

PHASE RELATIONS OF THE URANYL OXIDE HYDRATES AND THEIR
RELEVANCE TO THE DISPOSAL OF SPENT FUEL

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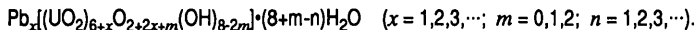
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ABSTRACT

Uranyl oxide hydrates, formed by the alteration of uraninite, are natural analogues for the long-term corrosion products of spent fuel in a geologic repository under oxidizing conditions. The uranyl oxide hydrates may be represented by the general formula:



Pb-bearing hydrates require the addition of a neutral uranyl group into the structural sheet $(UO_2(OH)_2)$ for each interlayer Pb ion. Distortion of the structure associated with the additional uranyl groups is reduced by replacing two structural hydroxyls with a structural oxygen and a molecular water. The general formula for the Pb-uranyl oxide hydrates is:



This hypothesis explains the paragenetic sequences:

- 1) schoepite \rightarrow billietite \rightarrow protasite \rightarrow bauranoite
- 2) schoepite \rightarrow vandendriesscheite \rightarrow fourmarierite \rightarrow masuyite \rightarrow wölsendorfit
- 3) schoepite \rightarrow vandendriesscheite \rightarrow fourmarierite \rightarrow \pm masuyite \rightarrow sayrite \rightarrow curite,

and indicates that, under relatively high pH conditions, schoepite will not be the long-term solubility-controlling phase for uranium in uranium-rich groundwaters.

INTRODUCTION

Spent fuel in contact with oxidizing groundwater corrodes and uranyl oxide hydrates form as corrosion products. These corrosion products will control the release of uranium from the spent fuel.

Natural analogue studies are used to validate geochemical models, employed in long-term extrapolation of corrosion behavior, but seldom are the naturally-formed alteration products properly and carefully described. For example, modelling the precipitation of many uranyl phosphates from solution requires anomalously high uranium and phosphate concentrations in the groundwater[1]; however, the likely role of the Pb-uranyl oxide hydrate, curite, as a "catalyst" for uranyl phosphate formation[2,3], even in groundwaters with relatively low U and P concentrations, is a process that has not been addressed. The Pb-uranyl oxide hydrates are ubiquitous in most uranium deposits ($> 1,000$ Ma), and they play an important role in the stable phase assemblage observed in an oxidized uranium ore body. However, as will be shown here, the Pb-uranyl oxide hydrates appear to represent a different formation sequence than other alkaline-earth uranyl oxide hydrates, and the lack of significant Pb in a spent fuel repository may significantly alter the final phase assemblage controlling uranium solubility. Understanding the conditions necessary for the formation of the uranium phases observed in nature is required before the long-term corrosion behavior of spent fuel may be anticipated.

Uraninite (UO_{2+x}) is a natural analogue used to confirm predicted corrosion behavior of spent fuel in an oxidizing aqueous environment. Uraninite remains relatively insoluble as it oxidizes from UO_2 to $UO_{2.25}$. In an aqueous environment, oxidation beyond $UO_{2.33}$ proceeds rapidly with concomitant hydration to produce the uranyl oxide hydrates, schoepite $(UO_3 \cdot 2H_2O)$ being formed first. No U_3O_8 has been identified in nature, but the structures of the uranyl oxide hydrates are based on sheets of edge-sharing coordination polyhedra which

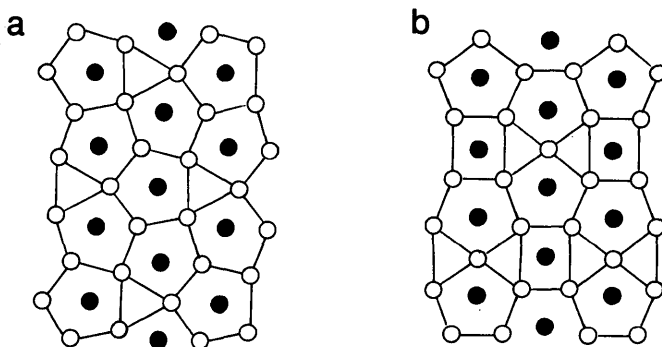


Figure 1. Sheet structures of a) α - U_3O_8 and b) β - U_3O_8 with coordination polyhedra outlined. Structural oxygens and hydroxyls are represented by open circles. Uranyl groups (UO_2^{2+}) are represented by filled circles (after Loopstra[4]).

contain oxidized uranium (U^{6+}), similar to the U_3O_8 structure[4] (Fig. 1). By bonding with two oxygens, the U^{6+} ion forms the stable linear uranyl ion, UO_2^{2+} , which is coordinated to either four or five equatorial oxygens (including structural hydroxyls). The resulting tetragonal and pentagonal dipyramids share their edges to form the structural sheets. Water molecules and cations occupy interlayer sites.

In nature, schoepite always coexists with the alkali and alkaline-earth uranyl oxide hydrates (Table 1), and schoepite alters readily to these phases, depending on pH and groundwater composition. Vochten[5] synthesized several alkaline-earth uranyl oxide hydrates by reaction of solid synthetic schoepite with alkaline-earth-containing aqueous solutions. Sobry[6] analyzed natural and synthetic uranyl oxide hydrates and postulated that a continuous substitutional series existed among them. Noe-Spirlet and Sobry[7] synthesized several Pb-uranyl oxide hydrates and showed that they exhibit unique chemical formulae rather than a continuous solid solution. The inverse relationship between metal/uranium ratio (M:U) and total water is well established[6]; however, the exact role of interlayer water in these structures remains undetermined. Grain size appears to decrease as M:U increases[8]; this is also unexplained. Unfortunately, the fine-grained nature of the uranyl oxide hydrate phases and their tendency to grow in intimate association with one another makes their structural and chemical characterization difficult. The paragenesis among these phases has not been resolved.

Table 1 Uranyl Oxide Hydrates

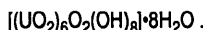
schoepite	$UO_3 \cdot 2H_2O$	meta:schoepite	$UO_3 \cdot H_2O$
Pb-uranyl oxide hydrates		Alkali and Alkaline-Earth Uranyl Oxide Hydrates	
vandriesscheite	$PbO \cdot 7UO_3 \cdot 12H_2O$	*becquerelite	$Ca[(UO_2)_6O_4(OH)_8] \cdot 8H_2O$
*fourmarierite	$Pb[(UO_2)_4O_3(OH)_4] \cdot 4H_2O$	*billietite	$Ba[(UO_2)_6O_4(OH)_8] \cdot 8H_2O$
richetite	$PbO \cdot 4UO_3 \cdot 4H_2O$	*compreignacite	$K_2[(UO_2)_6O_4(OH)_8] \cdot 8H_2O$
masuyite	$3 \cdot 4PbO \cdot 9UO_3 \cdot 10 \cdot 12H_2O$	*protasite	$Ba[(UO_2)_3O_3(OH)_2] \cdot 3H_2O$
*sayrite	$Pb_2[(UO_2)_8O_8(OH)_2] \cdot 4H_2O$	agnirierite	$(K_2, Ca, Sr)O \cdot 3UO_3 \cdot 5H_2O$
wölsendorfite	$(Ca, Pb)O \cdot 2UO_3 \cdot 10H_2O$	rameauite	$(K_2, Ca)O \cdot 3UO_3 \cdot 4H_2O$
clarkeite	$(Na_2, Ca, Pb)O \cdot 2UO_3 \cdot nH_2O$	bauranoite	$BaO \cdot 2UO_3 \cdot 4 \cdot 5H_2O$
*curite	$Pb_3[(UO_2)_8O_8(OH)_8] \cdot 2H_2O$	calciouranoite	$(Ca, Ba, Pb)O \cdot 2UO_3 \cdot 2 \cdot 5H_2O$

* Phases with refined structures.

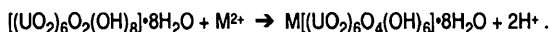
FORMATION OF THE URANYL OXIDE HYDRATES

In order to explain the observed phase relations among the uranyl oxide hydrates, we propose sequential formation by incorporation of cations into interlayer sites coupled with the loss of hydrogen ions from hydroxyls within the structural sheets (thus maintaining charge balance). As the interlayer cation occupancy increases, available water sites are reduced, resulting in dehydration.

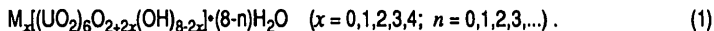
Based on the structures of the becquerelite-group phases, we postulate the fundamental structural formula



The terms within the square brackets define the sheet structures: the uranyl groups, (UO_2^{2+}) , are coordinated to the equatorial oxygens and hydroxyls, O and (OH). Molecular water occupies eight available interlayer sites[9]. This is a possible structural formula for schoepite. Formation of the becquerelite-group phases from schoepite only requires the incorporation of a divalent ion (or, more rarely, two monovalent cations) into the interlayer coupled with the loss of two hydrogen ions:



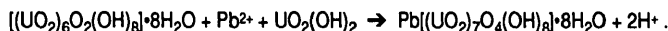
For $\text{M} = \text{Ca}$ or Ba , becquerelite or billietite, both well-known structures, result[10,11]. This does not reflect possible dehydration through the loss of interlayer water, and the coefficient on H_2O may be less than 8. This series is represented by the ideal structural formula



The value of n varies as interlayer water is lost. For $\text{M} = \text{Ba}$, $x = 2$ and $n = 2$, protasite, a well-refined structure, results[11,12]. $\text{M} = \text{Ca}$, $x = 3$ and $n = 3$ may result in meta-calcicouranoite.

Pb-Uranyl Oxide Hydrates

In the case of the Pb-bearing phases, formula (1) must be rewritten to reflect the addition of a neutral uranyl group, chemically equivalent to dehydrated schoepite $(\text{UO}_3 \cdot \text{H}_2\text{O})$, coupled with the addition of each interlayer Pb^{2+} ion. Thus, the reaction of schoepite in the presence of Pb becomes:



This is a possible structural formula for vandendriesscheite, a structure not yet confirmed. The next step in this sequence results in the structural formula $\text{Pb}_2[(\text{UO}_2)_8\text{O}_6(\text{OH})_8] \cdot 8\text{H}_2\text{O}$, which is fourmarierite, a well-refined structure[13].

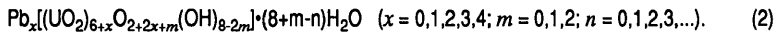
Increasing the number of neutral uranyl groups per formula unit reduces the ratio of uranyl ions (UO_2^{2+}) to equatorial oxygens and hydroxyls (hereafter referred to as $\text{U}^6:\text{O}$). The

becquerelite-group U⁶:O ratio is 3:5 (see Fig.1). It is possible to increase the U⁶:O ratio by replacing two structural hydroxyls with a single structural oxygen and a water molecule. The water may be incorporated into an interlayer site (though this will become increasingly difficult at higher M:U) or it may be eliminated.

The effect of the changing U⁶:O ratio complicates the formation sequence of the Pb-bearing phases, however, it is possible to use known structures to predict the compositions at which the ideal U⁶:O ratio is approached. For example, fourmarierite has U⁶:O = 3:5.25. The next phase in the formation sequence after fourmarierite is masuyite (Table 1). Though the structure of masuyite is not known, protasite is compositionally analogous to masuyite (with Ba = Pb); thus, protasite may be used as a structural analogue for masuyite[9]. Protasite has U⁶:O = 3:5, instead of 3:5.33 as predicted for this composition without replacement of structural hydroxyls. So, the structure of masuyite should be distinctly different from that of fourmarierite, requiring restructuring of the sheets as well as incorporation of an additional inter-layer Pb²⁺ ion.

Another resolved structure is sayrite[14], having U⁶:O = 3:4.8. Formation of sayrite also requires restructuring of the sheets from the masuyite structure. The sayrite structure has both five-coordinated uranyl ions and four-coordinated uranyl ions[14]. Both polyhedral types are also present in the curite structure[15,16]. Three sheet types are defined for the Pb-uranyl oxide hydrates based on hydroxyl occupancy within the sheet: (1) a fourmarierite sheet type with eight hydroxyls per structural formula unit; (2) a protasite sheet type with six hydroxyls per structural formula unit; and (3) a sayrite sheet type with four hydroxyls per structural formula unit. As the formation sequence continues, the sheet structure seen in masuyite may persist, or the sayrite type of sheet structure may form.

The general structural formula for the Pb-bearing phases is



The value of m depends on the type of structural sheet: for the fourmarierite type, $m = 0$; for the protasite type, $m = 1$; for the sayrite type, $m = 2$. As with formula (1), n varies indepen-

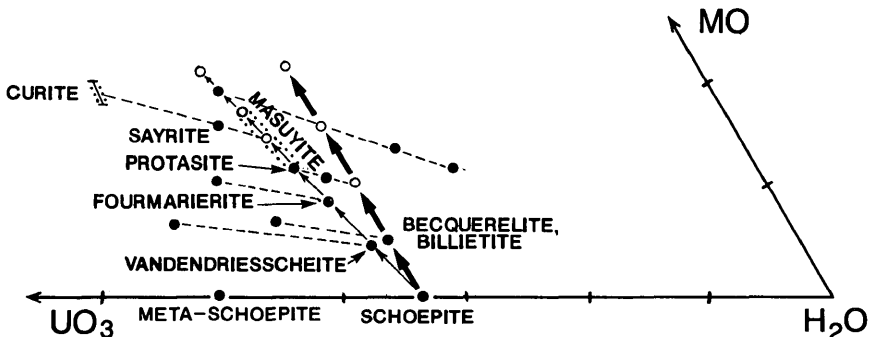


Figure 2. Portion of ternary diagram with apices MO-H₂O-UO₃ showing reaction paths for the uranyl oxide hydrates.

Compositions predicted by the formation sequence presented here.

● Known or reported phase compositions.

○ Unknown phase compositions.

→ Formation path for simple ion exchange (formula 1).

➔ Formation of the Pb phases (ion exchange coupled with the a neutral uranyl group; formula 2).

--- Dehydration reaction paths between known and/or predicted compositions.

⋯ Phases reported as solid solutions or as a range of compositions.

dently as interlayer water is lost. The compositions corresponding to the suggested formulae are plotted on a ternary diagram, $\text{UO}_3\text{-H}_2\text{O-MO}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Pb}, \text{K}_2$), and compared with known phase compositions in figure 2. The Pb-bearing phases follow a reaction path distinct from the other uranyl oxide hydrates as M:U increases. Dehydration is an important mechanism driving alteration; as M:O increases, the known phases are commonly more dehydrated than compositions predicted with $n = 0$. The structural formulae for the formation of the Pb phases are given in Table 2 as a function of Pb content along with U⁶:O ratios and prospective sheet types.

Table 2
Structural Formulae Suggested for the Pb-Uranyl Oxide Hydrates. $\text{Pb}_x[(\text{UO}_2)_{6+x}\text{O}_{2+2x+m}(\text{OH})_{8-2m}] \cdot (\delta+m-n)\text{H}_2\text{O}$

Structural Formula	sheet type ¹	U ⁶ :O	Alternative Structural Formula ²	sheet type ¹	U ⁶ :O
$[(\text{UO}_2)_6\text{O}_2(\text{OH})_8] \cdot 8\text{H}_2\text{O}$	F	3:5			
$\text{Pb}[(\text{UO}_2)_7\text{O}_2(\text{OH})_8] \cdot 8\text{H}_2\text{O}$	F	3:5.14			
$\cdot\text{Pb}_2[(\text{UO}_2)_8\text{O}_6(\text{OH})_8] \cdot 8\text{H}_2\text{O}$	F	3:5.25			
$\text{Pb}_3[(\text{UO}_2)_9\text{O}_9(\text{OH})_6] \cdot 9\text{H}_2\text{O}$	P	3:5			
$\text{Pb}_4[(\text{UO}_2)_{10}\text{O}_{11}(\text{OH})_6] \cdot 9\text{H}_2\text{O}$	P	3:5.1	$\cdot\text{Pb}_4[(\text{UO}_2)_{10}\text{O}_{12}(\text{OH})_4] \cdot 10\text{H}_2\text{O}$	S	3:4.8
$\text{Pb}_5[(\text{UO}_2)_{11}\text{O}_{13}(\text{OH})_6] \cdot 9\text{H}_2\text{O}$	P	3:5.2	$\text{Pb}_5[(\text{UO}_2)_{11}\text{O}_{14}(\text{OH})_4] \cdot 10\text{H}_2\text{O}$	S	3:4.9
$\text{Pb}_6[(\text{UO}_2)_{12}\text{O}_{15}(\text{OH})_6] \cdot 9\text{H}_2\text{O}$	P	3:5.25	$\text{Pb}_6[(\text{UO}_2)_{12}\text{O}_{16}(\text{OH})_4] \cdot 10\text{H}_2\text{O}$	S	3:5

¹ Sheet type: F = fourmarierite-type, P = protasite-type, S = sayrite-type (see text for discussion)
² Alternative Structural Formula indicates the sheet structure type that may exist instead of, or coexist with, the sheet structure in the first column for a given composition. Both sheet types are compatible with the sequence described by formula (2)
^{*} Structural formulae corresponding to refined structures, see Table 1.

SUMMARY

The series of alkali and alkaline-earth uranyl oxide hydrates is explained by a formation sequence based on the becquerelite-group structure. As pH and M^{2+} concentration increases in solution, the sequential formation of phases possessing unique chemical formulae is proposed. Interlayer water may be lost as M:U increases. The compositional and structural variation observed in several phases, especially masuyite, may result from interstratification similar to that found in mixed-layer clays, each layer corresponding to a unique chemical formula, as given in Table 2. The interstratification of variable proportions of these layers produces compositions encompassing the full range of compositions reported in nature (Fig. 2).

The structural sequence described here has several applications to modelling the corrosion of spent fuel. Schoepite is generally considered the solubility-limiting phase for uranium released from spent fuel in contact with oxidizing groundwater. However, schoepite alters readily to other uranyl oxide hydrates[4]. Becquerelite and several uranyl silicates have been identified in studies of the corrosion of spent fuel[17,18] and UO_2 pellets[19]. Such studies have identified only a small number of the phases found in nature. The unidentified phases are important in moderately high pH solutions, which may be present in a repository. Finally, the paragenesis of the uranium phases in nature must be determined and understood before the relevance of a natural analogue study to spent fuel corrosion may be ascertained.

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