

Affects of Hydrogen Peroxide on the Stability of Becquerelite

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ABSTRACT

While the majority of studies of alteration of UO_2 and commercial spent nuclear fuel under simulated geological repository conditions have emphasized the importance of uranyl oxide hydrates and uranyl silicates, the potential influence of peroxide on repository performance has been largely overlooked. There is considerable evidence that uranyl peroxides may be important alteration phases of nuclear waste, and that these phases may impact the long-term performance of a geologic repository. Here we report the thermodynamics and kinetics of becquerelite, $\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6](\text{H}_2\text{O})_8$, in the presence of solutions containing hydrogen peroxide. Thermodynamic calculations reveal that in solutions containing 3.5×10^{-6} M hydrogen peroxide, studtite formation is thermodynamically favorable over becquerelite at 298 K. To access the kinetics of this reaction, batch experiments were conducted by the reaction of becquerelite and solutions containing hydrogen peroxide. In the presence of 0.1 M hydrogen peroxide, becquerelite altered to studtite within eight hours.

INTRODUCTION

Uranyl oxide hydrates, such as schoepite, dehydrated schoepite, becquerelite, and compreignacite, are significant constituents of the oxidized portions of uranium deposits [1]. These minerals can occur in soils contaminated by actinides [2] and are likely to be important in the oxidative alteration of nuclear waste in a geological repository [3-8]. Laboratory experiments have demonstrated that schoepite and meta-schoepite rapidly alter to becquerelite in Ca-bearing solutions [9-11]. Becquerelite is expected to be the most stable phase in the $\text{UO}_3(\text{H}_2\text{O})_2$ -CaO- H_2O system under normal geochemical conditions.

While the majority of studies of oxidative alteration of UO_2 and commercial spent nuclear fuel under simulated repository conditions have emphasized the importance of uranyl oxide hydrates [4,8], the potential influence of peroxide on repository performance has been largely overlooked. Recently, McNamara et al. [12] found extensive formation of the peroxide mineral studtite, $(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_4$, on the surface of spent nuclear fuel reacted at 25 °C with deionized water for 1.5 years under ambient conditions. Sattonnay et al. [13] observed the formation of metastudtite, $(\text{UO}_2)(\text{O}_2)(\text{H}_2\text{O})_2$, on the surface of UO_2 irradiated with an α -particle beam, and concluded the peroxide was provided by alpha-radiolysis of water. Burakov et al. [14] reported that uranyl peroxides formed on the surface of fuel-containing material following the Chernobyl Nuclear Plant accident. Thus, there is considerable evidence that uranyl peroxides will be important alteration phases of nuclear waste, and that these minerals may impact the long-term performance of a geologic repository.

The long-term alpha radiation associated with spent nuclear fuel in a geological repository is substantial, because of long-lived radionuclides such as ^{237}Np , ^{235}U and ^{238}U , and their daughter products. Alpha-radiolysis of water produces oxidizing reactants (H_2O_2 , OH , etc.) and reducing species (H_2 , e^-_{aq} , etc.) in equal proportions. Under favorable conditions, uranyl peroxides may dominate at the expense of more common uranyl minerals, such as becquerelite, which has also been found as alteration phases on spent fuel in laboratory studies. As such, the stability and solubility of uranyl oxide hydrates in the presence of hydrogen peroxide will ultimately impact the fate and transport of uranium in the environment. Here we report the stability of becquerelite in the presence of hydrogen peroxide.

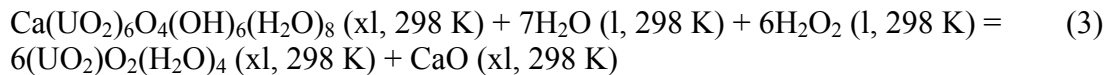
THERMODYNAMICS

Drop-solution enthalpies of becquerelite and studtite have been obtained using high-temperature drop-solution calorimetry of synthetic phases [15-16]. Measured drop-solution enthalpies of becquerelite and studtite were used in thermodynamic cycles to establish the enthalpies of formation from the binary oxides. Reference data were used for the standard enthalpies of formation of the binary oxides to calculate the standard enthalpy of formation, ΔH°_f , of becquerelite and studtite from the elements. The following standard enthalpies of formation were calculated:

$$\Delta H^\circ_f(\text{becquerelite}) = -11389.2 \pm 13.5 \text{ kJ mol}^{-1} \quad [16] \quad (1)$$

$$\Delta H^\circ_f(\text{studtite}) = -2344.7 \pm 5.0 \text{ kJ mol}^{-1} \quad [15] \quad (2)$$

To investigate the stability of becquerelite in the presence of solutions containing hydrogen peroxide, produced from the alpha-radiolysis of water, the enthalpy of becquerelite was compared to that of studtite. The enthalpy of the following reaction was calculated: (Table 1)



$$\Delta H^\circ_{r, 298 \text{ K}} = -186.7 \pm 18.0 \text{ kJ mol}^{-1}$$

The standard enthalpy of reaction suggests that studtite is the stable phase relative to becquerelite, H_2O , and H_2O_2 in their standard states. While ΔS° for this reaction is unknown, it is expected to be small as no gas is evolved or consumed during the reaction. Relatively low peroxide concentrations ($3.5 \times 10^{-6} \text{ M H}_2\text{O}_2$, Table 2) must be present in solution for studtite to be stable relative to becquerelite. If H_2O_2 is constantly produced locally in a geological repository, and the temperature is not too high, studtite will be stable relative to becquerelite above this concentration. While becquerelite is an alteration product that is often found in the paragenetic sequence involving uranyl oxide hydrates and uranyl silicates, studtite is thermodynamically favored where hydrogen peroxide is present.

Table 1. Calculation of the enthalpy of reaction, ΔH°_r .

Reactions	ΔH (kJ/mol)
(1) ΔH°_f (studtite) U (xl, 298 K) + $4H_2$ (g, 298 K) + $4O_2$ (g, 298 K) = $(UO_2)O_2(H_2O)_4$ (xl, 298 K)	-2344.7 \pm 5 [15]
(2) ΔH°_f (becquerelite) Ca (xl, 298 K) + $6U$ (xl, 298 K) + $11H_2$ (g, 298 K) + $15O_2$ (g, 298 K) = $Ca(UO_2)_6O_4(OH)_6(H_2O)_8$ (xl, 298 K)	-11389.2 \pm 13.5 [16]
(3) $\Delta H^\circ_f(H_2O)$ H_2 (g, 298 K) + $1/2O_2$ (g, 298 K) = H_2O (l, 298 K)	-285.8 \pm 0.1 [17]
(4) $\Delta H^\circ_f(H_2O_2)$ H_2 (g, 298 K) + O_2 (g, 298 K) = H_2O_2 (l, 298 K)	-187.8 [18]
(5) $\Delta H^\circ_f(CaO)$ Ca (xl, 298 K) + $1/2O_2$ (g, 298 K) = CaO (xl, 298 K)	-635.1 \pm 0.9 [19]
Thermodynamic Cycle	ΔH (kJ/mol)
$\Delta H^\circ_r = 6\Delta H^\circ_f(1) + \Delta H^\circ_f(5) - \Delta H^\circ_f(2) - 7\Delta H^\circ_f(3) - 6\Delta H^\circ_f(4)$	
$\Delta H^\circ_r = 6\Delta H^\circ_f(\text{studtite}) + \Delta H^\circ_f(CaO) - \Delta H^\circ_f(\text{becquerelite}) - 7\Delta H^\circ_f(H_2O) - 6\Delta H^\circ_f(H_2O_2)$	
$Ca(UO_2)_6O_4(OH)_6(H_2O)_8$ (xl, 298 K) + $7H_2O$ (l, 298 K) + $6H_2O_2$ (l, 298 K) = $6(UO_2)O_2(H_2O)_4$ (xl, 298 K) + CaO (xl, 298 K)	-186.7 \pm 18

Table 2. Calculation of minimum hydrogen peroxide.

Reaction	ΔH (kJ/mol)
ΔH°_r $Ca(UO_2)_6O_4(OH)_6(H_2O)_8$ (xl, 298 K) + $7H_2O$ (l, 298 K) + $6H_2O_2$ (l, 298 K) = $6(UO_2)O_2(H_2O)_4$ (xl, 298 K) + CaO (xl, 298 K)	-186.7 \pm 18.0
Calculation	
$\Delta G_{rxn} = \Delta G^\circ + RT \ln K$	<i>assumptions: at equilibrium $\Delta G_{rxn} = 0$; ΔS° is negligible and therefore $\Delta G^\circ = \Delta H^\circ$; $a_{H_2O} = 1$; $a_{studtite} = 1$; $a_{becquerelite} = 1$</i>
$\Delta G^\circ = -RT \ln K$	$K = 1/(a_{H_2O_2})^6$ $T = 298.15$ K $R = 8.314$ J mol ⁻¹ $\Delta G^\circ = \Delta H^\circ = -186700$ J mol ⁻¹
$K = 5.13 \times 10^{32}$	
$a_{H_2O_2} = 3.53 \times 10^{-6}$	

KINETICS

Thermodynamic calculations suggest that in the presence of solutions containing 3.5×10^{-6} M hydrogen peroxide studtite is stable in enthalpy relative to becquerelite. This thermodynamic calculation does not, however, suggest a time frame for which this reaction may occur. Here we report preliminary kinetic data for the transformation of becquerelite to studtite in the presence of excess hydrogen peroxide.

Synthesis

Becquerelite was synthesized under mild hydrothermal conditions by the reaction of 0.165 g UO_3 , 0.25 g calcite (5 crystals), and 5 mL H_2O . The pH of the water was adjusted to 3 by the addition of dilute HCl. The reactants were placed into a Teflon-lined Parr reaction vessel and heated to 453 K for 10 days. Upon cooling, the products were recovered by filtration and rinsed using H_2O . Synthesis experiments were run multiple times to achieve desired quantities of material.

Powder X-ray Diffraction

Aliquots of each sample were ground to a fine powder and deposited onto the surface of a zero-background oriented silicon wafer. X-ray powder diffraction patterns were collected for each aliquot. Data was collected using a Bruker D8 Discovery powder diffractometer over the 2θ range 20 to 140° with a step-width of 0.01° and one second spent counting per step. All powder diffraction patterns exhibit sharp profiles and no peaks that are attributable to impurity phases.

Batch Experiments

Becquerelite crystals were ground to a powder using a mortar and pestle and separated into three 0.2 g aliquots. Each aliquot was placed into a plastic reaction vial with 20 mL of 0.1 M H_2O_2 . The solid phase in each aliquot was analyzed by powder X-ray diffraction every five minutes for the first hour, and every 20 minutes thereafter. The reaction vial was shaken continuously during the experiment.

Results

Within the first three hours of the reaction of becquerelite and 0.1 M hydrogen peroxide solution, becquerelite was the only detectable phase present. After three hours, studtite was detectable in the powder X-ray diffraction profile. Within nine hours the only detectable crystalline phase in the powder diffraction profile was that of studtite. A three-dimensional diffraction profile is shown in Figure 1.

In the presence of 0.1 M hydrogen peroxide, becquerelite converted to studtite within nine hours. This reaction would presumably take longer for lower concentrations of hydrogen peroxide, such as 3.5×10^{-6} M, as calculated from the thermodynamics (Table 2). This initial research demonstrates that not only is the alteration of becquerelite to studtite in the presence of hydrogen peroxide thermodynamically favorable, but it occurs in time scales measurable in laboratory experiments.

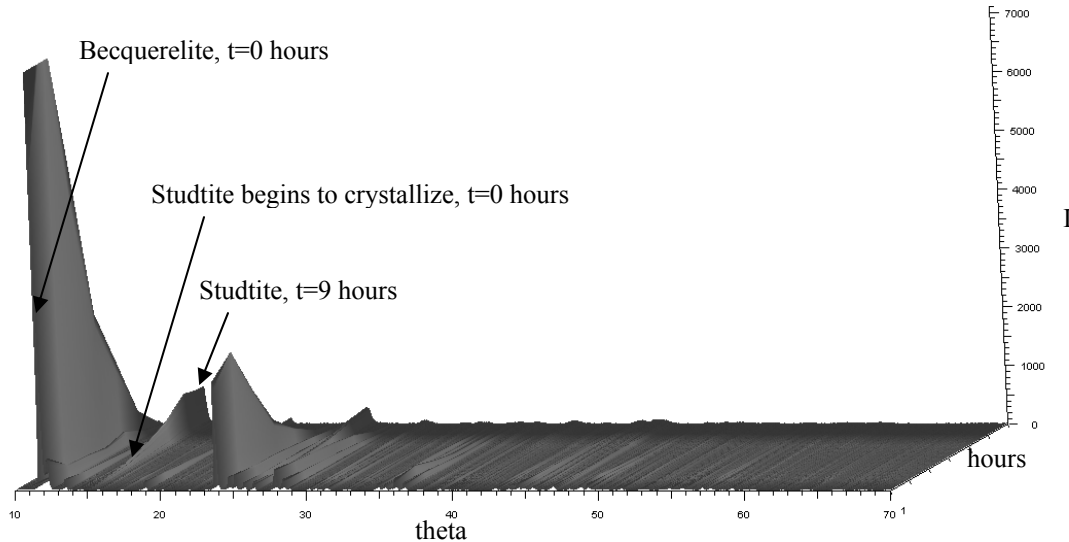


Figure 1. Powder diffraction patterns as a function of time for the reaction of becquerelite in the presence of 0.1 M hydrogen peroxide. After 9 hours, studtite is the only detectable crystalline phase.

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