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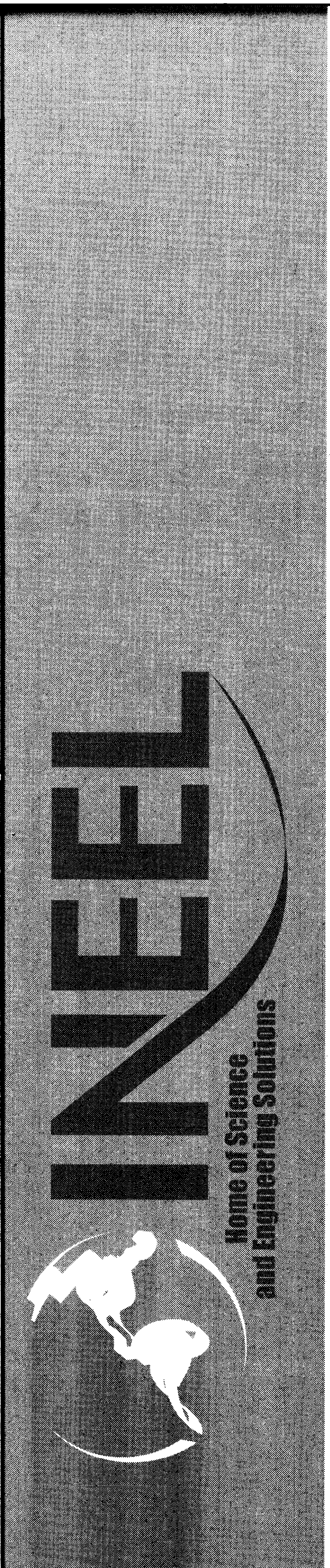
Rev. 0

Actinide Solubility Experiments in INEEL Perched Simulant Solution Final Report

November 2000



Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC

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Actinide Solubility Experiments in INEEL Perched Simulant Solution Final Report

Gregory R. Choppin

Department of Chemistry
Florida State University
Tallahassee, Florida

November 2000

Idaho National Engineering and Environmental Laboratory
Environmental Restoration Project
Idaho Falls, Idaho 83415

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Actinide Solubility Experiments in INEEL Perched Simulant Solution

Final Report

Principal Investigator: Gregory R. Choppin

Department of Chemistry

Florida State University

Tallahassee, FL 32306-4390

Signature: Gregory R. Choppin 11/1/00

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Final Report

Actinide Solubility Experiments in INEEL Perched Simulant Solution

Summary of Research

Subsurface sampling at the Idaho National Engineering and Environmental Laboratory has raised concerns that actinides may have migrated to the interbeds. Although some mechanisms have previously been proposed to explain this possible transport, validation of such mechanisms or a thorough analysis of the available data are lacking. Research programs are underway, and are being planned, to explain and understand the behavior of actinides in the subsurface.

Solubility studies were performed on samples of uranium oxide powder in simulated water at pH8. The studies were the batch type in duplicate sample containers at room temperature and the uranium was allowed to attain equilibrium from dissolution of a fraction of a sample of U_3O_8. The aqueous phase simulated INEEL perched water.

The batch solutions were sampled after one day, 3 days, each week for the first month, and biweekly after the first month. After sampling the batch solution the pH were readjusted to approximately 8.0 with either concentrated NaOH or HCl. The samples were centrifuged for 5 minutes and filtered through a 20 micron acetate filter to remove any colloidal particles. The samples were acidified (5 ml of 1 M HCl) in order to keep the U from hydrolyzing before analysis. The experiments were terminated once steady state has been observed.

Introduction

The possibility of container compromise within nuclear waste repositories makes it necessary to investigate potential interactions between the repository environment and the materials purposed for storage. Dissolution of the repository contents into the groundwater could result in migration of the radionuclides from the repository. This possible scenario necessitates the investigation of the waste materials solubility in groundwater.

The goal of this research was to determine the solubility of mixed uranium oxides in synthetic groundwater of the Snake River plain, under oxic and anoxic conditions at constant pH, in the presence and absence of humic acid. The values for the uranium solubility obtained experimentally and by calculations were compared.

Experimental

Anoxic experiments were performed in a glovebox containing a water saturated, dinitrogen atmosphere at ambient temperature (20±2°C). All anoxic pH and Eh measurements as well as sampling and sample preparation were performed within the glovebox. Oxic experiments were performed on a bench top, exposed to ambient conditions.

Synthetic groundwater resembling the Snake River Aquifer was used for all experiments (see table below). Mixed uranium oxides were used as the source of uranium. The humic acid used had a 4.3% ash value and when present in solution, its concentration was 1 ppm.

Fluorinated, high-density polyethylene (HDPE) 2 L bottles stirred with a teflon coated magnetic stir bar, were filled with 1.80 L of the synthetic groundwater, to which approximately 0.330 g of uranium oxide was added. The pH was measured with a semi-micro glass combination electrode and adjusted to a value of 8.00. The Eh measurements were performed using a platinum/silver-silver chloride combination electrode and their accuracy was checked using "Zobell's" solution.

Sampling procedures

Stirring was ceased approximately two hours before sampling. A bottle was sampled by withdrawing approximately 2 mL of solution with a 5 mL disposable syringe. The Eh and pH were measured. Sample aliquots were filtered through a 0.22 μm hydrophilic nylon syringe filter into a silanized glass vial. Using a calibrated pipette, 1.00 mL of a 1.00 M ultra pure nitric acid solution was placed into a 5 mL glass vial, followed by the addition of 1.00 mL of the filtered solution. The vial was stoppered and stored until measured for uranium content. Duplicate samples from each bottle were taken. The pH was adjusted to 8.00.

Uranium concentrations were measured on a high-resolution, magnetic-sector ICP-MS instrument.

Results

The solubility experiment was performed for a total of 180 days. After a period of 104 days all samples reached equilibrium. A plot of uranium concentration in solution versus time is given in the figure below, with error bars set at 2σ (95.5% confidence). In the absence of humics, the solubility of uranium was 0.098±0.002 g/L in anoxic conditions and 0.114±0.002 g/L in oxic conditions. In the presence of humics, the solubility of uranium was 0.094±0.003 g/L in anoxic conditions and 0.112±0.001 g/L in oxic conditions.

Uranium solubility calculations were performed using published data for uranium stability constants and solubility products. Results indicated that in the absence of humic acid, the oxic uranium solubility should be 0.117 g/L, which is very close to the experimental value. Calculations indicated that $CaUO_4$ controls the overall uranium solubility.

Eh reached a stable value of +138±4 mV for anoxic samples and +220±5 mV for oxic samples. The pH of oxic solutions between samplings increased to approximately 8.2, while for anoxic solutions it remained around 8.0. BET analysis showed that oxides had a surface area of 3.561±0.003 m^2/g. Sieving resulted in approximately 33% of the oxides being less than 170 mesh. XRD analysis indicated that a mixture of uranium oxides were present in the sample.

The results of these experiments imply the possibility of uranium oxides leaching into groundwater. Uranium entering the groundwater from a mixed oxide form is not a slow process on a geological time scale. The presence of humic acid at 1ppm levels does not influence the uranium concentration as significantly as the presence of oxic conditions. Uranium solubility is less under anoxic conditions than under oxic conditions. The difference between oxic and anoxic solubility though does not imply that anoxic solubility should be ignored. The solubility calculations support the experimental findings of this research.

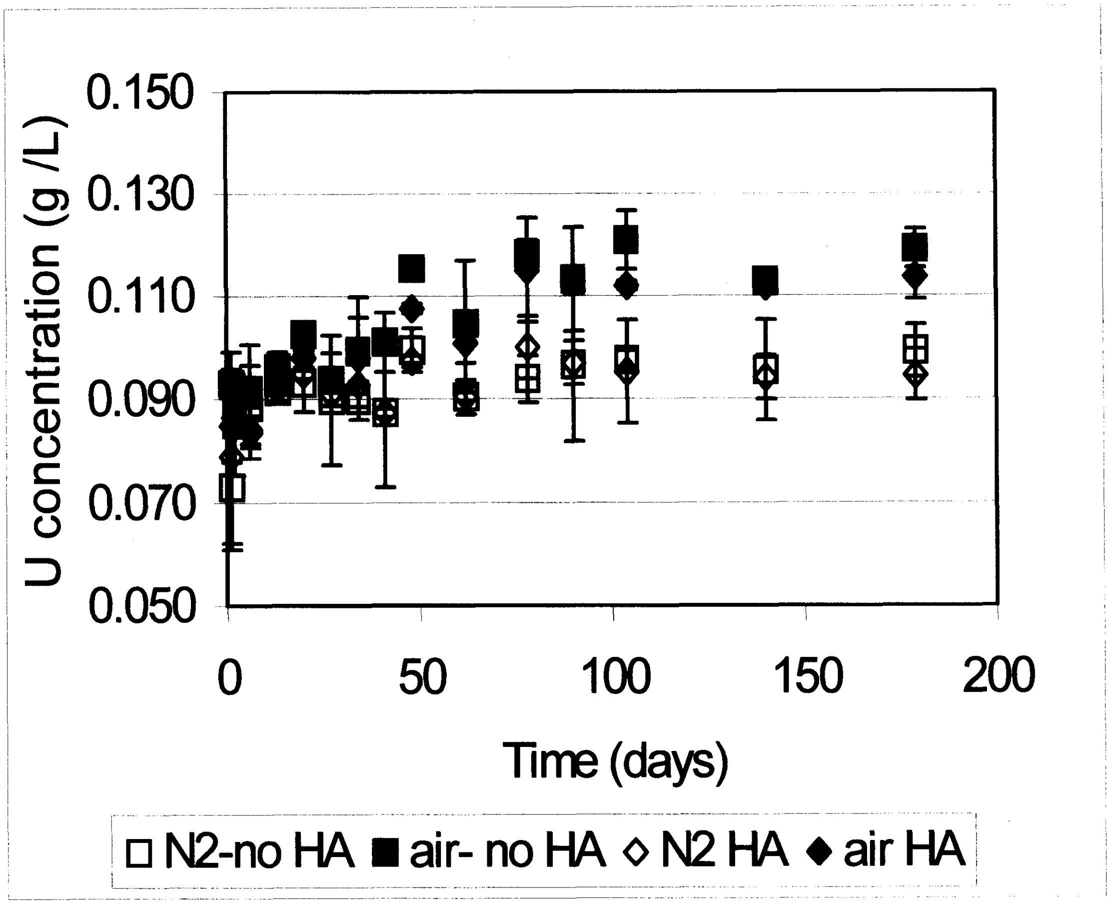
Publication

A paper (essentially the same as this Final Report) was presented at the Plutonium Futures Conference, Santa Fe, N.M., July 2000. It is published in the conference proceedings by the American Institute of Physics.

Synthetic groundwater formulation:

Sodium	$2.48\ 10^{-2}$ M
Magnesium	$7.00\ 10^{-4}$ M
Calcium	$2.50\ 10^{-4}$ M
Potassium	$2.56\ 10^{-4}$ M
Silicon	$3.57\ 10^{-4}$ M
Carbonate	$1.23\ 10^{-2}$ M
Sulfate	$3.65\ 10^{-3}$ M
Chloride	$6.21\ 10^{-3}$ M
Fluoride	$1.05\ 10^{-3}$ M
Nitrate	$1.26\ 10^{-4}$ M

Uranium concentration in solution vs. time:



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David N. Kurk, Gregory R. Choppin, and James D. Navratil

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GREGORY R. CHOPPIN   David N. Kurk

Name (print)

Gregory R. Choppin   8 March 2000

Signature   *Date*

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K. K. S. Pillay
K. C. Kim
Los Alamos National Laboratory,
Los Alamos, New Mexico

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Interactions of mixed uranium oxides with synthetic groundwater and humic acid using batch methods; Solubility determinations, experimentally and calculated

David N. Kurk[1], Gregory R. Choppin*,[1], and James D. Navratil[2,3]

1. Florida State University, Chemistry Department, Tallahassee, FL 32306-4390, USA

2. Bechtel BWXT Idaho, LLC, INEEL, P.O. 1625, Idaho Falls, ID 83415-3915, USA

3. currently located at Environmental Engineering and Science, Clemson University-Clemson Research Park, Anderson, SC 29625-6510 USA