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Dissolution of studtite $[UO_2(O_2)(H_2O)_4]$ in various geochemical conditions

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ABSTRACT

This study determined the dissolution rate of studtite, $(UO_2)O_2(H_2O)_4$, which can be formed by reaction between H_2O_2 and UO_2^{2+} that leaks from spent nuclear fuel (SNF) in deep geological repositories. The batch dissolution experiments were conducted using synthesized studtite under different solution conditions with varying pHs and concentrations of HCO_3^- and $[H_2O_2]$ in synthetic groundwater. The experimental results suggested that carbonate ligand and H_2O_2 in groundwater accelerated the dissolution of studtite and uranium (U) release. Above 10^{-5} M of H_2O_2 initial concentration, the released uranium concentration in solution decreased, possibly as a result of reprecipitation of studtite due to reaction between uranium and H_2O_2. The results will be useful to assess the comprehensive transport of uranium from both nuclear waste and SNF stored in deep geological repositories.

1. Introduction

Deep geological disposal is considered as one of the methods to dispose of spent nuclear fuel (SNF) in several countries (e.g., Canada, Finland, Germany, Spain, Sweden, England, and USA) (Hogselius, 2009). Deep geological disposal entails placing SNF in a canister and burying it at a depth of 500–1000 m below the ground in stable bedrock (Fuel, 2011). However, because fission products and other radionuclides may leach from the weathered SNF, the radionuclide transport should be correctly predicted and prevented to ensure safe operation and long-term performance assessment of repositories. The release of radionuclides from grains of UO_2 matrix depends on solubility of the alteration phases and the location of fission products within SNF (Shoesmith and Sunder, 1992).

SNF buried in a repository can irradiate the groundwater surrounding canisters and the radiation dose rate is mainly effected by α-radiation because the dose rates of β- and γ-radiations after 1000 years will be reduced to 10^{-3} and 10^{-5} times their initial values respectively, compared with α-radiation emitted from CANada Deuterium Uranium (CANDU) SNF (burn up 220 MWh/(kg U)) (Sunder, 1995). Consequently, over the long term, α-radiation is the main cause of groundwater radiolysis. This α-radiolysis decomposition produces H_2O_2, OH·, H·, e_{aq}^-, and H_2 of which H_2O_2 has the greatest (99.9–100%) effect on the stability of uranium dioxide (UO_2) (Choppin et al., 2002; Ekeroth et al., 2006). Reaction between H_2O_2 and uranyl ions (UO_2^{2+}) that may leach from SNF forms peroxide-bearing uranium mineral, studtite, $(UO_2)O_2(H_2O)_4$ (Sattonnay et al., 2001).

The crystal structure of natural studtite consists of chains of edge-sharing UO_8 polyhedron with water molecules between the chains. Chains are linked by H bonds that extend to and from an interstitial H_2O group (Burns and Hughes, 2003). The solubility of studtite varies with pH from 3 to 11; the best fit of the model to the experimental solubility data for the studtite dissolution reaction (Eq. (1)) is log $(K_{s0}) = -2.7 \pm 0.2$ and the pH_{pzc} of studtite was determined to be 4.0 ± 0.2 (Gimenez et al., 2014). Studtite that forms on the SNF surface (McNamara et al., 2003) can impede the further corrosion of SNF (Shoesmith, 2000), which retards the release of neptunium (Douglas et al., 2005), cesium (Gimenez et al., 2010), and strontium (Sureda et al., 2010) by surface sorption reactions. However, if studtite exists at the SNF surface in contact with groundwater in repositories, the release of radionuclides such as uranium and thorium is also controlled by studtite dissolution (Eq. (1)).

$$UO_2(O_2)\cdot 4H_2O_{(s)} + 2H^+ \leftrightarrow UO_2^{2+} + 4H_2O + H_2O_2 \tag{1}$$

Therefore, the dissolution kinetics of studtite in various natural environmental conditions is an important factor in modelling

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radionuclides transport and to assess the risk of burying SNF in deep geologic repositories. Dissolution of studtite in groundwater should be quantified under varying conditions, but research for studtite dissolution kinetics and mechanisms after its formation is still lacking. In this study, batch dissolution experiments were conducted in different solution conditions (pH), bicarbonate concentration [HCO_3^-], hydrogen peroxide concentration [H_2O_2], synthetic groundwater composition, and provided valuable information on uranium release due to studtite dissolution.

2. Material and methods

2.1. Synthesis of studtite [$(UO_2)O_2(H_2O)_4$]

Studtite was synthesized using $UO_2(NO_3)_2{\cdot}6H_2O$ (0.004 M of ^{238}U, PerkinElmer Pure Plus) and H_2O_2 (9.79 M, Junsei) solutions. These two stock solutions were mixed in 1: 3 vol ratio (2.5 mL of $UO_2(NO_3)_2{\cdot}6H_2O$ and 7.5 mL of H_2O_2 stock solution) in 15-mL polypropylene conical tubes (BD Falcon, #352096) and reacted for 12 h at room temperature. Uranium and hydrogen peroxide concentrations of the mixed solution were 0.001 M and 7.34 M, respectively. Uranium concentration was determined by inductively coupled plasma mass spectroscopy (ICP-MS, NexION 300D, PerkinElmer). The concentration of H_2O_2 of all samples was determined using a UV-VIS spectrophotometer (UV-1800, Shimadzu). Titanium(IV) oxysulfate ($TiOSO_4 \cdot xH_2SO_4 \cdot xH_2O$) solution (~15 wt.% in dilute sulfuric acid, Sigma-Aldrich) was used as the indicator solution and absorbance of the sample was recorded at 405 nm (Buck et al., 2012). A calibration curve was developed using diluted H_2O_2 stock solutions (1.96 μM, 39.2 μM, 97.9 μM, 0.29 mM, 0.98 mM, 2.94 mM, and 4.90 mM) and used to determine H_2O_2 sample concentration.

After mixing the uranyl nitrate and hydrogen peroxide solution, yellow particles precipitated at the bottom of the tube and the pH value of the final solution was close to 1.0. The yellow precipitates were separated by filtration using a nylon membrane filter paper (pore size = 0.45 μm, Whatman), washed five times using deionized water (DIW), and dried at 40 °C in an oven (OF-11E, Lab Companion) for 1 day before use.

2.2. Characterization of studtite and dissolved uranium species

X-ray diffraction (XRD, Rigaku Miniflex II) was used to identify studtite mineralogy. The XRD pattern of the synthesized uranium sample was analyzed with Jade software (Materials Data Incorporated, California) using the International Centre for Diffraction Data (ICDD) XRD database.

Chemical bonds of the synthesized studtite were analyzed using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR Nicolet iS10, Thermo Scientific). The IR spectrum was classified using ATR-FTIR equipped with a Fast-recovery deuterated triglycine sulfate (DTGS) detector, Mid-infrared Ever-Glo source and KBr/Ge mid infrared optimized beam splitter. After cleaning the ATR diamond crystal using ethanol, IR spectra of the synthesized studtite and background spectra of air in the wavenumber ranging from 525 to 4000 cm^{-1} were obtained by conducting 32 scans with a resolution 4 cm^{-1}. All IR spectra were processed using OMNIC 9 software (Thermo Scientific) with a transmittance scale.

The Brunauer-Emmett-Teller (BET) (Brunauer et al., 1938) specific surface area of the synthesized studtite was measured by nitrogen adsorption-desorption isotherm measurements at 77.38 K using a surface analyzer (Accelerated Surface Area and Porosimetry System, ASAP 2010, Micromeritics).

The pH of all batch solution samples was measured using a pH meter (Orion Star A211 pH Benchtop Meter, Thermo Scientific) that was calibrated using pH 4.0, 7.0, and 10.0 standard solutions (Thermo Scientific). The oxidation-reduction potential (ORP) of synthesized groundwater was determined using the same meter with an ORP probe. After the ORP electrode (Orion 9179BNMD) was calibrated with an ORP standard solution (Orion 967901), corrected E_h (mV) values were read and used. Dissolved oxygen (DO) was measured using a DO meter (Horiba D-75) and DO electrode (Horiba 9551-20D) after conducting a calibration.

The Geochemist's Workbench Professional version 10.0.10 (Bethke and Yeakel, 2014) was used to develop Eh-pH diagrams (Act2 program), synthetic groundwater (GSS program), and balancing chemical reaction (Rxn program). The default thermo dataset, *thermo.tdat*, complied by Lawrence Livermore National Laboratories (LLNL) was used and modified to add the equilibrium constant of studtite (Gimenez et al., 2014).

2.3. Batch dissolution experiments

2.3.1. Different solution conditions (pH, HCO_3^-, and H_2O_2 concentration)

To determine how pH effects studtite dissolution and uranium release, six solutions of 50 mL, one each at pH = 1, 3, 5, 7, 9, or 11 were prepared in DIW (Millipore Type 1 Ultra-Pure Water Systems, 18 MΩ cm) by adding 13.5 M HNO_3 (Daejung) or 0.1 M NaOH (Daejung).

$NaHCO_3$ (0.21 g, 99.7–100.3% purity, Sigma-Aldrich) was dissolved in 250 mL of DIW in a glass beaker and diluted using DIW to make 50 mL of different HCO_3^- concentrations, 10^{-2}, 10^{-3}, and 10^{-4} M of [HCO_3^-] as background solutions. These solutions were adjusted to pH = 9 by adding 0.1 M NaOH before use.

H_2O_2 stock solution (9.79 M) was diluted with pH = 9 DIW to prepare two H_2O_2 concentrations solutions, [H_2O_2] = 0.979 M and 9.79×10^{-2} M. Then, these hydrogen peroxide solutions were more diluted using pH = 9 DIW to make 50 mL of solutions with different [H_2O_2] concentrations, 10^{-1}, 10^{-2}, and 10^{-3} M as background solutions. The pHs of these solutions were also adjusted to maintain pH = 9 by adding 0.1 M NaOH before use.

Synthesized studtite (1 mg) was mixed into each dissolution solution (50 mL); the initial pH of each batch dissolution solution was continuously maintained close to pH = 9 using 0.1 M NaOH or 4.5 M HNO_3, and the batch dissolution tests were conducted continuously for 2 months. Each sample (2 mL) was collected at different times of 3, 12, 24, 72, 168, 336, 528, 672, 842, 1008, 1176, and 1344 h from different dissolution batches and the same volume of the appropriate background solution was added to keep the total volume constant. All the collected samples were filtered using a 0.45-μm PVDF syringe filter and diluted with 4.5 M HNO_3 solution before uranium analysis using ICP-MS.

2.3.2. Groundwater and H_2O_2–spiked groundwater conditions

Synthesized groundwater was prepared using reagent-grade chemicals to simulate a typical natural granitic groundwater (Table 1) obtained from a borehole in the Korea Atomic Energy Research Institute (KAERI) Underground Research Tunnel (KURT) (Kim et al., 2010). The Geochemist's SpreadSheet (GSS) program and SpecE8 program of the Geochemist's Workbench (GWB) software were used to develop a recipe for synthetic groundwater. This mimicked groundwater solution was completely mixed on a platform shaker using a magnetic stirring bar for 24 h at room temperature, then filtered using nylon-membrane filter paper (0.45 μm) before use.

The synthesized groundwater was used for dissolution tests with 1:50 ratio of studtite (1 mg) powder in 50 mL of filtered groundwater under both anoxic and oxic conditions. Anoxic conditions were maintained by preparing the sample inside an Ar-filled glove box (4% H_2 + 96% Ar gas); before the studtite was added, the water was deaerated by Ar-gas sparging and left for 1 day inside the glove box. Oxic conditions were obtained naturally by performing the dissolution tests open to the atmosphere. The dissolution experiments were performed at room temperature and the initial pH was continuously maintained by adding 0.1 M NaOH or 4.5 M HNO_3 as needed. As in the previous