starting at Si/Al $\geq$ 20. It showed an increase compared to the previous results without Ca^{2+}



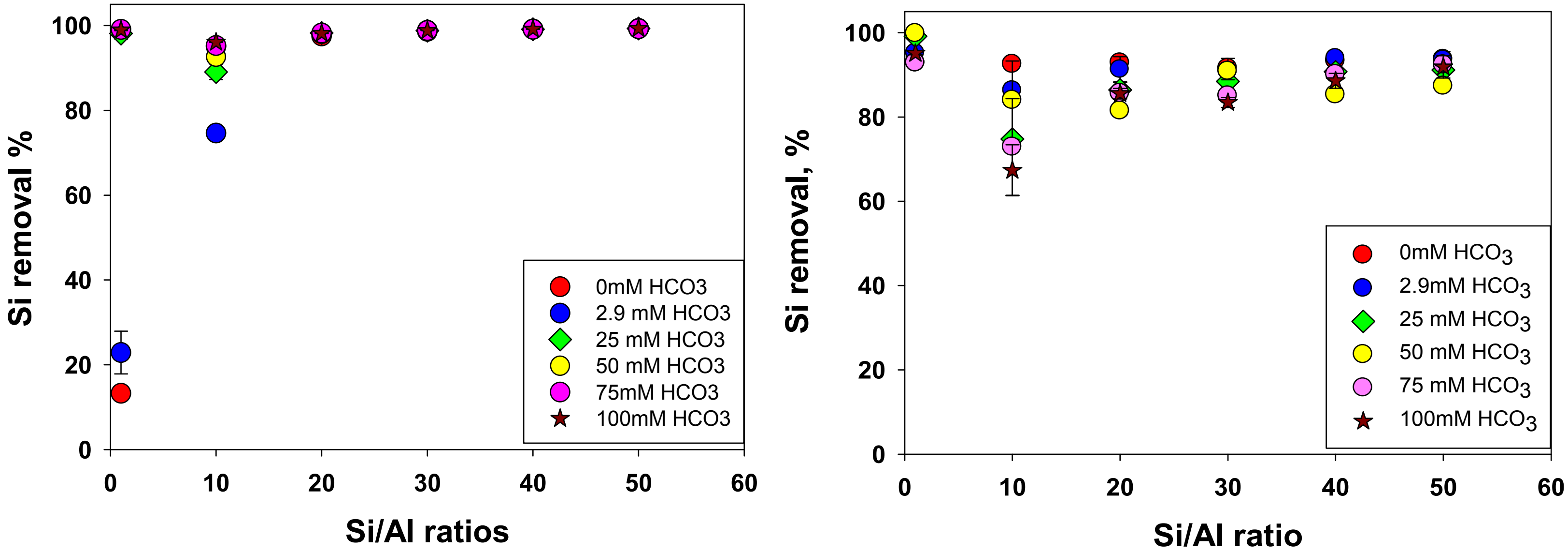
Removal of U(VI) in the solution mixture prepared with 5 mM (left) and 10 mM (right) of Ca.

Removal of U(VI)

- Si/Al molar ratio and HCO_3^- concentration affect U(VI) removal.
- The U(VI) removal was largely controlled by the Si/Al ratios and Ca^{2+} concentrations.
- The % of U(VI) removal increased as Si/Al ratios and HCO_3^- concentrations increased.
- The U(VI) removal varied between 87% and 100% starting at Si/Al ratio 10 for all HCO_3 tested.

Removal of Silica

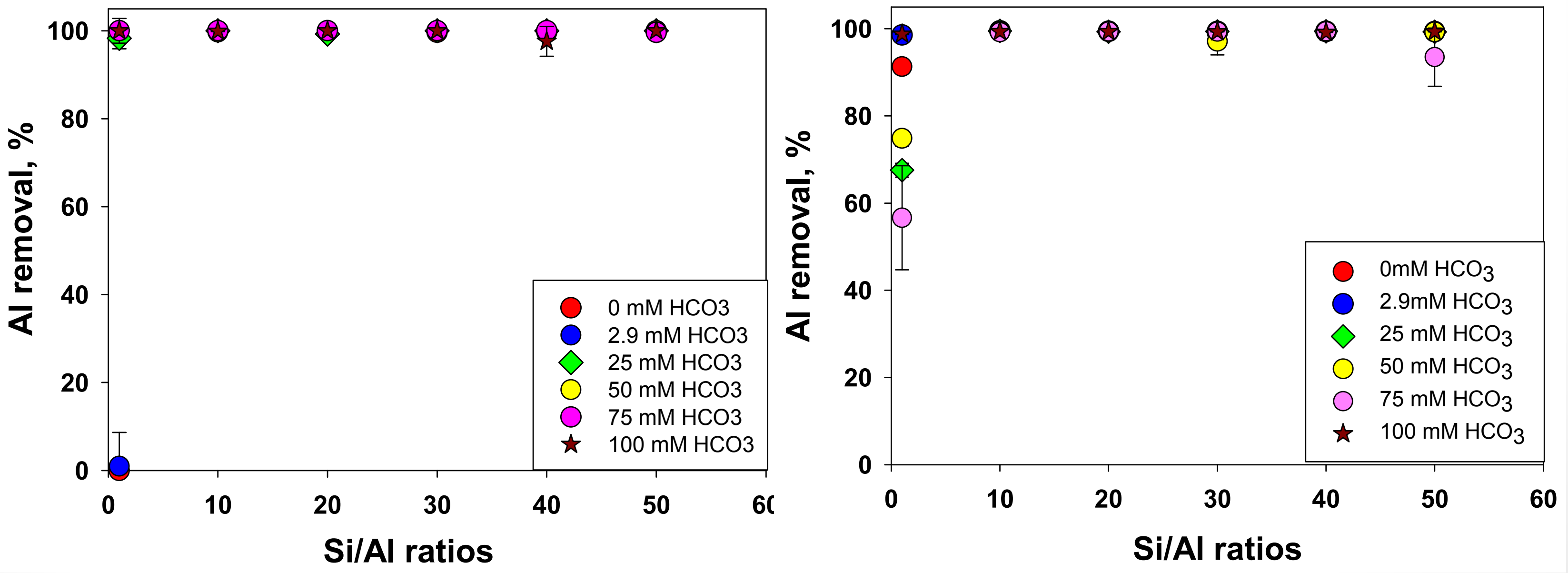
- 5 mM of Ca^{2+} (HCO$_3^-$ 0 and 2.9 mM), the percentage of Si removal at Si/Al ratios of 1 remained between 13% and 23%.
- 5 mM and Si/Al >10, Si removal remained between 89% and 99%
- At 10 mM of Ca the efficiency of Si removal at Si/Al =1 was increased up to 93-97%.



Removal of Si in the presence of 5 mM (left) and 10 mM (right) of Ca.

Removal of Al

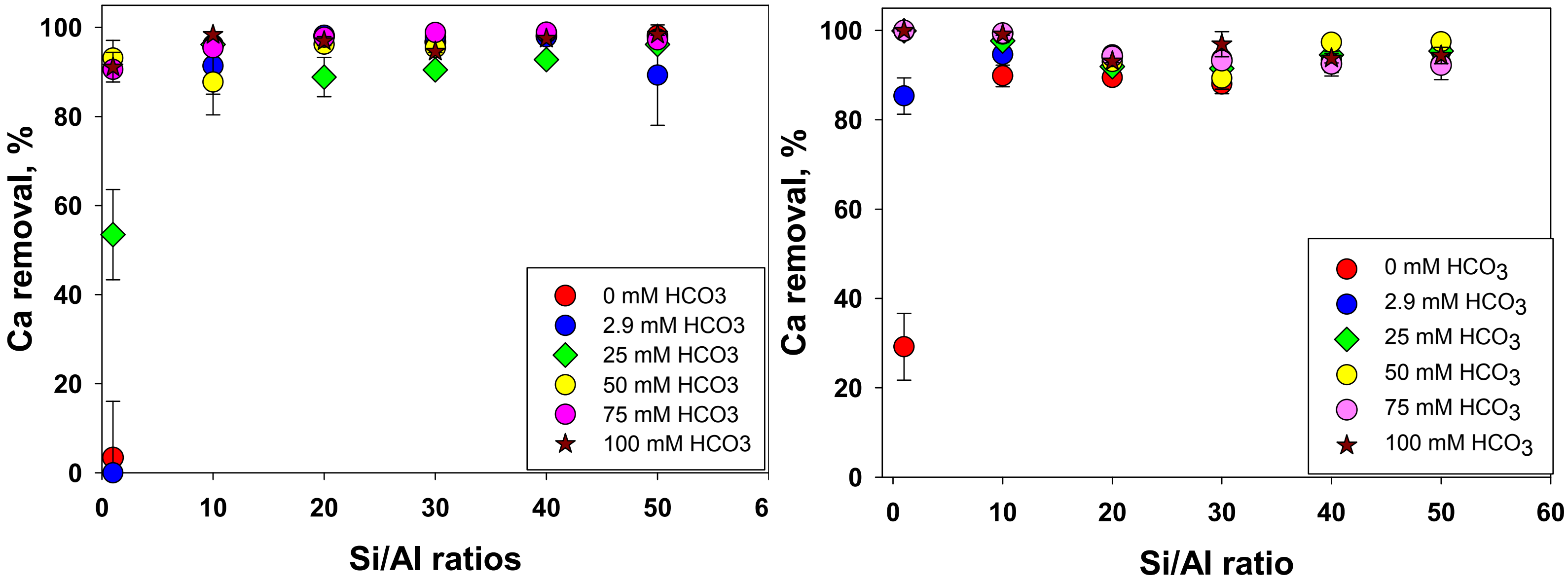
- At Si/Al =1, Al showed some variability.
- At Si/Al molar ratio ≥10, Al concentration dropped to an almost undetectable level.
- Monomeric silica reacts with Al^{3+} ions following its precipitation due to a reaction between $Si(OH)_4$ and crystalline $Al(OH)_3$.



Removal of Al prepared with 5 mM (left) and 10 mM (right) of Ca.

Removal of Ca

- When the Ca^{2+} concentration was increased up to 10 mM, the percentage of Ca removal at Si/Al ratio 1 was increased to 83-99% except if no bicarbonate is present.
- The removal of Ca^{2+} ion from the solution apparently is due to the precipitation of calcium carbonate.



Removal of Ca in the solution mixture prepared with 5 mM (left) and 10 mM (right) of Ca.

MINTEQ / Results

- The SM hasn’t predicted the formation of calcium silicate at elevated pH.
- The removal of Ca^{2+} ions from the solution is apparently due to the precipitation of calcium carbonate (Ca plot).
- At 0 mM HCO_3^-, U(VI) is present in the solution dominantly as $UO_2\,(OH)_3^{-}$.
- In the solutions with bicarbonate, $Ca_2UO_2(CO_3)_3$ and $CaUO_2(CO_3)_3^{-2}$ are the predominant species accounting for 30%- 84% of the total U species.

MINTEQ / Results

- SI showed that potential U-bearing secondary phases are undersaturated at all conditions tested.
- SM predicted the formation of aragonite and calcite in addition to various aluminosilicate and aluminum hydroxide solid phases created out of elements present in the solution.

Conclusions

- Higher Si concentrations tended to greater removal efficiencies of U(VI).
  - The highest percent removal of U(VI) 98-99% was observed at Si conc. between 150 mM - 250 mM.
- In the presence of 5 mM and 10 mM of Ca, the removal of U(VI) have overshadowed previous results without Ca ions.
- The removal of Si correlated with the removal of U(VI) from solutions.
- At Si:Al ratio =1, the increase in Ca concentration up to 10 mM increased Si removal to 93-99%.

Conclusions

- The formation of precipitate always correlated with the removal of U(VI), Si, Al and Ca from the solution.
- If no precipitate formation was observed, there was no U removal from the supernatant solution.
- SM predicted U(VI) present dominantly as $Ca_2UO_2(CO_3)_3$ and $CaUO_2(CO_3)_3^{-2}$ and Ca-UO_2-CO_3 ternary complexes constitute up to 84% of uranyl species.

Future Work

- Solubility experiments to evaluate for the stability of U- bearing precipitates via isopiestic method
- Complete the mineralogical and morphological characteristics of U-bearing precipitates
  - scanning electron microscope energy-dispersive spectroscopy (SEM-EDS)
  - X-ray diffraction (XRD)
  - Raman spectroscopy

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