The Characterization of Uranium Phases Produced by the NH$_3$ Injection Remediation Method Under Hanford 200 Area Conditions

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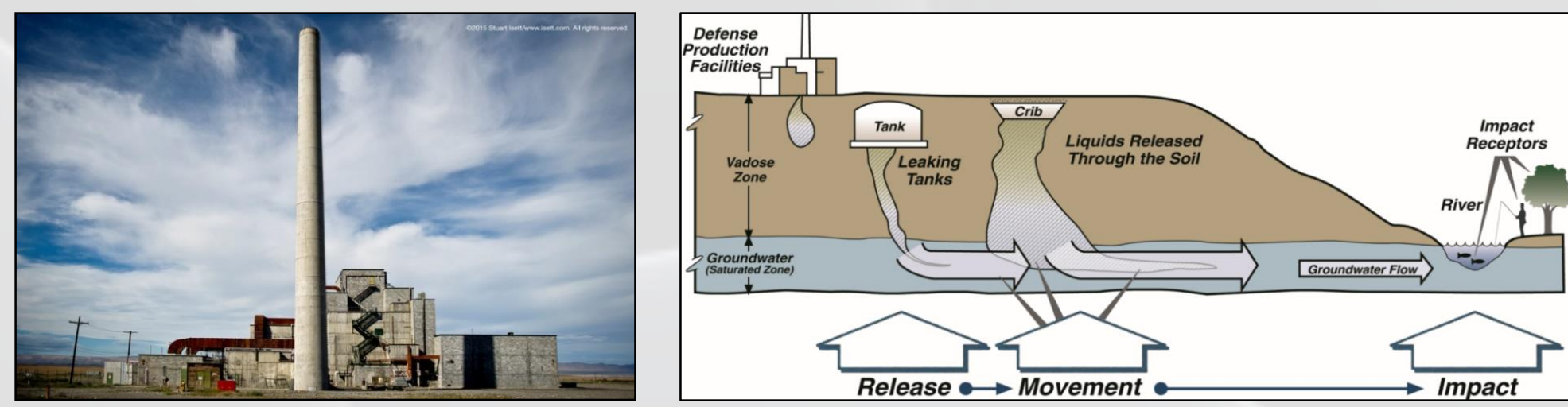
Background

Improper discharge and failed storage tanks have resulted in the contamination of the Hanford vadose zone with radiologically contaminated waste

Remediation methods considered for the area include sequestration of uranium by injection of ammonia (NH$_3$) gas

- Increases the pore water pH, promoting the dissolution of soil minerals
- Re-establishment of natural conditions is believed to cause the recrystallization of minerals and the co-precipitation of uranium phases

Objectives & Significance

Characterization of the precipitates formed when the ammonia (NH$_3$) injection method is applied to synthetic pore water on a laboratory scale. This involves:

- Identification of the uranium-bearing phases
- Study of the impact of major pore water constituents

This study will supplement the ongoing research into the application of the NH$_3$ remediation method to the Hanford vadose zone uranium contamination while working to broaden the understanding of the roles constituents play in the subsurface remediation technology

Sample Preparation & Analysis

Synthetic pore water solutions were prepared to mimic selected major constituents of the pore water from the Hanford 200 Area

- Varying concentrations of calcium and carbonate in solutions will be used to evaluate effects
- Prior results led to method modifications such as
  1. Preparation of duplicate (Group B) samples
  2. Vacuum filtration of all samples
  3. DI-water rinse of duplicate samples (5 mL)

Samples were subject to NH$_3$ gas treatment to pH 11-12 and allowed to re-establish pre-treatment pH before vacuum filtration to isolate solid and liquid phases for analysis
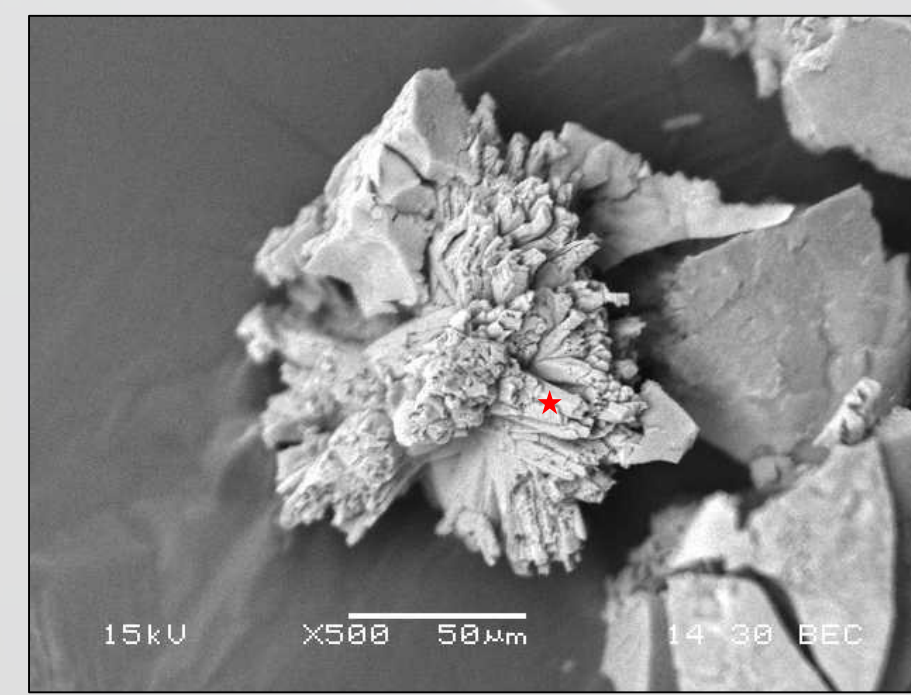
Ammonia gas injection and vacuum filtration steps of the modified sample preparation

Precipitate and supernatant were analyzed by scanning electron microscope with energy dispersive spectroscopy (SEM/EDS) and kinetic phosphorescence analyzer (KPA), respectively
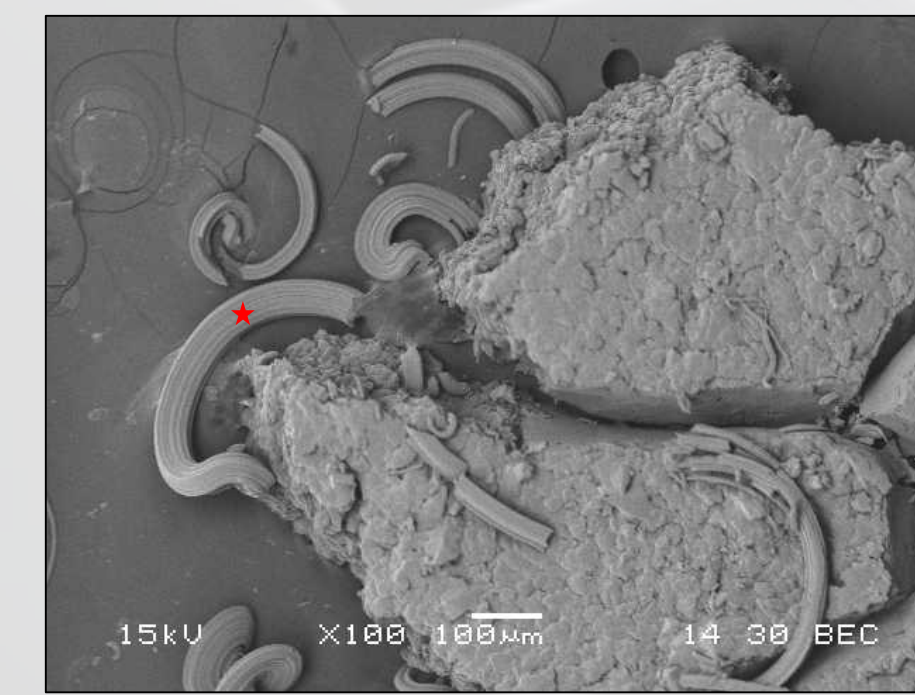
Results

Precipitate Analysis

Scanning electron microscopy showed eye-catching structures likely to be mineralogically significant though EDS analysis revealed no significant uranium content.

Element	Wt%	At%
C K$_\alpha$	18.43	28.04
N K$_\alpha$	03.11	04.05
O K$_\alpha$	46.75	53.41
Na K$_\alpha$	00.73	00.58
Al K$_\alpha$	00.08	00.06
Si K$_\alpha$	00.19	00.13
U M$_\alpha$	00.70	00.05
Ca K$_\alpha$	30.01	13.69

SEM image w/ EDS data for specimen 25-05A, prepared using a 25mM of HCO$_3^-$, 5mM Ca^{2+}, and 200ppm uranium pore water solution

Element	Wt%	At%
C K$_\alpha$	03.30	04.82
N K$_\alpha$	16.02	20.08
O K$_\alpha$	42.34	46.46
Na K$_\alpha$	36.79	28.10
Al K$_\alpha$	00.26	00.17
Si K$_\alpha$	00.35	00.22
U M$_\alpha$	00.72	00.05
Ca K$_\alpha$	00.21	00.09

SEM image w/ EDS data for specimen 50-00A, prepared using a 50mM of HCO$_3^-$ and 200ppm uranium pore water solution

- EDS analysis suggests that these are likely calcium carbonate (CaCO$_3$) (left) or nitratine (NaNO$_3$) (right), two precipitates expected based on composition and X-ray diffraction analysis of previous samples

Continued SEM analysis revealed areas of high average atomic weight which were then confirmed to be uranium-rich by EDS analysis

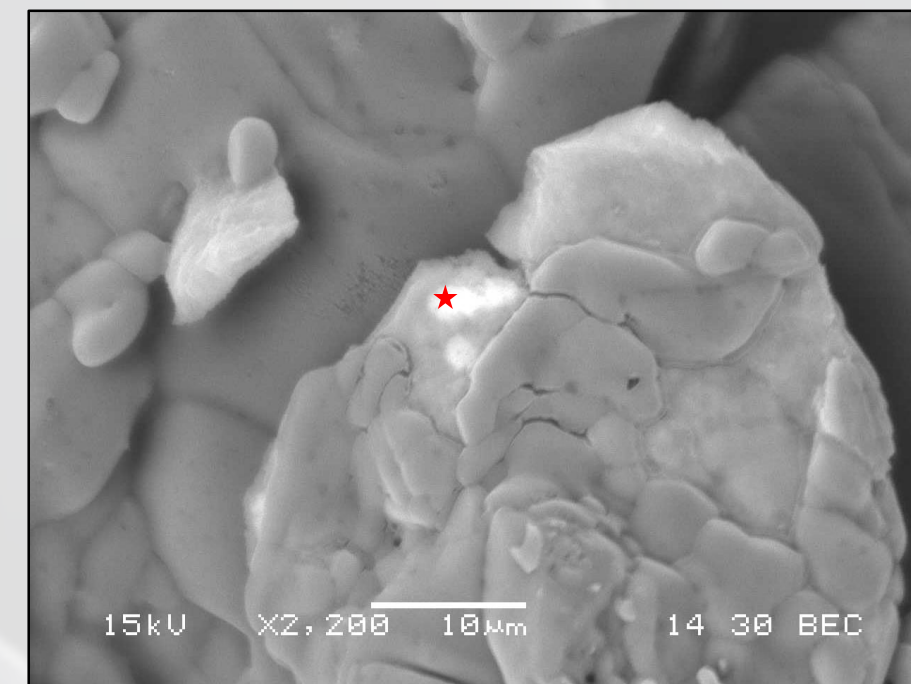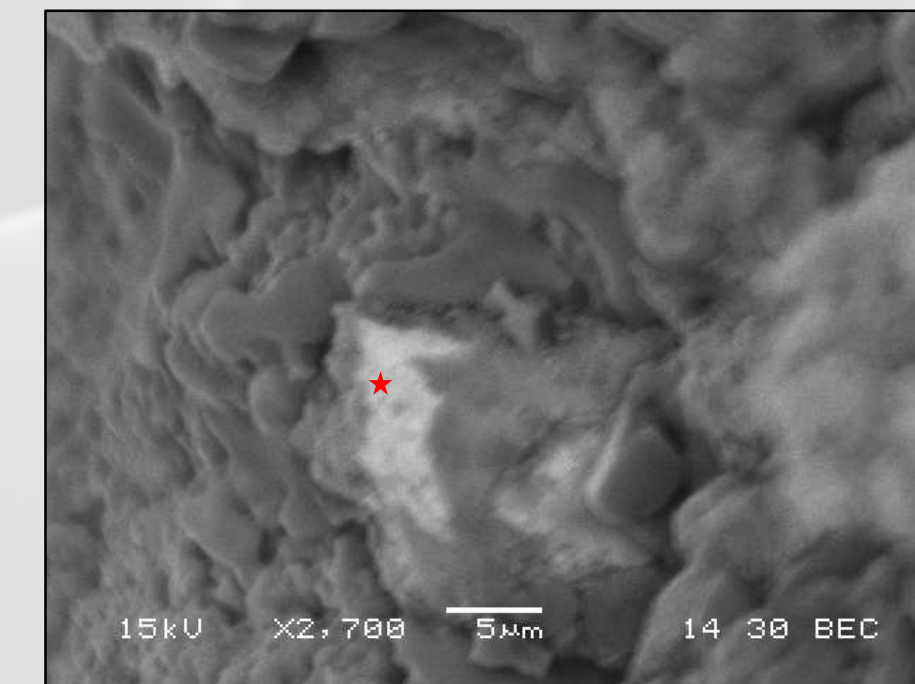| Element	Wt%	At%
C K$_\alpha$	06.33	11.22
N K$_\alpha$	03.61	05.48
O K$_\alpha$	41.41	55.08
Na K$_\alpha$	06.60	06.11
Al K$_\alpha$	01.78	01.40
Si K$_\alpha$	25.58	19.38
U M$_\alpha$	14.69	01.31

SEM image w/ EDS data for specimen 50-00A, prepared using a 50mM of HCO$_3^-$ and 200ppm uranium pore water solution

Element	Wt%	At%
C K$_\alpha$	06.96	12.37
N K$_\alpha$	04.68	07.13
O K$_\alpha$	39.29	52.44
Na K$_\alpha$	11.00	10.22
Al K$_\alpha$	01.59	01.26
Cl K$_\alpha$	00.91	00.55
Si K$_\alpha$	19.05	14.48
U M$_\alpha$	16.40	01.47
Ca K$_\alpha$	00.12	00.06

SEM image w/ EDS data for specimen 50-05A, prepared using a 50mM of HCO$_3^-$, 5mM Ca^{2+}, and 200ppm uranium pore water solution

- These uranium phases were exclusively found in the non-rinsed (Group A), high bicarbonate samples

Supernatant Analysis

The kinetic phosphorescence analyzer results were used to determine the concentration of uranium retained in the supernatant filtrates and, by difference, precipitated in the solid phase

- Resulting data was used to prepare response surface diagrams, allowing for the visualization of the relationship between initial calcium and bicarbonate content and the retention of uranium in the aqueous solution.

Group A Filtrate - Response Surface Diagram

Group B Filtrate - Response Surface Diagram
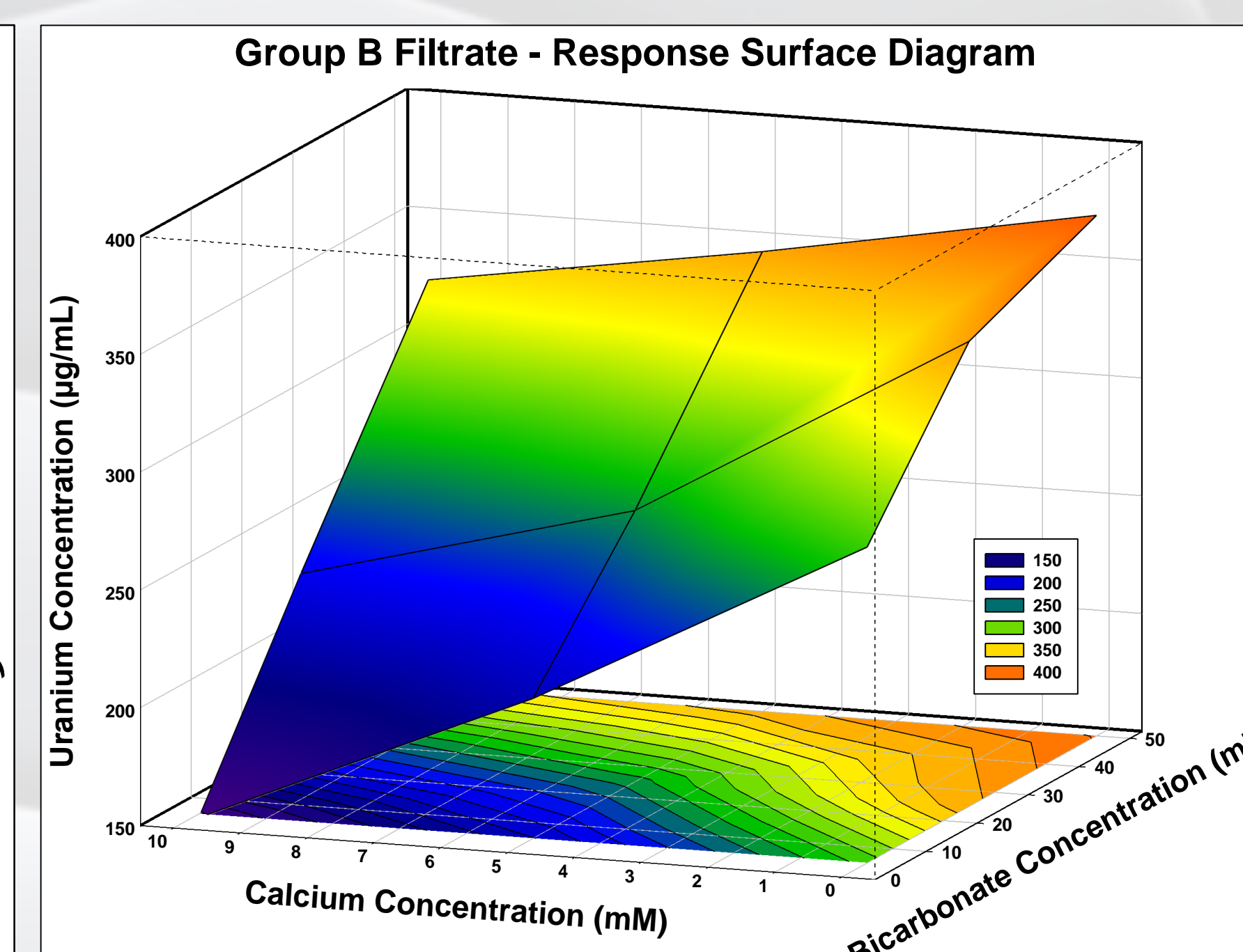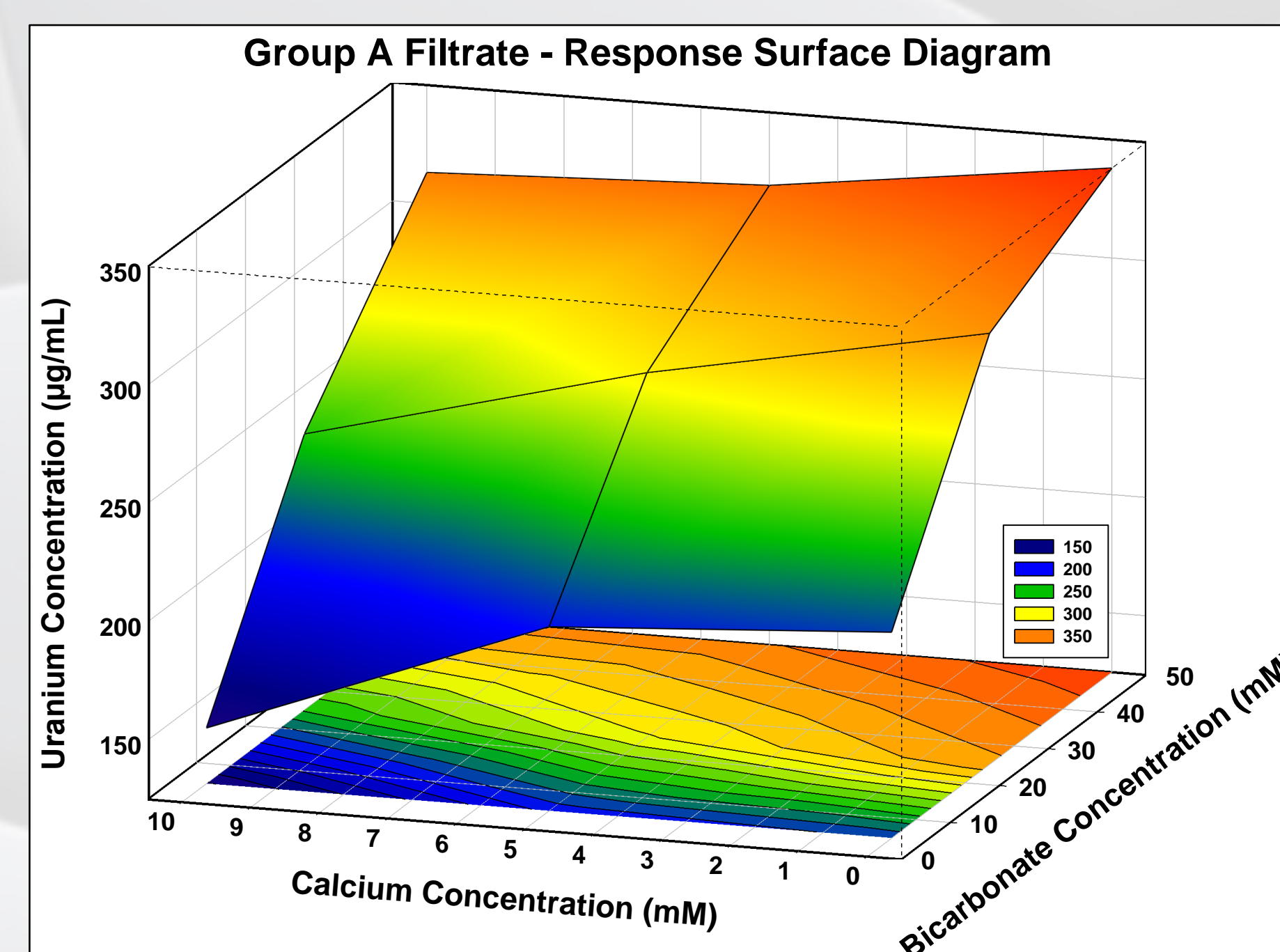
The diagrams display clear trends between uranium retained and initial pore water solution component concentrations

- High bicarbonate is associated with high uranium concentrations
- High calcium content is associated with low uranium concentrations

Group B Rinse - Response Surface Diagram
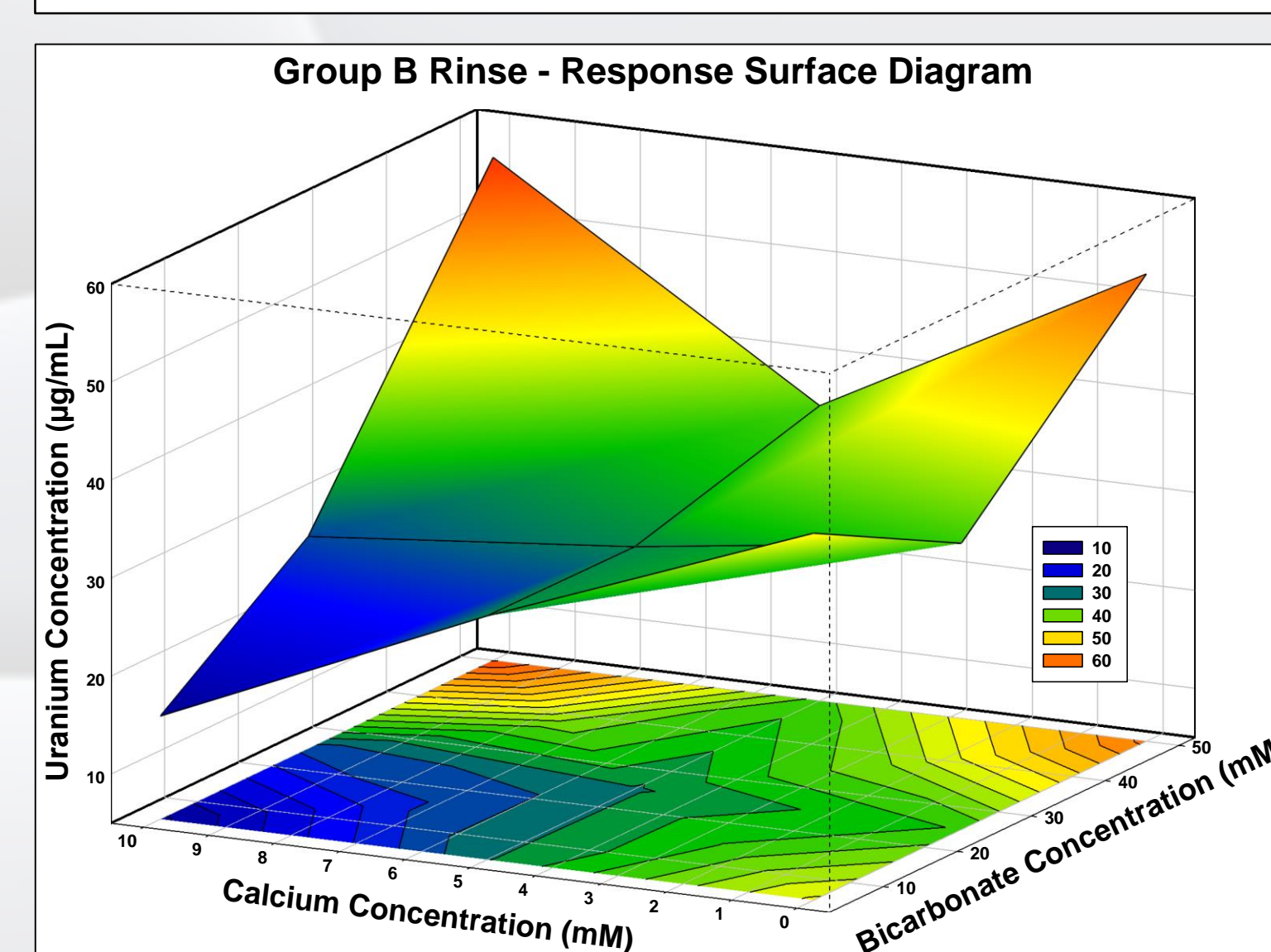
The response surface diagram for the filtered DI-water rinse resulted in concentrations an order or magnitude less than the filtered supernatant

- The rinse filtrates break from the trend established by the sample filtrates
- Similar to previous groups, the high calcium, low bicarbonate shows the lowest uranium retained in solution

Conclusions

With the exception of low bicarbonate samples, the structures suspected to be calcium carbonate were detected in nearly all calcium containing specimen, regardless of a rinsing step

The uranium rich solid phases detected by SEM/EDS were morphologically significantly different compared to the distinct phases observed in previous samples

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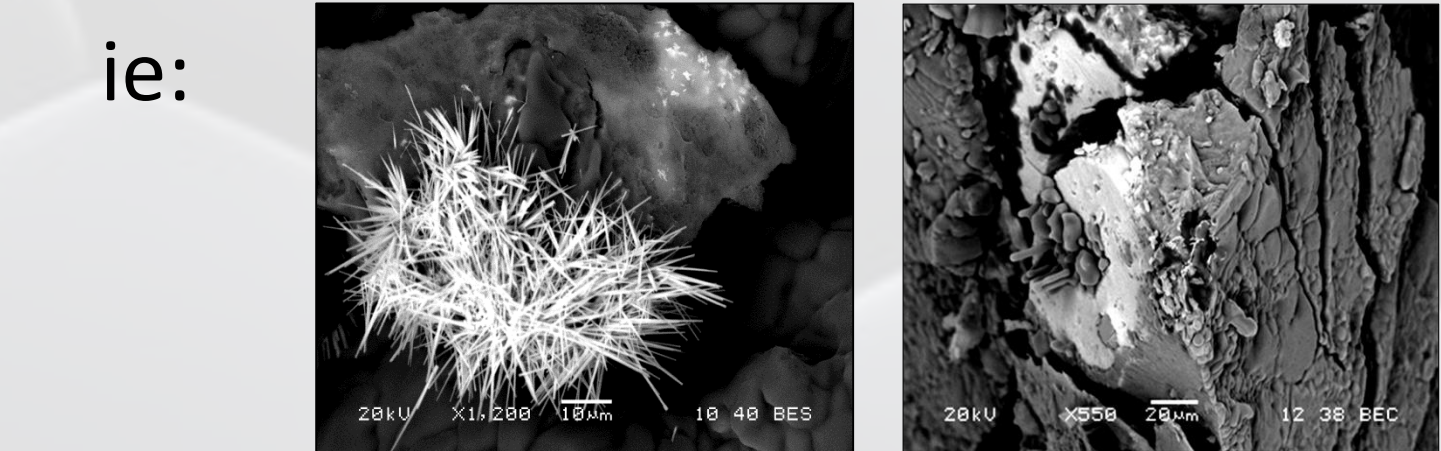
SEM images of uranium rich regions from prior 200ppm (L) and 500 ppm (R) samples

Analysis of the filtered supernatant solutions revealed that the concentration of uranium retained in solution after treatment was maximized with increased bicarbonate concentration and minimized by increased calcium content

- The high concentration of retained uranium in the low calcium, high bicarbonate supernatant solutions is undermined by the consistent identification of solid uranium phases by EDS analysis
- Similarly the data implies that the low bicarbonate, high calcium precipitates should contain the most solid uranium phases due to the low uranium concentrations retained in supernatants.
  - SEM/EDS analysis contradicts this implication due to the lack of any significant presence of uranium in the solid phase

Future Work

Electron microprobe will be used to analyze the elemental content uranium phases observed by SEM/EDS

- Samples will be mounted in epoxy prior to grinding and polishing with assistance from an appropriate facility

X-ray diffraction and transmission electron analysis will be used to attempt to determine a diffraction pattern for the crystalline uranium forms

Sequential extractions of sample precipitates will be used to characterize the uranium phases present based on solvent interactions

Acknowledgements