

Characterization of U(VI)-Bearing Precipitates Produced by Ammonia Gas Injection Technology for Unsaturated Sediments – 16600

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ABSTRACT

The processing of irradiated fuel to extract plutonium for the nuclear arsenal has resulted in a legacy of uranium contamination in the vadose zone (VZ) of the Hanford 200 Area. This contamination is a potential source for groundwater contamination, posing a risk to receptors through water uptake from contaminated wells or discharges to surface water. The injection of reactive gases is an innovative technology being evaluated for reducing the mobility of radionuclide contaminants in the Hanford vadose zone. Ammonia (NH₃) gas in particular has been used to reduce uranium mobility in laboratory scale studies and is being evaluated for field scale application.

The sediment of the Hanford vadose zone is composed of a complex of mineral phases including quartz, feldspar, mica, and calcium carbonates. The silica content in the 200 Area subsurface markedly outweighs the majority of elements, with aluminum following closely. The injection of ammonia gas into the vadose zone is associated with an increase in pH conditions as the gas partitions into the pore water. The resulting alkaline conditions significantly increase the solubility of some aluminum and silicate-containing minerals within the system. As pH decreases to natural conditions, the aluminosilicate minerals will precipitate, potentially coating and sequestering the uranium contaminants. Although previous laboratory scale tests have shown decreased uranium mobility, there are many questions regarding the application of the remediation method to 200 Area vadose zone conditions. In particular, additional testing is required to understand the impact of various environmental factors on the formation of uranium mineral phases with the application of the NH₃ injection method.

In order to answer some of the unknowns regarding this remediation technology for the 200 Area vadose zone, an effort was made to characterize the uranium-bearing precipitates being formed with the injection of ammonia gas. Rather than a sediment-water system, a synthetic pore water solution was prepared using the ion concentrations relevant to the 200 Area vadose zone. These solutions were limited to select constituents believed to play a major role in the remediation process. The use of this carefully composed solution allows for the thorough evaluation of the contribution the variable components make to the formation of the solid analyte.

The characterization of solid samples was attempted using a host of complementary analytical techniques including scanning electron microscopy with energy dispersive

spectroscopy (SEM-EDS) and X-ray diffraction (XRD). Though characterization of the samples is ongoing, the data produced thus far has allowed for the imaging and X-ray spectroscopy of the solid uranium phases produced as well as a tentative identification of cejkaite ($\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$) as the major uranium mineral phase.

INTRODUCTION

Past methods of radioactive waste disposal at the DOE Hanford's 200 Area allowed waste discharges to retention trenches, basins and cribs from which uranium contaminated liquids would leech into the vadose zone (VZ). Over 200,000 kg of uranium is known to have been discharged into the Hanford subsurface [1]. This uncontrolled leakage created a potential source for future groundwater contamination. This investigation targets uranium contamination in the VZ of the 200 Area with the potential to discharge to the Colombia River via groundwater migration. Remediation methods for reducing the potential for contaminant mobility are currently being investigated for application to the Hanford subsurface. Injection of a reactive gas [i.e.: ammonia (NH_3)], is an innovative method aiming to reduce uranium mobility in the subsurface without the addition of liquid amendments which could cause undesired downward contaminant migration. The injection of ammonia gas in the vadose zone prompts the formation of NH_4OH , accompanied by an increase in pH, as the gas partitions into the pore water. The alkaline conditions can greatly enhance the solubility of most Si-containing minerals. A subsequent decrease in pH, caused by the re-establishment of system equilibrium, will result in uranium co-precipitation with the recrystallization of minerals.

This study investigates the mineralogical and morphological characteristics of precipitates formed by application of the proposed remediation method to a synthetic pore water (SPW) solution. Precipitate samples were prepared using a variety of SPW solutions based primarily on the major vadose zone constituents described in a prior study [2]. The concentrations of various pore water components were varied to evaluate their impact on the uranium phases formed. Though the environmental matrix being simulated was simplified for the study, sample analysis required multiple complementary techniques to come to a defensible conclusion. Techniques like X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) were used to determine, with reasonable certainty, the identity of the uranium-bearing solid phases.

The objective of this experiment is to support the evaluation of the ammonia gas injection remediation method as an *in situ* amendment for subsurface contamination. Though studies have been published regarding the use of gaseous remediation amendments using Hanford soil, the use of synthetic pore water as a controlled system stands to allow for investigation into the roles of individual components without the additional complications of testing environmental samples [3, 4]. The characterizing of the uranium phases being formed in the artificial system is essential for furthering the ongoing investigation. More specifically, the identification of the resultant uranium solids is required for additional analyses

concerning their stability under various conditions and to provide insight into the overall viability of the remediation strategy.

MATERIALS AND METHODS

The experimental approach to conduct these studies involved preparation of multiple sets of samples with and without Ca; containing the desired Si, Al, and HCO_3^- concentrations; and amended with the desired concentration of U(VI). Stock pore water solutions were prepared for each set using a combination of various salt solutions formulated such that the concentration of the primary components of interest (HCO_3^- , Al, and Si) would be within the desired ranges when combined. The desired final concentrations were based on the characterization of vadose zone sediments from borehole 299-E33-45 performed by Serne et al. (2008) [2] at the Hanford 200 Area. The concentrations of the primary constituents of interest in the synthetic pore waters are given in (TABLE 1).

TABLE I. Desired Concentrations of Primary Constituents

[Si]	[Al]	[HCO_3^-]	[Ca]	[U]
100 mM	5 mM	3 & 50 mM	0 & 5 mM	200 ppm

The initial set of samples was comprised of 4 synthetic pore water solutions, prepared identically across all samples with the exception of the two variables being evaluated, bicarbonate (HCO_3^-) and calcium (Ca^{2+}). To observe the impact that these variables had on the uranium phase produced with the application of the remediation method, synthetic pore water sample solutions were formulated to have a combination of high and low bicarbonate concentrations and without the presence of calcium (TABLE 2). The concentrations of silica and aluminum were kept consistent based on what was determined to be the optimal silica to aluminum ratio for the system.

TABLE II. Stock Solutions and Sample Mixtures – 200 ppm U

Stock Solution	Stock Solution Concentration (mM)	Synthetic Pore Water Concentrations (mM)			
		Low bicarbonate w/o calcium	Low bicarbonate w/ calcium	High bicarbonate w/o calcium	High bicarbonate w/ calcium
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	147.01	0	5	0	5
KHCO_3	400.00	3		50	
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	50	100			
$\text{Al}(\text{NO}_3)_3$	422.24	5			

The sample preparation process began with the preparation of concentrated salt solutions of KHCO_3 , Na_2SiO_3 , and $\text{Al}(\text{NO}_3)_3$, which were then combined in a 50-mL vial at the ratios required to achieve the desired final concentrations when made up to volume with deionized water. Initially, only two sample solutions were prepared for the two HCO_3^- concentrations being evaluated. These solutions were split before adding highly concentrated calcium chloride and uranyl nitrate solutions in the final step to avoid errant side product formations in the synthetic pore water. This relatively alkaline solution was then adjusted to a pH of 8, using concentrated nitric

acid, to bring the solution down to a pH that better mimics the natural conditions of the Hanford 200 Area vadose zone [3]. At this point, prior to the addition of the calcium and uranium components, the remediation method was applied by basifying the solution by sparging ammonia (NH₃) gas until the pH range of 11-12 was achieved. From there, 10-mL aliquots of the 50 mL stock were dispensed into 15-mL sample vials, one for each calcium concentration. Solutions were finished by adding CaCl₂ and UO₂(NO₃)₂ solutions. The mixture was allowed to reach equilibrium over the course of 2 weeks, a period which has been shown in prior sample preparations, to be a significant enough for precipitation to occur. The separated supernatant was then decanted and reserved for analysis via KPA while the solid was dried in an oven at 30°C for two weeks. This precipitate was retained for SEM-EDS and XRD analysis.

The second set of samples was modified based on the observations during the sample prep and analysis of the first. Most notably, the uranium content was increased to 500 ppm and only the high bicarbonate concentration was used. Additionally, the range of calcium concentrations tested was expanded to include 10 mM. The reasoning for these revisions will be detailed in the results section.

TABLE III. Stock Solutions and Sample Mixtures – 500 ppm U

Stock Solution	Stock Solution Concentration (mM)	Synthetic Pore Water Concentrations (mM)	
		50 mM bicarbonate w/o calcium	50 mM bicarbonate w/ calcium
CaCl ₂ ·2H ₂ O	2500.00	0	5 10
KHCO ₃	400.00	50	
Na ₂ SiO ₃ ·9H ₂ O	422.24	100	
Al(NO ₃) ₃	50.00	5	

Similar to the aforementioned batch of samples, the modified sample preparation methods began with the combination of concentrated stock solutions of KHCO₃, Al(NO₃)₃, and Na₂SiO₃·9H₂O in a 50-mL vial to form two stock solutions for the two bicarbonate concentrations. This synthetic pore water solution was adjusted to pH 8 using concentrated nitric acid and allowed to equilibrate. Once again, the remediation method was applied with the increasing of pH by sparging ammonia gas. Three 10-mL aliquots were isolated from each synthetic pore water solution to which highly concentrated CaCl₂ and UO₂(NO₃)₂ solutions were added via minimal volume to reach each of the desired final concentrations for the synthetic pore water solutions. The mixture was allowed two weeks to reach equilibrium before decanting the supernatant and drying the precipitate phase for analysis.

Scanning Electron Microscopy and Energy Dispersive Spectroscopy

Scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) were used to study the surface morphology and composition of the dried precipitates. This was done at the Florida Center for Analytical Electron Microscopy (FCAEM) located on the Florida International University Modesto A. Maidique Campus (MMC). The SEM system used was a JOEL-5910-LV with acceleration potentials ranging

from 10 to 20 kV. EDS analysis was produced using an EDAX Sapphire detector with UTW Window controlled through Genesis software. Any required gold coating was done with an SPI-Module Control and Sputter unit for 1-2 minutes to produce a thin layer of gold.

Small specimens were taken from each of the solid precipitates and mounted to aluminum studs with double-sided carbon tape. The specimen were coated with gold to enhance conductivity and analyzed in both standard and backscatter modes. The majority of analysis took place in backscatter electron capture mode, which is preferred for its property of distinguishing the differences in average atomic weight in an area. This was of particular use to this study for identifying areas of elevated uranium content.

Powder X-Ray Diffraction

In order to maximize resources, only the precipitate samples which showed the presence of potentially crystalline areas of high uranium content were chosen for X-ray diffraction analysis. Select samples were carefully ground into a fine powder using a mortar and pestle. Two method blanks, prepared identically to the experimental sample without the addition of uranium, were also ground and analyzed for comparison. The powdered samples were loaded into a custom plastic samples holder designed specifically for this study. Diffraction analysis was performed on the precipitate samples at 35 kV and 40 mA using a Bruker 5000D X-ray diffractometer. Diffraction patterns were obtained using a copper Cu K α radiation source ($\lambda=0.154056$ nm) with a tungsten filter over a 2-theta range from 5° to 60° with a 0.02° step size and 3s counter per step.

RESULTS AND DISCUSSION

The objective of SEM-EDS analysis was to identify areas of high uranium content and the morphology that it had taken with the application of the ammonia gas remediation method to a range of synthetic pore water solutions. Within the first sample set, precipitated from 200 ppm U(VI) in SPW solutions, the resulting data and images (not shown) for the low bicarbonate subset revealed no areas of concentrated uranium, regardless of the presence of calcium. Multiple specimen analyses from this subset showed neither the visual cues, like the bright areas expected of a sample containing a heavy metal, nor the quantitative EDS measurements to suggest a significant presence of uranium.

In contrast, the high bicarbonate precipitates showed areas of concentrated uranium formations in the samples prepared with and without calcium (Fig. 1). Primarily identified by the anticipated bright areas typical of regions with high average atomic numbers, the elevated presence of uranium was confirmed by EDS analysis.

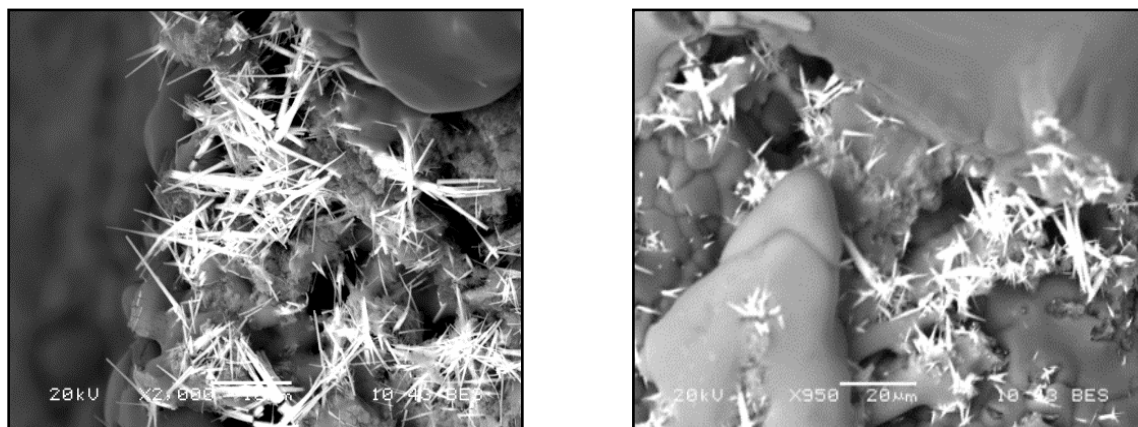


Fig. 1. Uranium bearing precipitates formed from calcium-free (left) and 5 mM calcium containing (right) 200 ppm uranium pore water solution

Morphologically, the structure of the uranium-rich phases pictured strongly suggests that the phase is a repeating crystalline structure, likely identifiable by diffraction. For this reason, powder XRD analysis was limited to samples from that first set which showed these seemingly crystalline structures and their associated blanks. Analysis produced diffraction patterns of well-defined peaks for all samples evaluated, confirming the presence of crystalline material. Several of the major peaks, including the most prominent at $2\theta \approx 29$, were present in all samples regardless of calcium, bicarbonate, or uranium content. The similarities in these patterns suggest the presence of a crystalline solid phase that is consistently present, despite the major differing variables.

Using *Match!* software for diffraction pattern identification, nitratine (NaNO_3) was recognized as the most likely major constituent of both the precipitate and blank samples. Considering the high concentrations of sodium and nitrates used in the synthetic pore water solutions, the formation of sodium nitrate salts is reasonable, though they should not precipitate under normal conditions. Direct comparisons of the sample diffraction patterns with the major peaks for nitratine show that the majority of major peaks align (Fig. 2) with the principal difference between the two patterns being the intensity of the peaks. The intensity of the most prominent peak in both patterns, $2\theta \approx 29$, peaks near 3500 and 1200 in the calcium-free and calcium-containing samples, respectively. In the calcium-free sample, the clear disparities occur at peaks present in the sample at $2\theta \approx 26.5$ & 47, though the relatively high background early in the pattern is believed to obscure other potentially significant peaks. Further comparison of the samples prepared with and without calcium shows peaks of relatively low intensity, which do not have corresponding peaks on the nitratine pattern (i.e., $2\theta \approx 23.5, 32.5, 34, \& 41$). If the nitratine identification is accurate, these unpaired peaks could signify the presence of a second crystalline phase. More specifically, they may represent the uranium-containing phase observed in prior SEM/EDS evaluation.

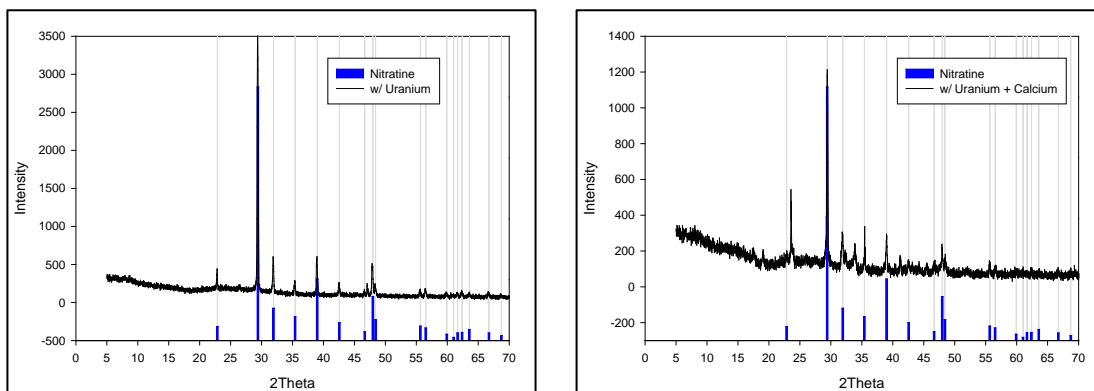


Fig. 2. Comparison of the diffraction patterns of the calcium-free (left) and 5 mM calcium (right) precipitate samples with the pattern for nitratine (NaNO_3)

The comparison of the sample diffraction patterns to reference patterns for species predicted by geochemical modeling software yielded no obvious matches. Though it was never predicted in modeling, cejkaite ($\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$) has emerged as a potential identity of the uranium-bearing phase that was observed in scanning electron micrographs. The comparison of the diffraction patterns revealed that two of the three most prominent peaks ($2\theta \approx 17.5$ & 19) appear to have a corresponding match in the experimental diffraction patterns for the calcium-containing sample (Fig. 3). A match for the third largest peak ($2\theta \approx 11$) could not be conclusively identified though it is believed to have been concealed by the noisy background. It is possible that the difficulty in identification comes from the low yield of the uranium phase, relative to the bulk of the sample. The comparison of the calcium-free sample to the cejkaite XRD pattern showed no apparent peaks at the same 2θ values. If it is assumed that cejkaite is not formed in this sample, the higher peak intensities relative to the calcium-containing sample could signify an indirect relationship between inclusion of calcium and the formation of cejkaite.

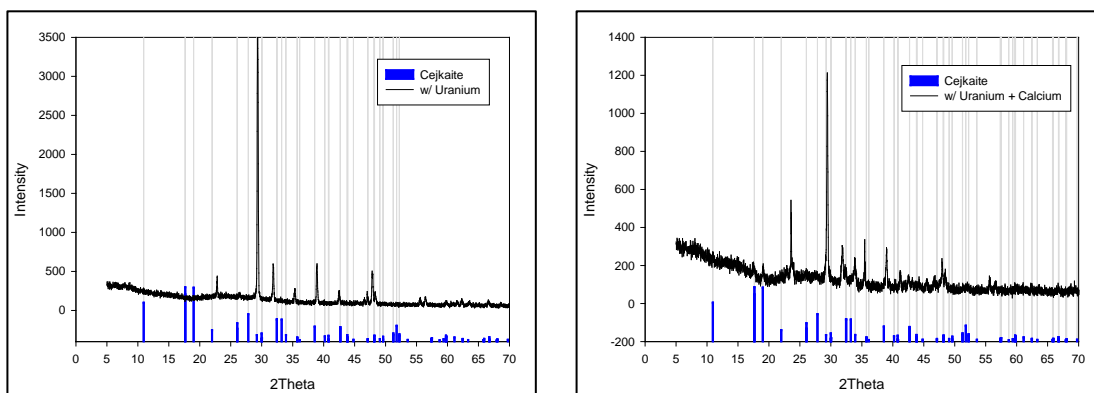
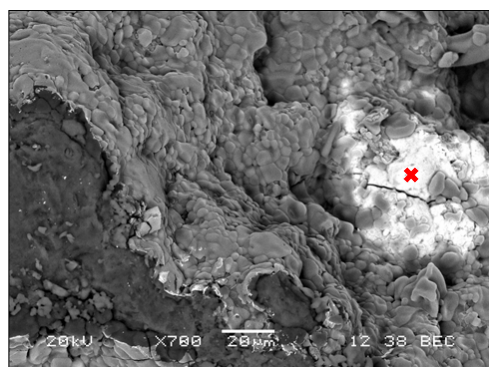


Fig. 3. Comparison of the diffraction patterns of the calcium free and 5 mM calcium-containing precipitate samples with the pattern for Cejkaite ($\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$)

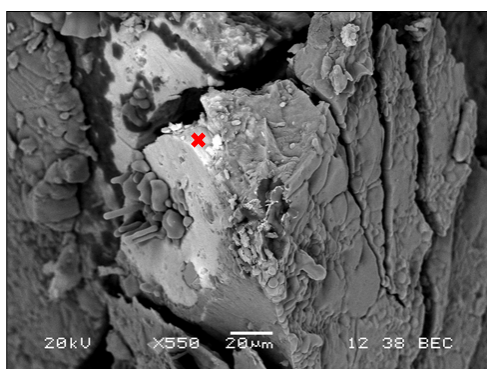
The preparation methods for the second set of samples were modified with the intention of minimizing the impact of less pertinent formations, such as nitratine, on solid phase analysis. This was done by more than doubling the uranium used in

sample preparation, from 200 ppm to 500 ppm, to increase the yield of the uranium-bearing analyte. The SEM images and EDS data of the resultant precipitates was different from what was anticipated (Fig. 4 & Fig. 5).



Element	Wt%	At%
C K _α	11.07	26.67
N K _α	12.19	25.18
Na K _α	16.99	21.39
Al K _α	01.39	1.49
Si K _α	18.62	19.18
U M _α	37.73	04.59
K K _α	02.02	01.49

Fig. 4. Uranium phases on the surface of samples prepared using 50 mM of bicarbonate and 500 ppm U (no calcium)



Element	Wt%	At%
C K _α	13.72	29.97
N K _α	15.08	28.24
Na K _α	15.77	18.00
Al K _α	02.14	02.08
Si K _α	17.26	16.12
Cl K _α	00.27	00.20
U M _α	33.20	03.66
K K _α	02.57	01.72
Ca K _α	00.00	00.00

Fig. 5. Uranium phases on the surface of samples prepared using 50 mM of bicarbonate, 5 mM of Ca, and 500 ppm U

Unexpectedly, the elevated uranium samples showed no sign of the crystalline structures targeted and expected based on the observations of the first set. The possible reason for the difference is limited to either the increase in uranium or a change, intentional or otherwise, in the sample preparation procedures. Though no obvious crystallinity was observed, diffraction analysis could be used to definitively determine if a discernable crystal pattern is present. This XRD data is not yet available for publication.

CONCLUSIONS

The SEM-EDS analysis of the first set of samples, prepared with 200 ppm of uranium, suggested that the low bicarbonate synthetic pore water solutions would form no crystalline uranium phases under the experimental conditions. The lack of any significant presence of uranium under the microscope precluded the subset of samples from further analysis by X-ray diffraction. To the contrary, the high bicarbonate subset saw widespread crystal-shaped uranium phases. The promising observations made on the surface of the calcium containing samples yielded a

positive identification of nitratine (NaNO_3) and a tentative identification of cejkaite ($\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$), which were not phases predicted during modeling. Geochemical modeling software has yet to support the precipitation of cejkaite under the experimental conditions.

Analysis of the second set of precipitates, formed using the elevated 500 ppm of uranium, is incomplete. It was thought that increasing the concentration of uranium injected into the synthetic pore water solution would increase the yield of the uranium-bearing analyte, facilitating diffraction analysis. Though this set of samples showed none of the obviously crystalline structures observed in the initial 200 ppm samples, areas of concentrated uranium phases were identified by SEM and EDS. This change in uranium phase structure is likely due to either the dramatic increase in uranium concentration or a misstep in sample preparation, but further evaluation is required to draw a conclusion. In particular, repeated sample preparation and powder X-ray diffraction analysis are ongoing. Alternatively, transmission electron microscopy is being investigated for the ability to do selective area electron diffraction.

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