U_3O_8 AND AMORPHOUS $UO_2(OH)_2$ SOLUBILITY AT ELEVATED TEMPERATURE IN SODIUM CHLORIDE BRINE

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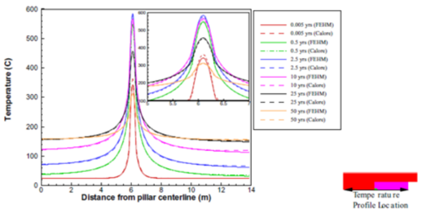
BACKGROUND

The permanent disposal of defense high-level nuclear waste or spent fuel in a salt repository would lead to elevated temperatures. It is important, by analogy with the WIPP safety case, to know the concentration of mobile actinide species as a function of temperature to account for actinide release in the event of low-probability human intrusion scenarios. An understanding of uranium speciation and solubility, especially in the case of spent fuel, is a key to predicting wasteform behavior should brine inundation occur.

The predicted repository-scale increase in temperature is dependent on the final repository design and heat loading but is typically estimated to be ~ 40-70°C for defense high-level waste and as high as ~130-160°C for spent fuel [see Figure below]. These temperatures will impact water movement and availability within the host rock prior to inundation, but will also lead to a heating of the brine introduced into the repository that will interact with the waste at elevated temperature.

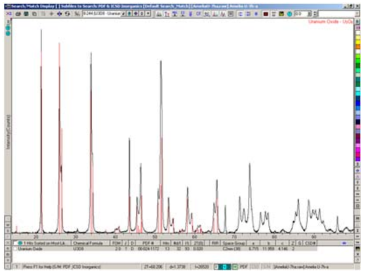
Herein we report progress to date on an undergraduate/graduate student project to investigate the effect of temperature and pH on the time evolution of uranium solubility and phase transition. Two uranium solid phases were used: crystalline U_3O_8 and amorphous uranyl hydroxide precipitate. The overall research strategy was to use the phase transition of the crystalline uranium oxide phase to the amorphous phase as an indicator of rate of reaction as the temperature is varied and link this to the observed uranium speciation and solubility. Experimental results for 30 and 60°C in 5 M sodium chloride are reported but it is planned to extend this to higher temperatures to cover the full temperature range for the HLW/SF repository case. The working hypothesis for this research is that phase transitions will drive aqueous uranium concentration/solubility and will evolve through an amorphous phase with the development of increased crystallinity at long times and higher temperature.



Temperature vs. Distance through the center line and perpendicular to the waste package reported in *3-D Thermal Analyses of High-Level Waste Emplaced in a Generic Salt Repository* [Clayton & Gable 2009].

SYNTHESIS AND CHARACTERIZATION OF THE URANIUM(VI) SOLID PHASE

Several U_3O_8 preparation methods were evaluated. In the end, U_3O_8 the was prepared by direct calcination of $UO_2(NO_3)_2{*}6H_2O$ [S.M. Thein, and P.J. Bereolos, "Thermal Stabilization of $^{233}UO_2$, $^{233}UO_3$, and $^{233}U_3O_8$", ORNL/TM-2000/82]. This was done by heating stepwise in a furnace to 750°C. This led to the formation of crystalline U_3O_8 (see Figure 1) that was confirmed by XRD (Bruker D8 Advance XRD with LynxEye detector). Uranium (VI) hydroxide was prepared by the precipitation of dissolved uranyl from 3 M NaCl brine solution at pH ~ 6 using PIPES to buffer/control the pH. For the experiments performed, quantitative XRD analysis was used to track phase evolution; ICP-MS (Agilent 7500ce ICP-MS) was used to analyze for uranium and verify brine composition; pH was measured using a Ross combination electrode and corrected for ionic strength and dissolved carbonate concentration was determined by GC analysis (Bruker 430 GC configured with a CO_2-methane conversion reaction cell and FID detector) of the gas phase for carbon dioxide following acidification of the brine samples



XRD results from the direct synthesis of U_3O_8 from $UO_2(NO_3)_2{*}6H_2O$.
Library pattern for U_3O_8 in red.

U_3O_8 Powder Synthesized by calcining $UO_2(NO_3)_2{*}6H_2O$

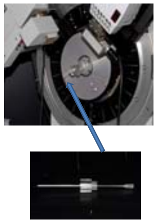
Dried uranium (VI) hydroxide

QUANTITATIVE AND CAPILLARY XRD ANALYSIS

The ability to accurately determine the relative percentages of phases within solid-state samples was examined using a simple halite/natrite ($NaCl/Na_2CO_3$) mix that was nominally and compared to the corundum reference at three points: ~25/75, ~50/50 and ~75/25% ratios. The MDI Jade program was used as a whole pattern fitting routine to produce satisfactory results with modest effort. The primary requirement is that a standard (the NIST 1976 corundum plate) is acquired under the same exact conditions as the unknown. The results of the fits are shown in the Table below.

Additionally, a capillary sample approach was developed and implemented (see Figures to the right). This worked well and allowed the use of small sample sizes, however, the ability to be quantitative was lost.

Comparison of actual vs. measured phase % for halite/natrite mixture				
Phase	(actual)%		(fit)%	
	Halite	Natrite	Halite	Natrite
Phase %	74.8	25.2	76.3	23.7
	49.6	50.4	51.0	49.0
	25.2	74.8	22.4	77.6

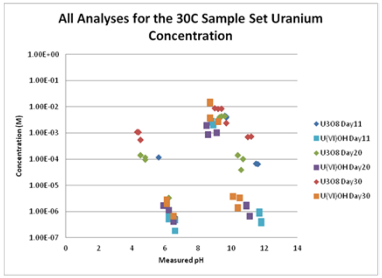


Capillary XRD Analysis

URANIUM SOLUBILITY STUDIES

EXPERIMENTAL APPROACH

- 5 M NaCl brine under oxic conditions
- PP bottles that were pre-equilibrated at temperature for a month
- 25 mM carbonate added as sodium carbonate – this was sustained at 20 mM for pH 9,12 but reduced to 6 mM at pH ~6 throughout the experiment
- Triplicate samples.
- All aqueous sampling was filtered immediately with 20 nm filters then analyzed by ICP-MS
- Solids were cooled and preserved at room T prior to XRD analysis

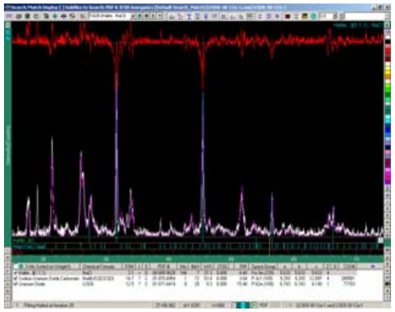


Initial Solution Trends

Uranium Phase Evolution with Time Based on Visual Evidence#				
Time	30 °C		60 °C	
	Uranyl Hydroxide	U_3O_8 Crystalline	Uranyl Hydroxide	U_3O_8 Crystalline
1 week	Yellow precipitate	Black solid	Yellow precipitate	Black solid
3 weeks	No change	No change	No change	Mixed yellow-black noted at pH ~ 9 and 12
3 months	No change	No change	No change	No change at pH ~ 6, complete conversion to yellow-orange phase noted
8 months	No change at pH 6 and 9, orange-yellow at pH ~ 12	Mixed yellowish dark/black precipitate at pH 6, 9. Mostly black solid at pH ~ 12	~ No change	Slightly yellow/mostly dark phase mixture at pH ~6. Orange/yellow precipitate at pH ~ 9 and 12
Final (~ 1 Year)	~ no change from 8 months	~ no change from 8 months	~ No change	Slightly yellow/mostly dark phase mixture at pH ~6. Orange phase at pH ~9 that gets more orange at pH ~ 12
# - at 90 °C complete conversion to an orange-colored (amorphous) phase noted in less than one week for oxide phase – these experiments were discontinued.				

MATRIX FOR THE URANIUM SOLUBILITY STUDIES						
	Uranium Oxide (U_3O_8)			Uranium (VI) Hydroxide		
pH Value	Temp = 30°C	Temp=60° C	Temp=90° C	Temp = 30°C	Temp=60°C	Temp=90°C
~6	U_3O_8-30-6	U_3O_8-60-6	U_3O_8-90-6	U(VI)OH-30-6	U(VI)OH-60-6	U(VI)OH-90-6
~9	U_3O_8-30-9	U_3O_8-60-6	U_3O_8-90-9	U(VI)OH-30-9	U(VI)OH-60-9	U(VI)OH-90-9
~12	U_3O_8-30-12	U_3O_8-60-12	U_3O_8-90-12	U(VI)OH-30-12	U(VI)OH-60-12	U(VI)OH-90-12

*Final Uranium Concentrations (M) and pC_{H+}			
Experiment (Starting Phase and nominal pH)		30 °C	60 °C
U_3O_8 Crystalline Solid	6	$pC_{H+} = 5.0$, $[U] = 3.6 \times 10^{-3}$	$pC_{H+} = 4.8$, $[U] = 4.9 \times 10^{-4}$
	9	$pC_{H+} = 9.4$, $[U] = 1.5 \times 10^{-3}$	$pC_{H+} = 9.3$, $[U] = 1.9 \times 10^{-4}$
	12	$pC_{H+} = 10.7$, $[U] = 2.7 \times 10^{-4}$	$pC_{H+} = 10.6$, $[U] = 1.4 \times 10^{-3}$
Uranyl Hydroxide Precipitate	6	$pC_{H+} = 7.1$ $[U] = 8.1 \times 10^{-7}$	$pC_{H+} = 6.5$, $[U] = 1.9 \times 10^{-5}$
	9	$pC_{H+} = 9.7$, $[U] = 1.6 \times 10^{-3}$	$pC_{H+} = 10.0$, $[U] = 1.9 \times 10^{-4}$
	12	$pC_{H+} = 11.7$, $[U] = 3.1 \times 10^{-5}$	$pC_{H+} = 10.8$, $[U] = 6.5 \times 10^{-5}$
*pC_{H+} measure with a Ross combination electrode and corrected for I~ 5 M, concentration data based on ICP=MS analysis after 20 nm (100K) filtration			



CAPILLARY XRD ANALYSIS OF SOLIDS

The majority of solids recovered after extended reaction in solution at various temperatures and pH values yielded amorphous patterns. One exception to this is the 30°C case at pH = 12. The fit to the overall pattern yielded hits on halite (i.e., the brine solution), the starting U_3O_8 material and a resulting sodium uranium oxide carbonate species, $Na(UO_2(CO_3)_3)$. Further work is needed to general more solids in the other cases to yield enough material to obtain a usable signal to noise ratio in the XRD pattern.

CONCLUSIONS AND OBSERVATIONS:

Although this is very much a work in progress, the overall approach is qualitatively validated. Significantly enhanced rates of phase conversion are noted even with relatively small changes in temperature. This can be used to provide insight into the effects of temperature on the long-term stability and rate towards equilibrium in complex systems. This however does not immediately lead to "equilibrium" uranium concentrations and these remains largely dependent on the original solid phase present. This is however solved by longer times and higher temperature (as expected) and crystalline phase are appearing in some cases at long times. Future efforts are to increase the extent of quantitative XRD analysis and extend this approach to higher temperature.