Dissolution Kinetics of Studtite ($UO_4 \cdot 4H_2O$) in HCO_3^- Solution and Synthetic Ground Water

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1. Introduction

Deep geological disposal is a promising method to dispose of spent nuclear fuel (SNF) that is being evaluated by Canada, Finland, Germany, Spain, Sweden, England, USA etc. Ground water beside the SNF canister can be decomposed by alpha (α), beta (β) and gamma (γ) radiation emitted from the SNF. Radiolysis can produce H_2O_2, OH^-, H^-, e_{aq}^-, and H_2 through water decomposition. Studtite ($UO_4 \cdot 4H_2O$) is formed by reaction between uranyl ion (UO_2^{2+}) that may leaks from SNF and H_2O_2. The studtite formed on the SNF surface, can impede the corrosion of SNF and retard the transport of cesium and strontium [1] through sorption reaction. Therefore, the dissolution kinetics of studtite in natural environmental conditions is important factor for the performance and risk assessment of repositories. The objectives of this study is to investigate the dissolution kinetics and mechanisms of uranium release from studtite in different solution conditions.

2. Materials and Methods

2.1 Synthesis and characterization of studtite

To synthesize studtite, we used $UO_2(NO_3)_2 \cdot 6H_2O$ (1000 ppm ^{238}U, Perkinelmer Pure Plus) and H_2O_2 (30wt% in H_2O, Junsei). These two stock solutions were mixed in a 15 mL centrifuge tube to make uranium concentration of 0.001 M and H_2O_2 concentration of 7.34 M at room temperature. The final solution pH was close 1 after 24 hour mixing. A bright yellow solid material was precipitated at the bottom of the centrifuge tube. Solid was separated by filtration using a nylon membrane filter paper (pore size 0.45 μm, Whatman ™) and dried at 40°C in an oven (OF-11E, Lab Companion) for 48 hour. The solid material was characterized using an x-ray diffractometer (XRD, Rigaku Miniflex II) for mineralogy and attenuated total reflectance – fourier transform infrared spectroscopy (ATR-FTIR Nicolet iS10, Thermo Scientific) for chemical bonds analysis.

2.2 Batch dissolution experiments of studtite

$NaHCO_3$ (99.5–100.5%, Sigma-Aldrich) was added to 50 mL of deionized water for preparing three different concentrations (10^{-2}, 10^{-3}, and 10^{-4} M HCO_3^-) of background solutions. The pH of these solutions were adjusted to 9 by adding 0.1 N NaOH. Both aerobic and anaerobic synthetic ground water was prepared for 50 mL to mimic natural granitic groundwater (sampled at YS-1-6 borehole) [2]. Synthesized studtite (1 mg) was added to each solution (50 mL) and started for batch dissolution test for 2 month. In each sampling time (total 12 times for 2 month), a 2 mL sample was collected and the same amount of sampling volume was replaced by the same background solution. The uranium concentration in each filtered sample was determined using inductively coupled plasma mass spectrometer (ICP-MS, NexION 300D, Perkinelmer).

3. Results & Discussion

We confirmed that the synthesized material is studtite based on XRD mineral identification and ATR-FTIR chemical bonds analysis (Fig. 1 and 2).

The released amounts of uranium increased with increasing HCO_3^- concentrations in solution.

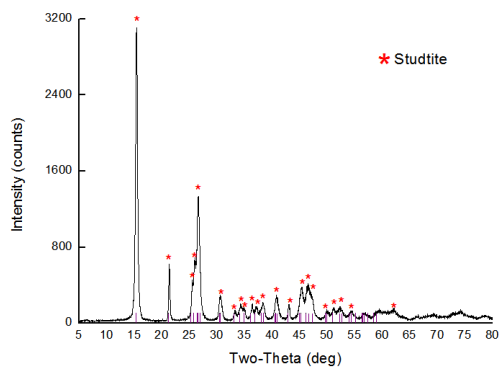Dissolution of studtite in 10^{-2} M of HCO_3^- was much faster than other 2 conditions (Fig. 3).
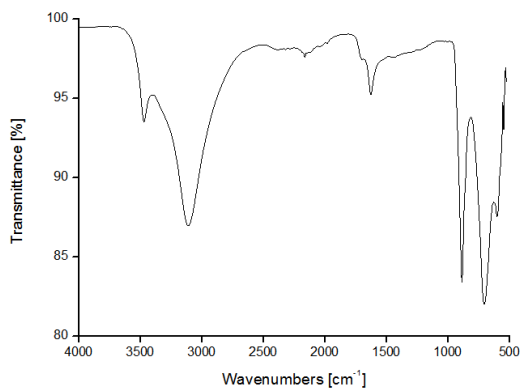

Fig. 1. XRD pattern of studtite.

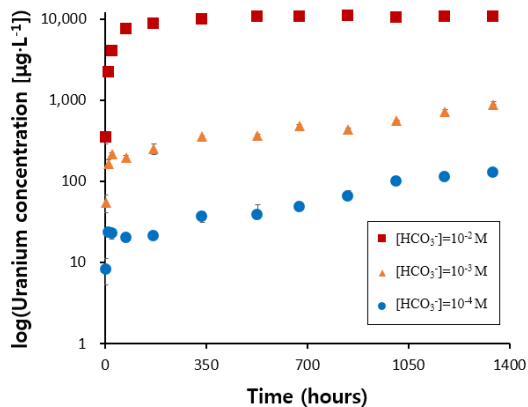Fig. 2. ATR-FTIR spectra of studtite.

Fig. 3. Log uranium concentration vs. time in three different [HCO3-] solutions with pH 9 in aerobic condition. Error bars were determined by standard deviation of duplicates.

The released amounts of uranium increased with increasing HCO_3^- concentrations in solution. Dissolution of studtite in 10^{-2} M of HCO_3^- was much faster than other 2 conditions (Fig. 3).

Dissolution kinetics between aerobic and anaerobic ground water showed small effect of dissolved

oxygen (DO) on studtite dissolution (Fig. 4). In addition, studtite dissolution was faster in aerobic groundwater with 3.11×10^{-5} M HCO_3^- compared to 10^{-3} and 10^{-4} M of HCO_3^- solutions.
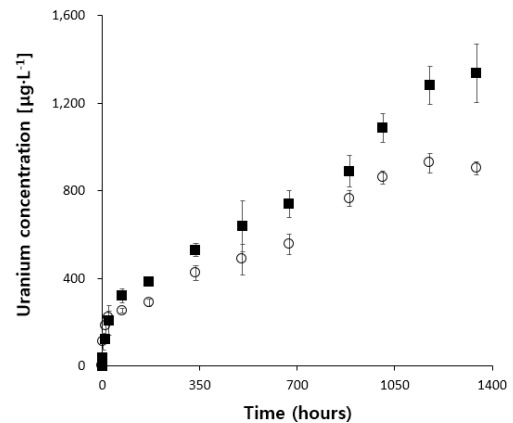

Fig. 4. Released uranium concentration vs. time in synthetic groundwater with pH 9 prepared under aerobic condition (filled squares, DO=4.92 mg·L-1) and anaerobic condition (clear circles, DO=0.31 mg·L-1). Error bars were determined by standard deviation of duplicates.

4. Conclusion

The effect of dissolved oxygen on studtite dissolution was found. Therefore, H_2O_2 effect should be investigated in the ground water, because H_2O_2 can be generated in groundwater by radiolysis and the relative oxidation effect of H_2O_2 to uranium dioxide (UO_2) is dominant. Single pass flow test (SPFT) will be conducted to determine studtite dissolution rate.

5. References

[1] Sureda R, Martinez-Llado X, Rovira M, de Pablo J, Casas I, Gimenez J., "Sorption of strontium on uranyl peroxide: Implications for a high-level nuclear waste repository", J Hazard Mater, 181, 881-885 (2010).

[2] B. Y. Kim, J. Y. Oh, M. H. Baik, and J. I. Yun, "Effect of Carbonate on the Solubility of Neptunium in Natural Granitic Groundwater," Nuclear Engineering and Technology, 42, 552-561, (2010).