



Chlorite alteration in aqueous solutions and uranium removal by altered chlorite



Eungyeong Kim^a, Hyangsig Ahn^a, Ho Young Jo^{a,*}, Ji-Hun Ryu^b, Yong-Kwon Koh^b

^a Department of Earth and Environmental Sciences, Korea University, Anam-dong, Seongbuk-gu, Seoul 02841, Republic of Korea

^b Korea Atomic Energy Research Institute, 1045 Daedeokdaero, Yuseong-gu, Daejeon 34057, Republic of Korea

HIGHLIGHTS

- Chlorite alteration and the U removal capacity of altered chlorite were investigated.
- Initial pH affected more chlorite dissolution than ionic strength.
- Chlorite dissolution at $\text{pH}_0 = 3\text{--}8$ was inversely proportional to the U removal capacity.
- Chlorite dissolution at $\text{pH}_0 = 10$ was proportional to the U removal capacity.
- The formation of Fe-containing secondary minerals affected the U removal capacity.

ARTICLE INFO

Article history:

Received 4 October 2016

Received in revised form

23 December 2016

Accepted 24 December 2016

Available online 26 December 2016

Keywords:

Chlorite

Alteration

Dissolution

Uranium

Sorption

ABSTRACT

Chlorite alteration and the U removal capacity of altered chlorite were investigated. Batch kinetic dissolution tests using clinocllore CCa-2 were conducted for 60 days in aqueous solutions of various pHs and ionic strengths. Batch sorption tests using these altered chlorite samples were conducted for 48 h with natural groundwater containing 3.06×10^{-6} M U. Chlorite dissolution was influenced more by pH_0 than by the ionic strength of the solution. TEM analysis revealed Fe(oxy)hydroxide aggregates in the solid residue from the batch dissolution test with 0.1 M NaClO_4 solution at $\text{pH}_0 = 10$. The U removal capacity of the reacted chlorite samples at $\text{pH}_0 = 6\text{--}10$ was higher than that of the reacted chlorite samples at $\text{pH}_0 = 3$. The degree of dissolution of chlorite samples reacted at $\text{pH}_0 = 3\text{--}8$ was inversely proportional to the U removal capacity, but that of chlorite samples reacted at $\text{pH}_0 = 10$ was proportional to the U removal capacity. The positive correlation between the U removal capacity and degree of chlorite dissolution at $\text{pH}_0 = 10$ might be due to the formation of Fe-containing secondary minerals and changes in the reactive sites.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

High-level radioactive wastes (HLRWs) should be kept isolated from the biosphere for a very long duration because of their long-term toxicity. A deep disposal facility for HLRWs (i.e., deep geological repository) has been considered as a long-term isolation option in many countries to prevent the migration of radionuclides into the biosphere.

Granite is considered a suitable host rock for deep geological repositories of HLRWs [1], and has been investigated as a potential host rock for a deep geological repository in South Korea [2]. Chlorite, which contains ferrous iron (Fe(II)), is a

major fracture-filling mineral in granite fractures. Chlorite has a 2:1:1 sheet structure, which is composed of talc-like layers (TOT: tetrahedral–octahedral–tetrahedral layers) and brucite-like layers (O: octahedral layers). Fe(II) is located in the octahedral sheet of the chlorite structure [3].

A deep geological repository can be affected by natural environmental processes (e.g., physical and chemical weathering processes) under natural conditions. Moreover, chlorite can be altered under natural conditions, which can cause various transitions in the surrounding environments: (1) chlorite dissolution affects the composition of groundwater and (2) secondary minerals are formed by redox processes [4–8]. Chlorite, which contains oxidizing ions (e.g., Fe(II)), can help to maintain reducing conditions in a deep geological repository through such dissolution and redox processes. Dissolution is an initial step for the formation of secondary minerals through the redox processes. Thus, the degree of

* Corresponding author.

E-mail address: hyjo@korea.ac.kr (H.Y. Jo).

dissolution can directly affect the formation of secondary minerals, which are related to the retardation of radionuclide migration.

Secondary minerals are formed due to mineral dissolution, and these secondary minerals generally have small particle sizes and large specific surface areas [9]. Uranium (U) can be sorbed onto chlorite and Fe-containing secondary minerals [10,11]. Krawczyk-Bärsch et al. [9] reported that Fe(oxy)hydroxides are formed by chemical weathering of chlorite and that the formed Fe(oxy)hydroxides sorb uranium. However, not many studies were performed to evaluate how the conditions of chlorite alteration affected the U removal capacity.

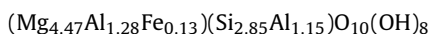
The objectives of this study were to evaluate the degree and kinetics of chlorite dissolution in aqueous solutions with various pH values and ionic strengths and to determine how chlorite alteration affects the U removal capacity. The pH of the groundwater can be affected by various substances (e.g., CO₂, sulfide minerals, and cement materials). The dissolution of CO₂ and sulfide minerals causes acidic conditions, whereas the dissolution of cement materials causes alkaline conditions. Cement materials can be used for the construction of deep geological repositories and to seal fractures, which can act as water flow pathways. In addition, seawater intrusion can cause a significant increase in the ionic strength of groundwater.

2. Materials and methods

2.1. Chlorite

The clinocllore chlorite (CCa-2) used in this study was obtained from the Source Clays Repository of The Clay Minerals Society at El Dorado County, California, USA. The chlorite was crushed and ground using a grinding machine. The ground chlorite was passed through a US #200 sieve to obtain particle sizes of less than 75 μm.

The mineral composition of the chlorite sample was determined using an X-ray fluorescence spectrometer (XRF; PW2404 Philips) at the Korea Basic Science Institute (KBSI), Seoul, South Korea. The chemical formula of chlorite was calculated based on the XRF results shown in Table 1 using the method described in detail by Foster [12]. The calculated chemical formula of chlorite used in this study is:



The mineral content was determined using an X-ray diffractometer (XRD; Philips X'Pert PW3040/00) at KBSI, Seoul. The XRD results indicate that the chlorite sample was composed mostly of clinocllore (Fig. 1). The specific surface area of the chlorite powder sample (<75 μm) determined by Brunauer-Emmett-Teller (BET) analysis using N₂ gas was 8.0 ± 0.04 m²/g. The morphology of the chlorite sample was analyzed using a scanning electron microscope/energy dispersive X-ray spectrometer (SEM/EDS; Quanta 250 FEG) at the Green Manufacturing Research Center (GMRC) of Korea University, Seoul.

Table 1
Chemical composition of unreacted chlorite obtained by XRF analysis.

Material	Chemical composition (%)						
	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃ ^a	TiO ₂	L.O.I. ^b	Total
Unreacted chlorite	29.9	21.7	31.5	1.8	0.3	12.9	98.1

^a Total Fe.

^b Loss on ignition.

2.2. Batch kinetic dissolution tests

Batch kinetic dissolution tests were conducted using the chlorite powder sample in aqueous solution at various pH values (3–10) and ionic strengths (0–0.2 M). Deionized (DI) water was used as a reference solution. NaClO₄ solution was used to control the ionic strength of the solution, and 0.1 and 0.2 M NaClO₄ solutions were prepared by dissolving NaClO₄ powder in DI water. Concentrated HCl and NaOH solutions were used to adjust the pH of the solution. The pH and electrical conductivity (EC) of the solutions before and after the batch kinetic tests were measured using pH/pH/conductivity portable meter (Orion).

The solution was poured into a 250 mL polypropylene copolymer centrifuge bottle that contained 3 g of the chlorite powder, which was vacuum-dried, corresponding to a solid-to-liquid ratio of 12.5 g/L. The centrifuge bottles containing the chlorite and solution mixtures were shaken using a precise shaking incubator (WIS-10RL) at 120 rpm. A total of 63 batch kinetic dissolution tests were conducted at 25 °C for various reaction times ranging from 30 min to 60 days. The centrifuge bottles were shaken by hand for about 1 min every day at the same time to disperse chlorite powder homogeneously in the solution. The tests were terminated at the designated reaction time (30 min and 10, 20, 30, 40, 50, and 60 days).

After terminating the test, the pH and EC of each mixture were measured in an anaerobic glove box that was filled with nitrogen gas. The mixture was then centrifuged using a centrifuge (MEGA 21R) for 1 h at 2500 rpm to separate the supernatant and solid particles. The solid particles after centrifuging were vacuum-dried and then stored in a 50 mL conical tube for material characterization and batch U sorption tests. The supernatant was filtered using a 0.45 μm membrane filter (Advantec®). Nitric acid was added to the filtered liquid to obtain pH < 2. The filtered liquid was stored in a refrigerator at approximately 4 °C for chemical analysis. The solid residue remaining on the membrane filter was vacuum-dried and then stored in a glass box for material characterization.

The concentrations of magnesium (Mg) and silicon (Si) in the supernatant samples were analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES; Optima 7300 DV, Optima 3300 DV) at the inter-university facility of Chungnam National University, Daejeon, South Korea. The concentrations of Al and Fe in the supernatant samples were analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS; Elan DRC II, Perkin Elmer) at KBSI, Seoul. The mineral components of the solid particles obtained after centrifuging was analyzed using XRD at KBSI, Seoul. The morphology and composition of the solid residue remaining on the membrane filter were analyzed using SEM/EDS at GMRC of Korea University and a field emission transmission electron microscope (FE-TEM; JEM-2000EX or JEM-3010, JEOL) at KBSI, Seoul. The samples for TEM were prepared by placing a drop of aqueous solution with the solid residue onto a 400 mesh carbon-coated copper grid.

2.3. Batch U sorption tests

Batch U sorption tests were conducted on the unreacted and reacted chlorite samples obtained after the batch kinetic dissolution tests using 0, 0.1, and 0.2 M NaClO₄ solutions at various pH values (3–10). The pH of the groundwater sample used in this study was 7.9.

The concentrations of the cations and anions in the groundwater sample were analyzed using ICP-AES and ICP-MS at KBSI, Seoul and ion chromatography (IC) at Korea University. The groundwater sample mainly contained calcium (Ca), sodium (Na), magnesium (Mg), silicon (Si), and potassium (K). The U concentration was 728.7 μg/L (Table 2). The U species in the groundwater sample

Download English Version:

<https://daneshyari.com/en/article/4979824>

Download Persian Version:

<https://daneshyari.com/article/4979824>

[Daneshyari.com](https://daneshyari.com)