

Solubility of Uranyl Phosphates in Nanocluster forming Environments

Final Research Report

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## **Abstract**

The fate and transport of uranium in the environment is an increasingly important issue as current plans of action are created for geologic repositories. The solubility of uranium bearing materials is of particular concern for industrial-scale spent fuel reprocessing. Uranium-based nuclear fuel dissolution in water can also be a route for uranium release into the environment. Uranyl phosphates may be important secondary mineral phases in various settings involving radionuclide contamination. Uranyl phosphates are of particular importance due to their insolubility in water, only releasing about 50-100 ppm U. Preliminary studies have shown autunite, a calcium uranyl phosphate, releases  $\sim 7000$  ppm U (as measured in water) when exposed to an alkaline environment containing peroxide. Along with autunite, other uranyl phosphates display similar qualities where the uranium release into solution increases as pH and peroxide concentration increase. At these conditions, the uranium content in the form of uranyl peroxide nanoclusters. This study investigated the role and effect additional cations have on uranium release from uranyl phosphates under nanocluster forming environments. The solubility was measured for three differing cations: calcium (autunite), copper (metatorbernite), and potassium (meta-ankoleite) uranyl phosphates. In order to understand uranium release under such conditions, peroxide concentration and pH levels were manipulated to favor nanocluster formation. Nanocluster formation was characterized by Electrospray Ionization-Mass Spectrometry (ESI-MS), and the concentration of uranium was measured at the end of the experiment using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

## **Background**

The goal of this experiment is to investigate the role of cations on the solubility of uranyl phosphates in nanocluster forming conditions. uranyl phosphates are found in the secondary mineral phases in spent nuclear fuel (SNF). They are mostly insoluble in water, only releasing about 50-100 ppm U in an aqueous solution. The current technology dictating how spent nuclear fuel is dealt with is PUREX. This process takes the SNF and dissolves the solution in boiling nitric acid. Not only is this not an environmentally conscience method, but also can be very costly in terms of temperature constrains and creating a safe environment to carry out this potentially dangerous procedure.

Previous unpublished studies have shown uranyl phosphate nanoclusters able to release about 7000 ppm, comparable to PUREX process, using an economical and environmental friendly mythology. The uranium in solution is in the form of uranyl peroxide cage clusters. Uranyl peroxide cage clusters readily assemble where counterions (such as Na and K), uranyl ions, and hydrogen peroxide are present in solution. These

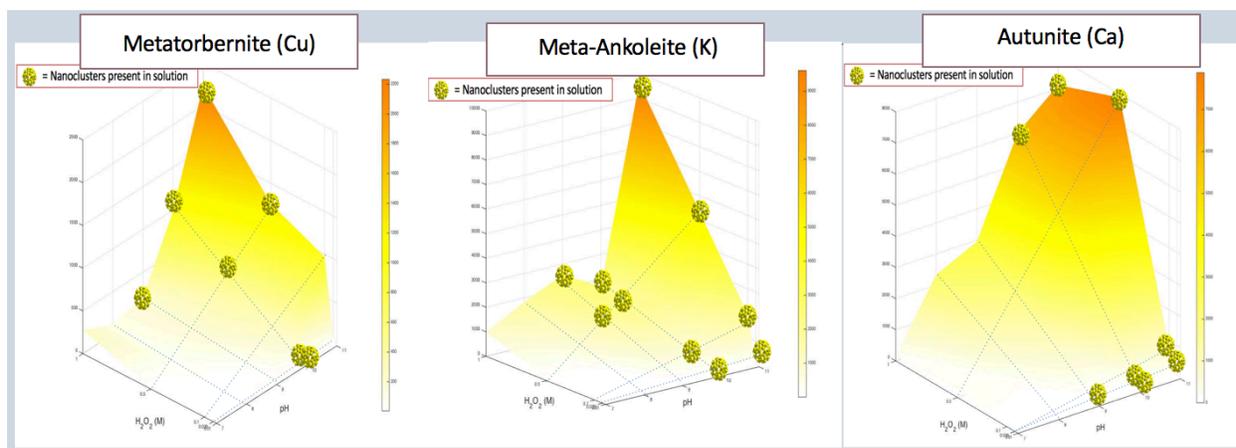
cage clusters are able to form and persist in aqueous environments, and behave uniquely compared to their ionic counterparts.

## Procedure and Instrumentation

The major tasks will be first synthesizing uranyl phosphate minerals through slow liquid diffusion techniques. Then, the minerals will be harvested and checked for purity with powder X-ray diffraction (PXRD). The Introduction of different phases to environments in pH range (7-11) and peroxide range (0.01M-1.0M) for 7 days will assist in the analysis of increased uranium release. Using ESI-MS (electrospray ionization-mass spectrometry), we will be able to see possible nanocluster formations and ICP-OES (inductively coupled plasma-optical emission spectroscopy) to determine amount of uranium released from mineral phases. Other instruments used to develop the project was a density meter that was used to verify the concentration of peroxide being used in all experiments. Powder-XRD (X-ray diffraction) was used to monitor the form and phase of minerals when the experiment concluded. Powder-XRD was also used to check the purity of minerals synthesized.

## Results and Discussion

After the 7-day experiment was concluded, ICP-OES data was collected for all samples and a graph display was created. This was done for all three minerals.



**Figure 1: Metatorbernite, Meta-Ankoleite, and Autunite on ICP-OES produced graph with nanocluster locations plotted using ESI-MS data. (X-axis: H<sub>2</sub>O<sub>2</sub>, Y-axis: pH, Z-axis: U release**

In figure 1, the graph was produced from ICP-OES data in order to reveal the amount of uranium that was released at the end of the experiment. The nanocluster formation points were plotted using data collected

using ESI-MS data in order to accurately pinpoint where nanoclusters were present. It is clear that as pH increase and peroxide concentration increase that uranium release also increases. Metatorbernite, Meta-Ankoleite and Autunite reached a maximum release of 2200 ppm U, 9000 ppm U, and 7100 ppm U, respectively. The type of cation used to develop the uranyl phosphate nanoclusters is important for uranium release and overall solubility. Controls were also used in this experiment in order to verify that without pH adjustment or addition of peroxide in any concentration did not lead to the formation of nanoclusters.

### **Future Research**

Through this experiment, it became clear that not only were uranyl phosphates important in recovery of uranium from spent nuclear fuel, but also that the cation used also made a significant difference in the amount of uranium that was recovered. Therefore, for future work, other cation will be used to further test this theory and find the optimal conditions of uranium release and create a more economic procedure. Other uranyl phosphates that can be found in SNF and replicated in the lab are saleeite, a magnesium cation, uranocircite, a barium cation, and bassetite, an iron cation. Another important experiment to conduct would be to see the effect of the base used to pH adjust the experiment on uranium release. For this experiment, tetraethylammonia hydroxide was used but tetramethylammonia hydroxide, lithium hydroxide, and potassium hydroxide will be tested in the future.