Characterization of the Uranium-Bearing Products of the Ammonia Injection Remediation Method

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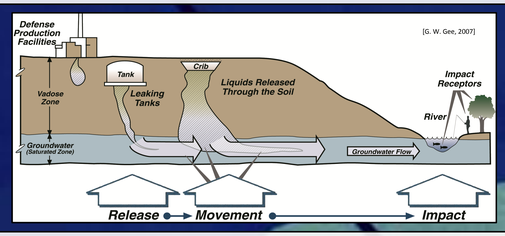
Background

- Commissioned in 1943, the Hanford Site is the home of the world's first full-scale nuclear production facility.
- After more than 40 years of processing, 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 the mobile uranium by injection of ammonia (NH_3) gas.
  - Injection of this reactive gas increases the pore water pH, promoting the dissolution of soil minerals; a subsequent re-establishment of natural conditions is believed to result in the recrystallization of those soil minerals and the co-precipitation of uranium phases.



Objective

- Characterization of the precipitates formed when the ammonia (NH_3) injection method, proposed for the Hanford vadose zone, is applied to synthetic pore water on a laboratory scale. This involves:
  - Identification of the uranium-bearing phases.
  - A study of the effect of pore water constitution on the phases produced.

Method

Sample Preparation & Analysis

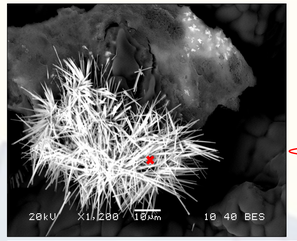
- Synthetic pore water solutions were prepared to mimic selected constituents of the pore water from the Hanford 200 Area.
  - Varying constituent concentrations
  - Observations led to modifications to increase relative uranium content
    - 200 ppm → 500 ppm U
    - Substituted sodium silicate for silicic acid
- Dried samples were analyzed by SEM-EDS and powder X-ray diffraction (XRD).
- A suspension in ethanol was prepared and analyzed by Transmission Electron Microscope (TEM) with Selective Area Electron Diffraction (SAED).

Technical Internship – Pacific Northwest National Laboratory

- Studied and applied geochemical modeling software (Visual Minteq & Geochemist's Workbench) for speciation & prediction of potential species formed.

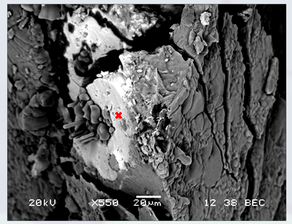
Results

SEM-EDS Analysis



Element	Wt%	At%
CK	07.78	15.31
NK	04.23	07.13
OK	37.08	54.76
NaK	17.69	18.18
AlK	00.18	00.16
SiK	00.62	00.52
ClK	00.12	00.08
UM	31.01	02.08
KK	01.11	00.67
CaK	00.20	00.12

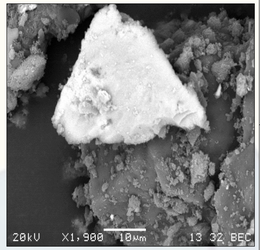
SEM image w/ EDS data for a 200 ppm uranium specimen

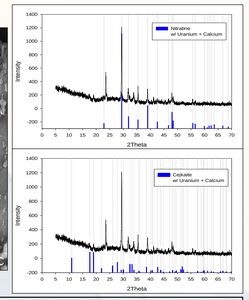


Element	Wt%	At%
CK	13.72	29.97
NK	15.08	28.24
NaK	15.77	18.00
AlK	02.14	02.08
SiK	17.26	16.12
ClK	00.27	00.20
UM	33.20	03.66
KK	02.57	01.72
CaK	00.00	00.00

SEM image w/ EDS data for an amplified 500 ppm uranium specimen

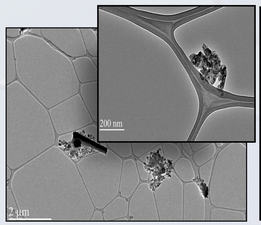
Diffraction Analysis





SEM image and XRD data for the pulverized sample

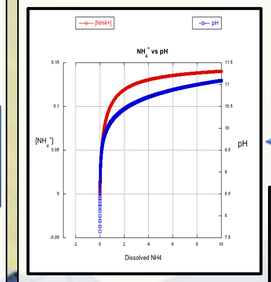
The comparison of resultant XRD patterns with reference patterns showed a match with nitratine ($NaNO_3$) [*top*] and a tentative match with cejkaite ($Na_4(UO_2)(CO_3)_3$) [*bottom*].



TEM & SAED data for the uranium bearing sample

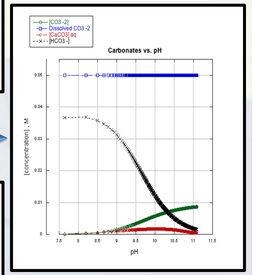
TEM/SAED analysis resulted in a discernible diffraction pattern consistent with a polycrystalline sample.

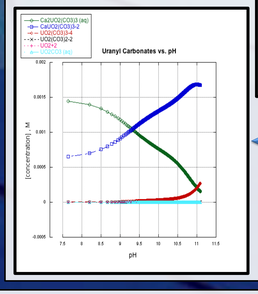
Geochemical Modeling



Graph showing the increase in system pH with increasing [NH_4^+] in solution.

Plot showing the change in carbonate species with increasing pH; altered using [NH_4^+] concentration.





Plot showing the change in uranyl-carbonate species with increasing pH; altered using [NH_4^+] concentration.

Discussion/Conclusions

SEM-EDS Analysis

- Scanning electron microscopy revealed areas of high average atomic weight which would be confirmed to be uranium-rich by energy dispersive spectroscopy analysis.
  - The samples prepared with a more than two-fold increase in uranium concentration did not show the crystal-like forms spotted in the lower [U] samples.
  - The samples prepared with silicic acid substituted in showed little to no uranium precipitation [*not shown*].

Diffraction Analysis

- Powder XRD analysis of the low [U] samples confirmed the presence of repeating crystalline patterns in the precipitate samples.
  - Nitratine ($NaNO_3$) showed a massive presence, potentially obscuring significant peaks in the low [U] samples.
    - Though it was not predicted, there was a tentative match for cejkaite ($Na_4(UO_2)(CO_3)_3$).
  - Elevated uranium samples showed none of the needle-like crystalline shapes [*diffraction data pending*].
- TEM – SAED confirmed the presence of a polycrystalline phase.
  - Data analysis is complex but a comparison of average d-spacings with those of reference minerals could further support a match with cejkaite.

Geochemical Modeling

- The system conditions were input into geochemical modeling software to predict the forms present throughout the reaction process.
  - The model was used to demonstrate that the pH of the system could be increased using [NH_4^+] in solution to better represent the system.
  - Using the [NH_4^+] increase, the changes in significant species with increasing pH were observed.

Future Work

- Repeat samples will be prepared and analyzed to bolster any potential identification.
  - Promising samples will be submitted to the PNNL's EMSL facility, which is better equipped to perform the required analyses.
- An expanded study on the impact of carbonate (CO_3^{2-}) on the phases produced.

Acknowledgements

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