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U.S. Nuclear Regulatory Commission
ATTN: Mrs. Deborah A. DeMarco
Two White Flint North
11545 Rockville Pike
Mail Stop T8A23
Washington, DC 20555

Subject: Programmatic Review of Poster

Dear Mrs. DeMarco:

The enclosed poster is being submitted for programmatic review. This poster will be submitted for presentation at the 8th International Conference on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere Migration '01, to be held September 16–21, 2001, in Bregenz, Austria. The title of this poster is:

"The Solubility of Uranophane in $CaCl_2$ and SiO_2(aq) Test Solutions"
by James Prikryl and William Murphy

This poster is a product of the CNWRA and does not necessarily reflect the view(s) or regulatory position of the NRC.

Please advise me of the results of your programmatic review. Your cooperation in this matter is appreciated.

Sincerely,

Budhi Sagar
Technical Director

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Enclosure

cc:	J. Linehan	J. Bradbury	J. Prikryl
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THE SOLUBILITY OF URANOPHANE IN $CaCl_2$ AND SiO_2(aq) TEST SOLUTIONS

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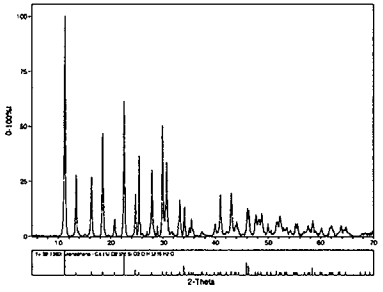
Introduction

Studies of uranium (U) deposits that are natural analogs to the proposed high-level nuclear waste repository at Yucca Mountain, Nevada (e.g., deposits in the Peña Blanca Uranium District of Chihuahua, Mexico) indicate that the calcium uranyl silicate, uranophane [$Ca(UO_2)_2Si_2O_7 \cdot 6H_2O$] is the end product of U mineralization hosted by siliceous volcanic rocks [1]. Similarly, long-term leaching studies of synthetic UO_2 and spent UO_2 fuel designed to mimic conditions in a Yucca Mountain repository indicate that uranophane is an end product of the alteration of spent fuel [2,3]. Natural uranophane has been noted to incorporate Th [4]. Therefore, uranophane that is secondary after spent fuel could incorporate part of the nuclear waste inventory and control its release from the engineered barrier system. Predictive modeling of uranophane formation and dissolution requires reliable thermodynamic data for uranyl minerals. In this study, the solubility of uranophane under oxidizing conditions was studied by reacting uranophane with Ca- and Si-rich solutions calculated to bracket uranophane solubility. Natural uranophane samples are typically of insufficient quantity and purity for use in solubility experiments. Thus, experiments were performed using synthesized uranophane.

SEM photomicrograph of synthesized uranophane.



X-ray diffraction pattern of synthesized uranophane compared to a reference pattern for uranophane taken from the ICDD database.

Experimental

Uranophane Synthesis and Characterization

Uranophane was synthesized based on the method of Cesbron et al. [5] using reagent grade uranyl acetate, sodium metasilicate, and calcium acetate. About 105 g of the reagents in the stoichiometric ratio Ca:U:Si = 1:2:2 were reacted with 1,350 g of deionized, degassed water (with pH lowered to about 1.0 by addition of HCl) in a teflon-lined stainless steel reaction vessel. The reaction was allowed to proceed for 10 days at 150 °C. Using measured analytical contents obtained by ICP-MS, stoichiometric coefficents for Ca:U:Si in the synthesized uranophane were calculated to be 0.99(±0.01):2.01(±0.01):2.01(±0.01).

Solubility Experiments

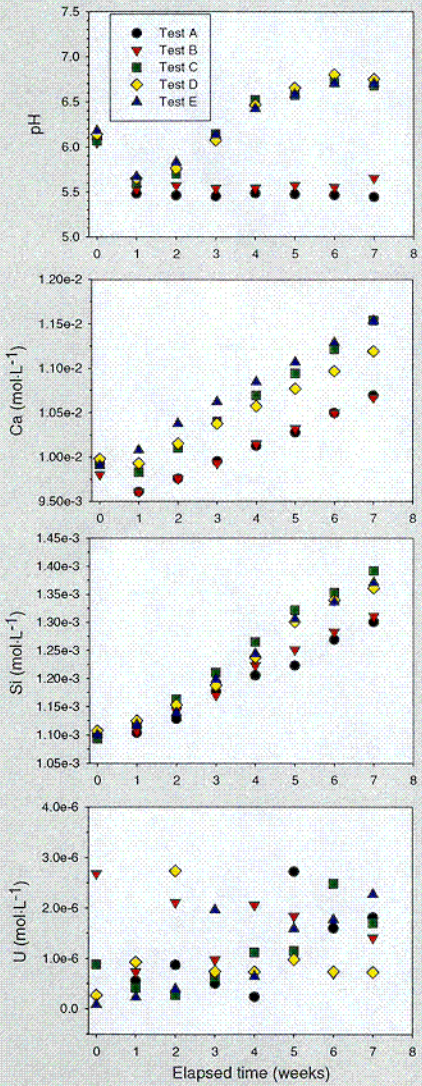
Solubility experiments were designed to approach uranophane equilibrium in both undersaturated and supersaturated solutions. Experimental solutions had initial U concentrations of 10^{-5} to 10^{-7} mol · L^{-1} in matrices of 10^{-2} mol · L^{-1} $CaCl_2$ and 10^{-3} mol · L^{-1} SiO_2(aq). Before addition of uranophane, the pH of solutions were adjusted to about 6.0 by addition of $CaCO_3$ and allowed to equilibrate with atmospheric CO_2(g). The U concentration and pH of experimental solutions before reaction with uranophane are shown in Table 1. The experiments were carried out by reacting known volumes of the test solutions (100 ml) with known amounts of synthetic uranophane (0.5 g) in polycarbonate bottles. Experiments were conducted at room temperature (20.5 ± 2.0 °C) under atmospheric PCO_2 conditions. Aliquots (5 ml) of the experimental solutions were taken at 1 week intervals for 7 weeks. The aliqouts were passed through 0.45 μm membrane filters during the sampling process. Experimental solution weights were measured before and after each sampling to track loss of solution due to sampling and evaporation. Concentrations of major cations in the sample aliquots were determined by ICP; U concentrations were measured by ICP-MS.

Table 1
U content and pH of starting solutions

Test Label	U(mol · L^{-1})	pH
A	1.0×10^{-5}	6.10
B	3.2×10^{-6}	6.05
C	1.1×10^{-6}	6.07
D	3.2×10^{-7}	6.14
E	1.0×10^{-7}	6.18

Results

Experimental Data



The pH and concentrations of Ca, Si, and U in test solutions plotted as function of time. The starting U concentration for Test A (1.0e-5 mol . L⁻¹) is not shown.

Thermodynamics

The uranophane dissolution reaction can be written as

$$Ca(UO_2)_2Si_2O_7 \cdot 6H_2O + 6H^+ \rightleftharpoons$$

$$Ca^{2+} + 2UO_2^{2+} + 2SiO_2(aq) + 9H_2O$$

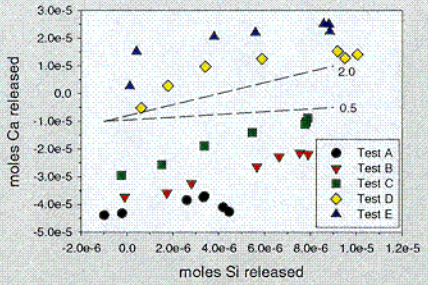
The reaction quotient for this reaction is

$$Q = [Ca^{2+}]\,[UO_2^{2+}]^2\,[SiO_2(aq)]^2\,[H^+]^{-6}$$

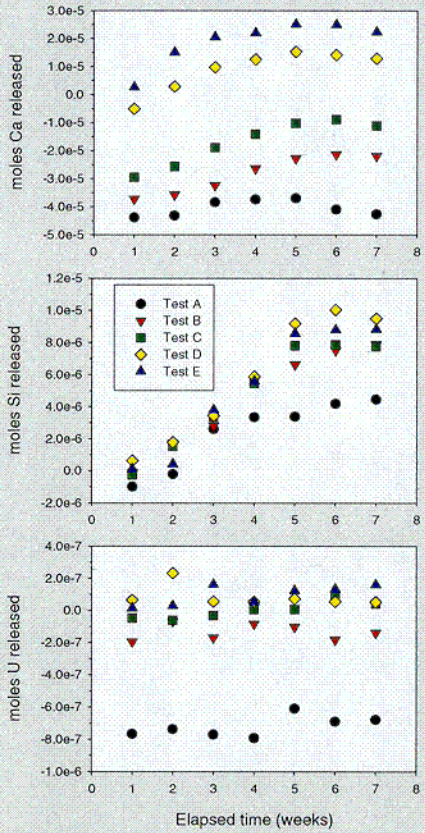
Logarithms of the reaction quotients for uranophane dissolution (log Q) for the last 3 sampling periods are listed in Table 2. Differences in the log Qs between tests A and B and C, D, and E are due primarily to differences in pH.

Table 2

Test Label	Sampling Time (wks)	pH	log Q
A	5	5.47	11.71
	6	5.46	11.28
	7	5.44	11.34
B	5	5.57	11.74
	6	5.55	10.89
	7	5.65	11.83
C	5	6.57	13.77
	6	6.71	14.62
	7	6.68	14.36
D	5	6.65	13.76
	6	6.80	13.84
	7	6.75	13.76
E	5	6.58	14.02
	6	6.70	14.33
	7	6.70	14.55



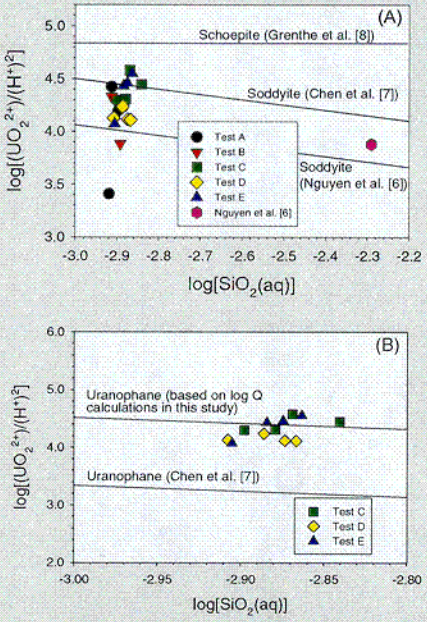
Mass Transfer Relations



Net moles of Ca, Si, and U released to solution plotted as a function of time. Erratic U release and fluctuating U contents (see experimental data) could have resulted from contamination by uranophane colloids, which were not retained on the 0.45 μm membranes used to filter experimental solutions.

Relative number of moles of Ca and Si released to solution. Dashed lines have slopes of 0.5 and 2.0 and are included to illustrate incongruent dissolution of uranophane (i.e., mole ratios of Ca to Si greater than 0.5) during weeks 1 to 4.

Uranyl Phase Relations



Logarithmic activity diagrams of $UO_2^{2+}/(H^+)^2$ versus $SiO_2(aq)$ illustrating position of test solution chemistries in the last 4 sampling intervals with respect to the solubility limit of (A) soddyite and schoepite and (B) uranophane.

(A) Solubility limits for soddyite are based on experimental data (Nguyen et al. [6]) and theoretical prediction (Chen et al. [7]). A single solution chemistry taken from a soddyite dissolution experiment conducted by Nguyen et al. [6] is also plotted. The solubility limit for schoepite is based on data from Grenthe et al. [8].

(B) Solubility limits for uranophane were derived from the average of log Q calculations presented in Table 2 for tests C, D, and E and from theoretical prediction (Chen et al. [7]). Solubility limits for uranophane were calculated by fixing $\log[(Ca^{2+})/(H^+)^2]$ at 11.08, which was averaged from test C, D, and E solution chemistries. Mass transfer results indicate that tests C, D, and E came closer to uranophane solubility because of increased uranophane dissolution and increase in pH. However, evidence for continued uranophane dissolution at the end of these experiments indicate that values of log Q are smaller than the equilibrium constant for uranophane dissolution.

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Interpretation

Mass transfer and thermodynamic analyses indicate that distinct types of reaction paths (A-type and E-type) were followed by solutions with higher and lower initial U concentrations. The characteristics of the reaction paths are summarized in Table 3.

Table 3

	A-type	E-type	Comments
Test	A (initial U 1.0×10^{-5} mol · L^{-1}) B (initial U 3.2×10^{-6} mol · L^{-1})	D (initial U 3.2×10^{-7} mol · L^{-1}) E (initial U 1.0×10^{-7} mol · L^{-1})	Test C (initial U 1.1×10^{-6} mol · L^{-1}), initially had characteristics of A-type then transitioned to E-type
pH	Initial pH drop Relatively constant at about 5.5	Initial pH drop Increased to values > 6.5	Initial pH drop was independent of initial U, suggesting a surface phenomenon such as OH^- sorption
Ca	Net precipitation Initial rapid precipitation	Net release	Precipitation of a secondary Si-bearing phase(s) led to excess Ca in solution in both A- and E-type experiments from week 1 to 4
Si	Small initial precipitation Net release	Net release	Only source of Si is uranophane, so solutions generally remained undersaturated with uranophane
U	Initial precipitation Erratic release (perhaps U colloids)	Small net release	In A-type reaction, Si precipitation was comparable to that of U suggesting precipitation of a uranyl silicate
log Q	10.89 to 11.83	13.76 to 14.62 (includes Test C)	Calculated from solution chemistries in last 3 sampling intervals; greater in E-type due to increased pH

Conclusions

Distinct types of reaction paths were followed by solutions with higher and lower initial U concentrations

- A-type experiments were characterized by initial precipitation of Ca, Si, and U, net precipitation of Ca, and relatively constant pH after an initial pH drop
- E-type experiments were characterized by net release of Ca, Si, and U and pH increase after an initial pH drop

After the initial effects (pH drop and strong Ca precipitation in A-type experiments), reaction paths were dominated by uranophane dissolution coupled to uranyl mineral precipitation

- Reaction progress was greater in the E-type experiments; higher initial U and strong initial Ca precipitation in the A-type experiments appear to have inhibited uranophane dissolution
- Uranyl mineral precipitation was balanced by uranophane dissolution which generally conserved U such that net U release and U concentrations in solution were steady

Based on mass transfer analyses, uranophane continued to dissolve at the ends of all the experiments indicating that all values of log Q are smaller than the equilibrium constant for uranophane dissolution

- Log Q values for uranophane dissolution were greater in the E-type experiments due to increased pH
- E-type experiments (with lower initial U concentrations) came closer to uranophane solubility because of increased uranophane dissolution and increased pH

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