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THE STABILITY OF URANIUM-BEARING PRECIPITATES CREATED AS A RESULT OF AMMONIA GAS INJECTIONS IN THE HANFORD SITE VADOSE ZONE

Master Thesis Oral Defense
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Background Information

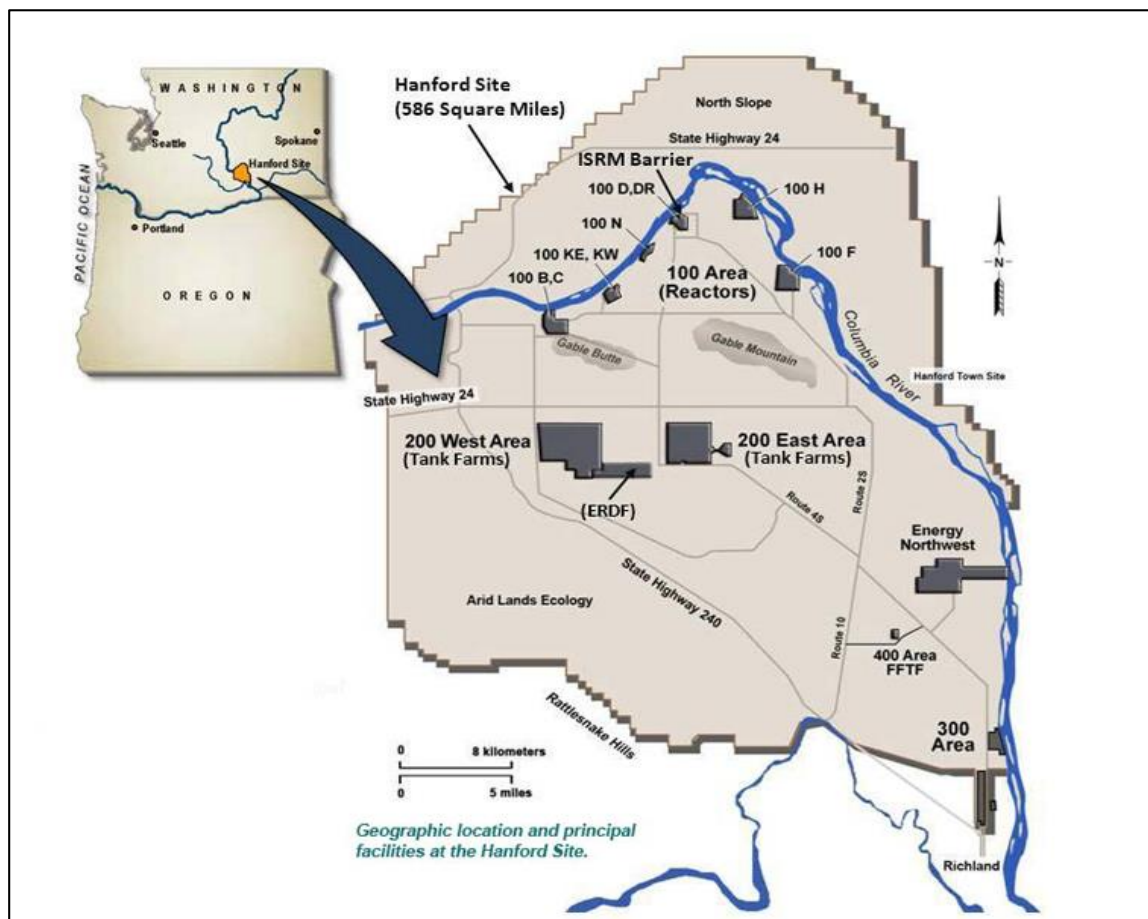


Figure 1: Hanford Site Area

Source : <http://www.hanford.gov/page.cfm/ProjectsFacilities#HM>

Department of Energy (DOE)

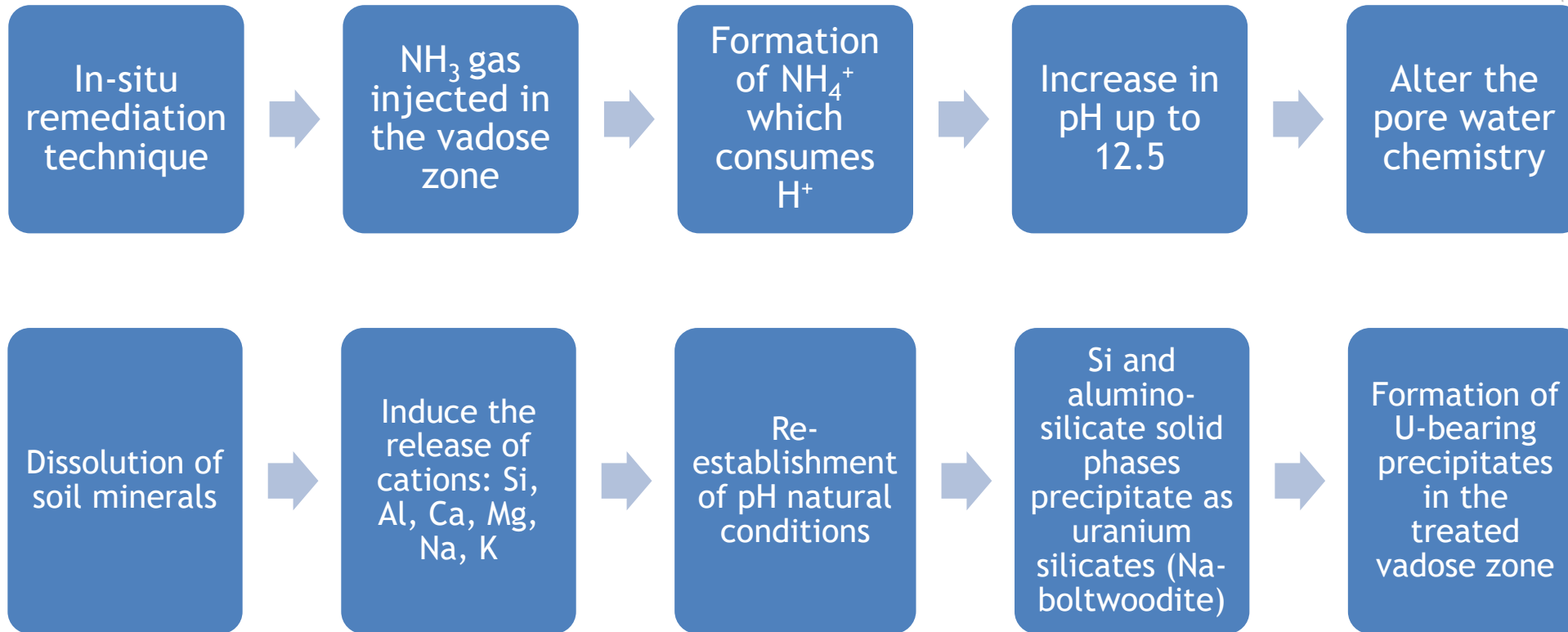
Hanford Site

200 Area

Uranium Contamination

Remediation Strategy

pH Manipulation via Ammonia (NH₃) gas injections



Remediation Strategy

- ▶ Addition of gas rather than liquid amendment to prevent potential downward U (VI) migration to the underlying aquifer.
- ▶ Decrease uranium mobility in the contaminated subsurface via creation of alkaline condition causing incorporation into solid precipitates that are stable in the natural environment and ultimately preventing the radioactive contaminant from spreading to the natural water resources.
- ▶ Szecsody et al. (2013) concluded that previous short-term laboratory evaluations showed a decrease in U mobility after NH_3 gas injections in the low water content sediments.
- ▶ Zhong et al., (2015) determined that the mass of U leaching from NH_3 -treated sediment was significantly less compared to the mass leached from the untreated sediment.

Research Objectives

- ▶ Evaluate the stability of the U-bearing precipitates created in the vadose zone as a result of ammonia gas injections.
- ▶ **Specific Objectives:**
 1. Description of the relevant environmental conditions prevailing in Hanford Site
 2. Preparation of artificial U-bearing precipitates mimicking those created in the vadose zone after injection of NH_3 gas replicating the subsurface conditions present in the Hanford Site 200 Area.
 3. Evaluation of U leaching from U-bearing precipitates via sequential extraction experiment.
 4. Evaluation of U precipitation/removal efficiencies from NH_3 -treated synthetic pore water solutions.

Procedures and Methods

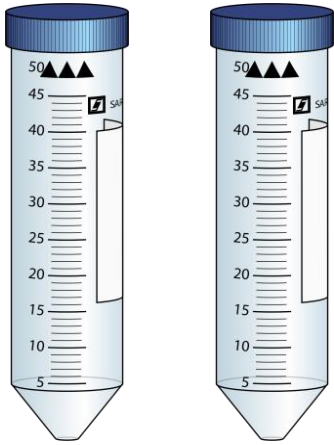
► I. Pore water composition and number of samples

Component	Concentration	Reference	Salt Used for Stock Solution
Uranium (VI)	2 ppm	Szecsody et al., (2012)	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Silica (Si)	50 mM	Zhong et al., (2015)	$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$
Aluminum (Al)	5 mM	Qafoku et al., (2004)	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
Bicarbonate (HCO_3)	3 and 50 mM	Katsenovich et al., (2016)	KHCO_3
Calcium (Ca^{2+})	0, 5 and 10 mM	Szecsody et al., (2012)	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$

Sample Number	Bicarbonate Concentration	Calcium Concentration
1	"Low" 3 mM	0 mM
2		5 mM
3		10 mM
4	"High" 50 mM	0 mM
5		5 mM
6		10 mM

Procedures and Methods

▶ II. Experimental Set up



1. Prepare two 50 mL test solutions mixing volumes of Si and Al
2. Add measured volumes of bicarbonate
3. Adjust pH via titration with HNO_3 to approximately 8
4. Inject ammonia gas until pH reaches 11
5. Distribute the mixture into six 10-mL centrifuge tubes
6. Add measured volumes of U and Ca
7. Shake at 100 rpm and 25°C . Let solid particles to settle for 24 hours
8. Centrifuge for 30 minutes at 5000 rpm and
9. Collect supernatant in different vials



Procedures and Methods

► Preparation of samples containing U-bearing precipitates

a) Unfiltered Samples (12)

10. The wet precipitates were set to dry in the oven at 35°C for 2-3 weeks

b) Filtered Samples (12)

Ensure pore water accumulated inside precipitates was removed before sample drying

11. Vacuum-filter all the samples using micro sized pore filters



Figure 2: Glass Setting for Vacuum-filtration

Procedures and Methods

▶ III. Sequential Extraction on Solid Precipitates

- Evaluate U leaching potential from solid precipitates
- Increasingly aggressive solutions each intended to target increasingly more difficult-to-remove uranium phases.

Step	Solution	Time of exposure (h)	Target Compounds
1	Deionized Water (DIW)	1	Aqueous U phases
2	Carbonate solution	1	Adsorbed U phases
3	Acetate solution	1	Dissolved some U-Carbonates
4	Acetic acid solution	120	Most U-Carbonates and hydrated boltwoodite (uranyl silicate minerals)
5	8 M Nitric Acid (HNO ₃) at 95° C	2	Dissolved harder U phases

Procedures and Methods

- ▶ IV. Analytical Procedure
 - Concentration of soluble U in all samples were analyzed using a Kinetic Phosphorescence Analyzer (KPA-11)



Figure 3: KPA instrument. Source: ChemChek Instruments

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RESULTS

Uranium Extraction Distribution for Unfiltered Samples

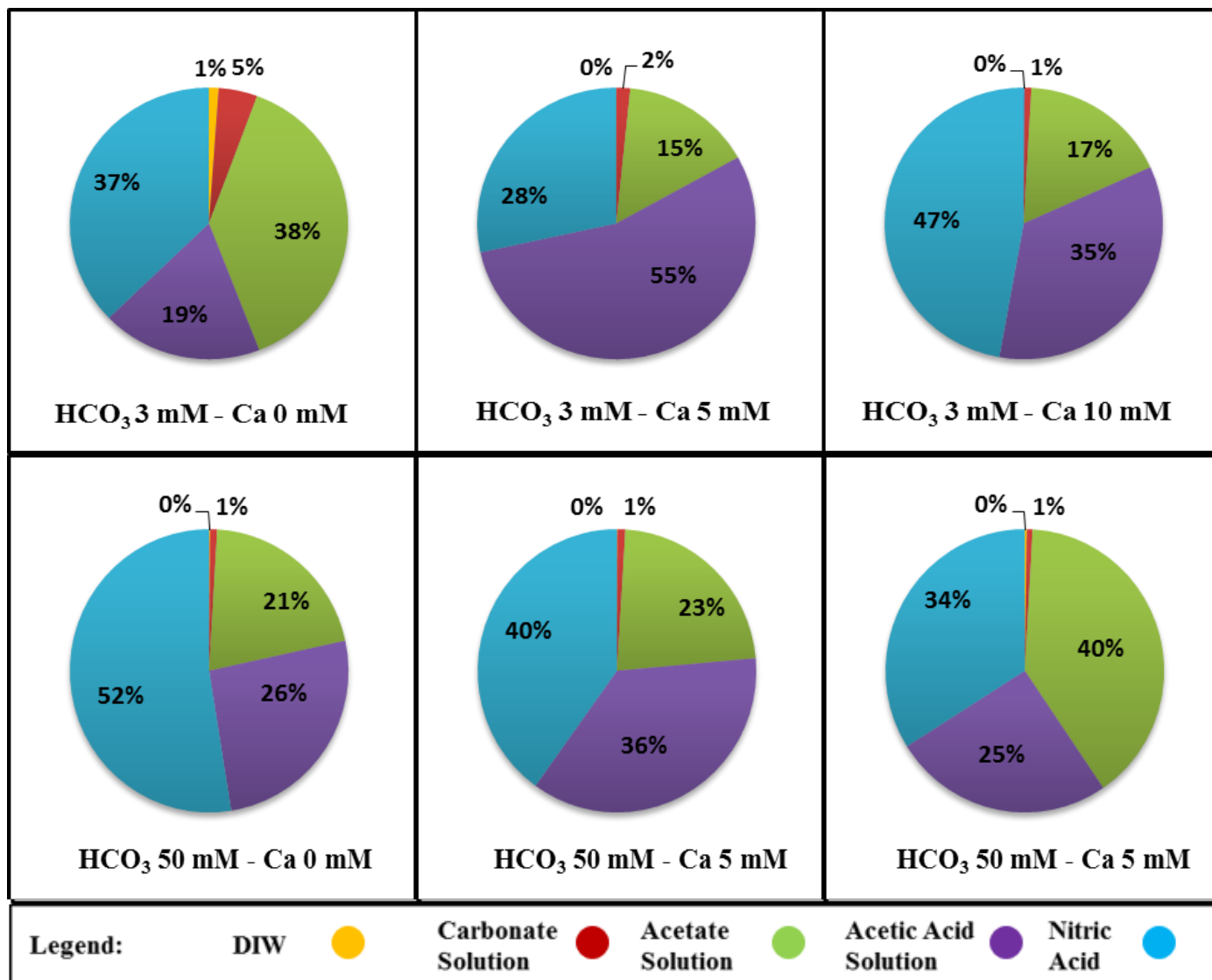


Figure 4

Uranium Extraction Distribution for Filtered Samples

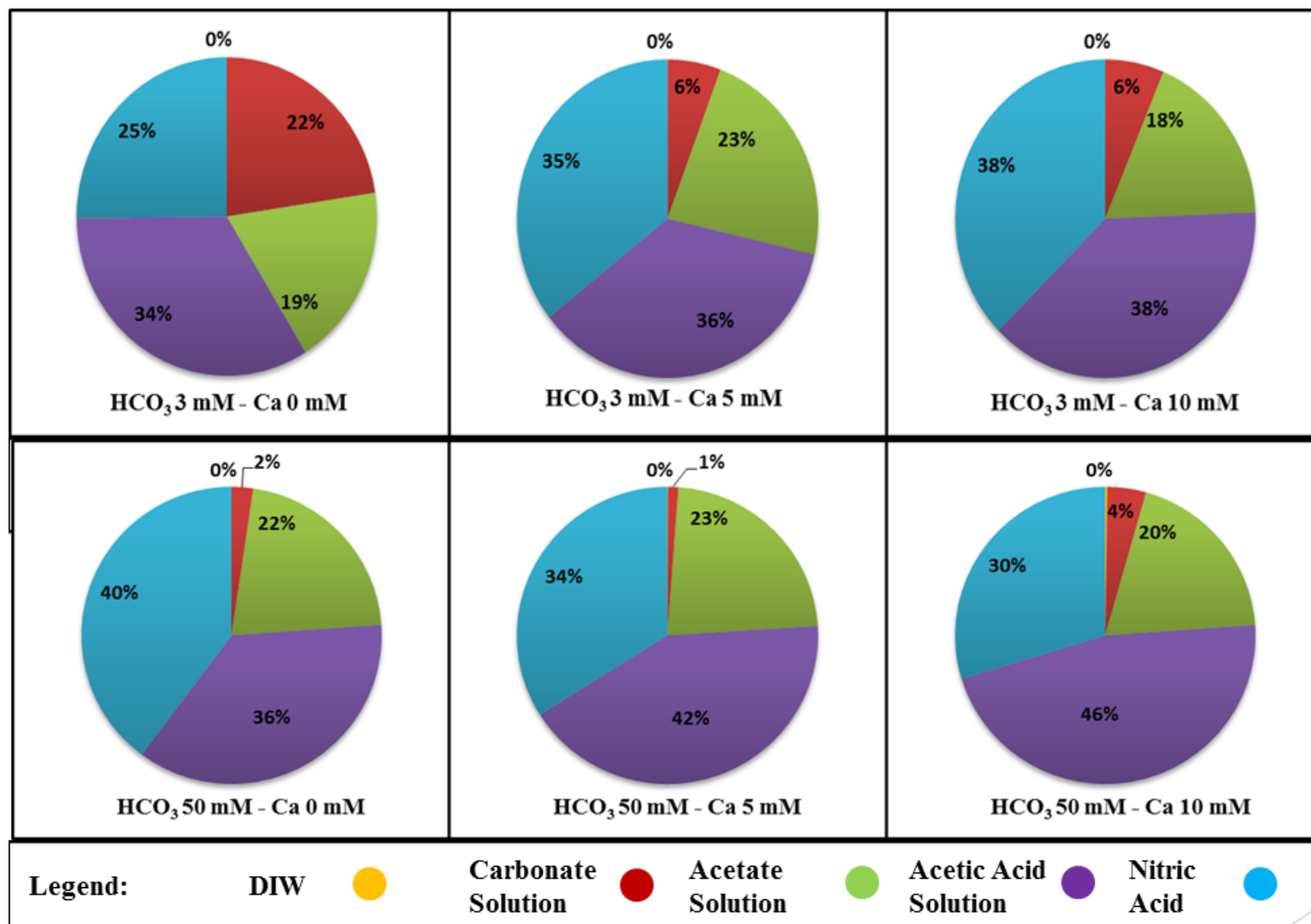


Figure 5

Sequential Uranium Extraction of Filtered Sample Precipitates on Mass Basis

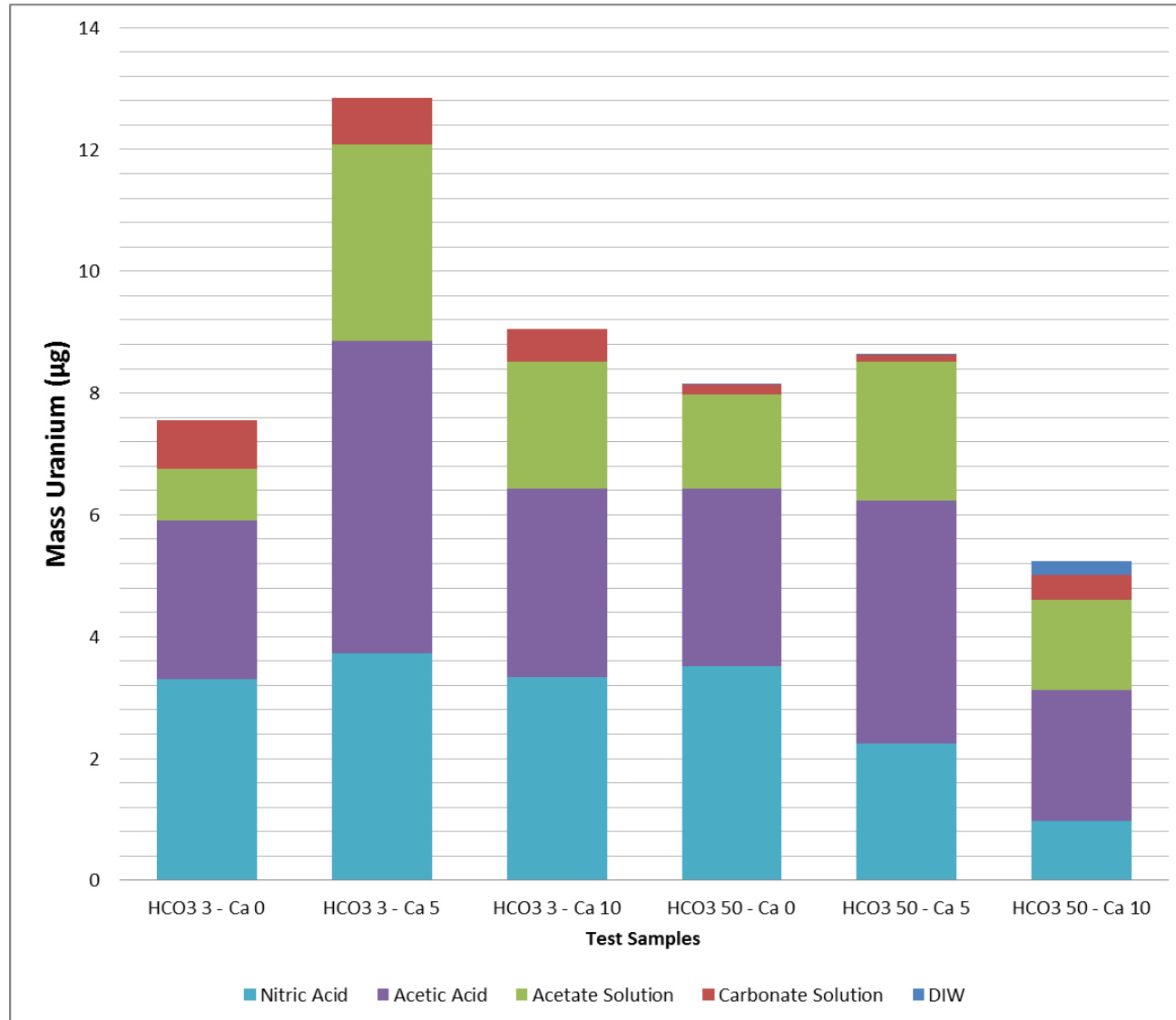
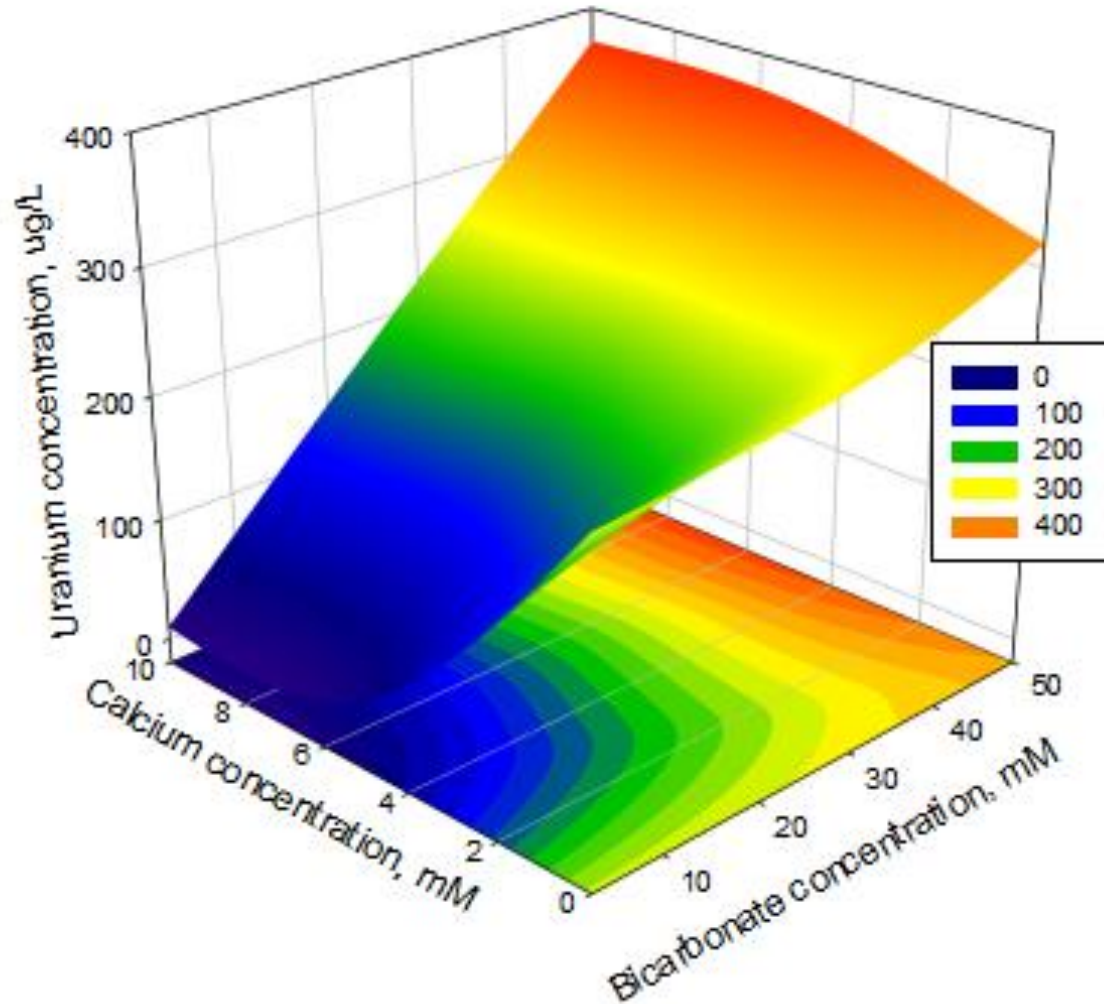


Figure 6

Mass of U In (µg)	Mass of U Out (µg)	Recovery (%)
17.535	7.54690	43.04
19.637	12.84220	65.40
19.896	9.05490	45.51
16.822	8.14720	48.43
16.316	8.63973	52.95
16.266	5.23459	32.18

Optimization Study - Analysis of Supernatant Solution



- Increasing bicarbonate concentration, the amount of U in precipitate decreases.
- Formation of uranyl carbonates under high bicarbonate concentrations
- Formation of uranyl silicates under low bicarbonate concentrations
- Increasing calcium concentration, the amount of U in precipitate increases.
- Precipitation of calcium carbonates or calcium silicates causing Si polymerization reactions
- U precipitation efficiency 75-99%

Figure 7: Response surface diagram displaying filtrated solution uranium retention in samples

Low Si concentrations experiment

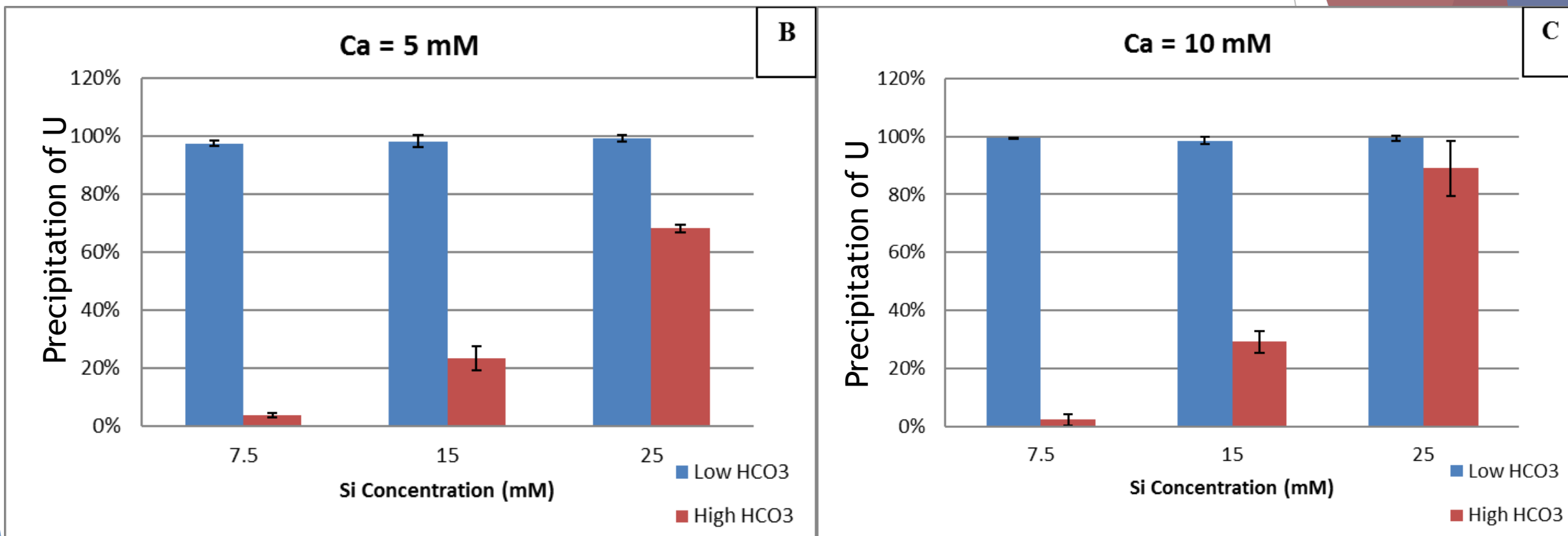


Figure 4: Percent removal of U (VI) tested at variable bicarbonate and silica concentrations in 5 mM Al amended solutions containing 2 mg/L U (VI) and (B) 5 mM; and (C) 10 mM of Ca

Low Si concentrations experiment

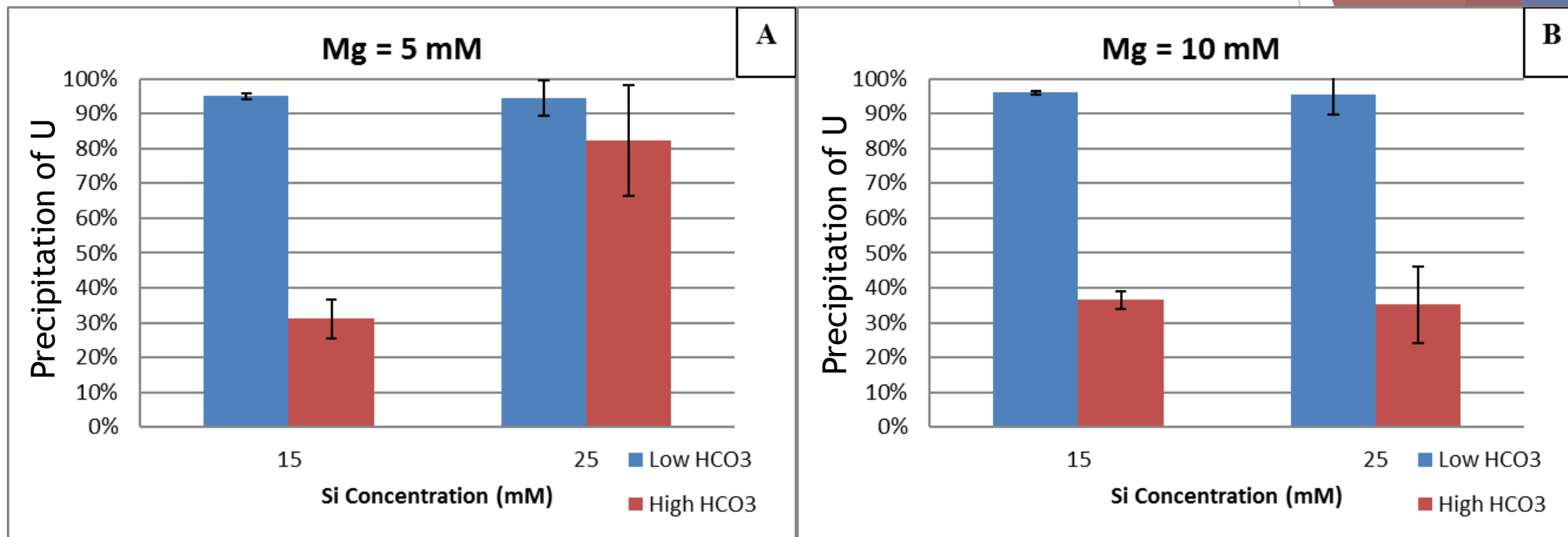


Figure 5: Percent removal of U (VI) tested at variable bicarbonate and silica concentrations in 5 mM Al amended solutions containing 2 mg/L U (VI) and (A) 5 mM; and (B) 10 mM of Ca

Conclusions

- pH manipulation via ammonia gas injections is an effective remediation technology to reduce mobility of U aqueous phases by converting them into lower solubility precipitates.
- The sequential liquid extraction experiment showed that U-silicates and even more solid stable U phases make up the majority of the precipitates composition created in NH₃ gas treated solutions. Low bicarbonate appears to guarantee effective U precipitation.
- There is evidence to suggest that U present in the solid particles has strong bond to sediments located in the vadose zone, causing the precipitates created after NH₃ gas injections to be stable in the natural environment, and therefore, the technology to be effective under the simulated conditions.
- The results obtained from the Low Si concentration experiment also confirmed its major role in the precipitation/removal efficiencies of U (VI).
- Results also showed that there were little soluble U phases found in solutions after NH₃ gas treatment. This findings are of great importance because further contamination potential caused by migration to groundwater or surrounding water resources in the Hanford Site will be significantly reduced.

Future Work

- ▶ Future experiments using different Si and bicarbonate concentrations could help understand the variances in U (VI) removal.
- ▶ Continuous leach extractions experiments would complement the results found in this study by evaluating the relative extractability of U and influence of contact time in U leaching potential.
- ▶ Other major constituents found in the Hanford Site Vadose Zone at different concentrations such as iron (Fe) combined with high concentrations of Si and bicarbonate could be used to prepare new U-bearing precipitates and evaluate their role in of U (VI) removal efficiency.
- ▶ Speciation modeling varying constituents concentrations and different environmental conditions could help better understand the species formed by studying their properties.

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