Corrosion of copper and authigenic sulfide mineral growth in hydrothermal bentonite experiments

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HIGHLIGHTS

- Experiments run at 300 °C and 150 bars for up to six weeks.
- Copper degrades to chalcocite (CuS2) and minor covellite (CuS) in presence of H2S.
- Corrosion rates between 8.8 and 116 μm/yr.
- Rate dependent on experiment duration, brine composition, and clay type.
- Sulfide corrosion products may inhibit further corrosion of copper.

ARTICLE INFO

ABSTRACT

The focus of this experimental work is to characterize interaction of bentonite with possible used-fuel waste container materials. Experiments were performed up to 300 °C at 150—160 bars for five to six weeks. Bentonite was saturated with a 1900 ppm K-Ca-Na-Cl-bearing water with Cu-foils. Copper rapidly degrades into chalcocite (CuS_2) and minor covellite (CuS) in the presence of H_2S. Chalcocite growth and corrosion pit depths were measured for four different experimental runs yielding corrosion rates between 8.8 and 116 μm/yr depending on duration of experiment, brine composition, and clay type (bentonite vs. Opalinus Clay). Results of this research show that although pit-corrosion is demonstrated on Cu substrates, experiments show that the reactions that ensue, and the formation of minerals that develop, are extraordinarily slow. This supports the use of Cu in nuclide-containment systems as a possible engineered barrier system material.

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1. Introduction

The United States' Department of Energy initiated the Used Fuel Disposition campaign to evaluate various generic geological repositories for the permanent disposal of used nuclear fuel and wastes. The development and evaluation of engineered barrier system (EBS) design concepts and their potential interactions with the natural barrier or with other EBS interfaces are inherently important to the long-term (i.e., tens of thousands of years) safety and performance assessment of the safety case [5]. One idea for a

high-level nuclear waste repository is to pack Dual Purpose Canisters with bentonite in an underground repository [7,17]. Dual purpose canister designs vary but most proposed canisters will be constructed from steel or stainless steel with a steel reinforced concrete overpack [21]. Copper cladding is added to the steel canister in several EBS design concepts [36]. Many of the European concepts are limited to four spent fuel assemblies (4 pressurized water reactors (4-PWR)), but these canisters can house up to 32 spent fuel assemblies (32-PWR) [17,36]. This increase in load of used fuel assemblies will generate a large amount of heat radiating into the EBS and the host rock. High-level thermal modeling suggests a 32-PWR waste package in a clay/shale host rock at 60 GW-days per metric ton burnup can heat the host rock to 299 °C within 1 m from the waste package after 85 years (25 years ventilation; 15 m package spacing) [17]. This is just one of many designs for a

U.S. nuclear repository but this particular model provides for a high temperature scenario. The long-term repository safety relies upon continued canister integrity while in contact with bentonite under repository conditions (e.g., increased temperatures, pressures, and radioactivity). The focus of this experimental work is to characterize the interaction between bentonite and copper and determine copper corrosion rates under elevated temperatures (up to 300 °C) and pressures (150—160 bars) associated with a shallow geological repository.

Copper corrosion has been studied extensively as a canister material for long-term disposal of radioactive waste [25,27,28,32,40—42]. For instance, [24,32]; and the review of [29] describe the effects of sulfides on copper corrosion. In the context of subsurface nuclear waste disposal, these authors attributed the source of sulfide ions and other S-bearing aqueous species in the bentonite clay barrier to dissolution of pyrite where it is present as an accessory mineral [32]. determined that sulfur-bearing species (e.g., (poly)-sulfides, -sulfates) associated with pyrite dissolution are among the most important to "activate" copper corrosion in repository environments. These studies also highlighted the importance of solution chemistry and the fact that pore solutions in subsurface repository setting are expected to be chloride-bearing. Studies performed by Ref. [30] show that copper corrosion is limited by copper diffusion away from the metal surface developing a chemical gradient away from the copper surfaces. Many factors therefore have an ability to control corrosion rates by either attacking the metal directly or influencing Cu diffusion. However, it was suggested [30] that under certain chemical conditions copper corrosion rates are independent from temperature and bentonite bulk density. The primary corrosive agents associated within a bentonite environments are oxygen, sulfur (i.e., sulfide), and chloride.

2. Methods

2.1. Experimental setup

Because the experiments were performed for a generic repository scenario, we sought to maximize peak temperature beyond expected canister maximum temperature. The pressure used would simulate hydrostatic pressure in a closed repository at 600 m. Additionally, clay/water ratio was set to saturate the bentonite. The intent of these conditions was to maximize copper corrosion and therefore provide a conservative limit. Much of the experimental setup was previously characterized in Ref. [11]; but key points are summarized here. The bentonite clay used originates from a reduced horizon in Colony, Wyoming and contained 0.4 wt % pyrite [11]. One experiment included Opalinus clay as a wall rock component (pyrite content of 1.1 wt %) and comprised 20% of the clay component (Table 2). The synthetic solution composition was chosen to represent that of a deep groundwater in crystalline rock (Table 1), Stripa sample V2 (69-4) [15], but not specifically the Stripa site and loaded at a 9:1 water: bentonite mass ratio. The redox conditions for each system were buffered using a 1:1 mixture by mass of Fe_3O_4 and iron-filings added at 7 wt % of the bentonite mass. Approximately 7 wt % of total mass Cu-foil was added to experiments representing the presence of a waste canister. Experiments were pressurized to 15.0—16.0 MPa (approximate lithostatic pressures for a shallow repository [26]) and were heated following three different temperature profiles: 1) ramped: 120 °C for two weeks, 210 °C for two weeks, and then 300 °C for one week, 2) isothermal: 300 °C for six weeks, and 3) long term cooling: 300 °C for four months, 210 °C for one month, and then 120 °C for one month. A summary of copper reaction conditions are summarized in Table 2.

Table 1
Synthetic groundwater compositions used in the experiments.

Species	Stripa V2.1	Stripa V2.3	Stripa V2.4	Opalinus Clay
	mg/L	mg/L	mg/L	mg/L
Ca^{2+}	93	43	61	426
Cl^-	931	686	882	6470
K^+	583	299	559	225
Na^+	171	162	201	3846
Si	1	2	1	1
SO_4^{2-}	46	31	53	998
Sr^{2+}	0.05	<0.05	0.06	0.16
TDS	1863	1226	1759	12153
pH	7.35	6.93	11.2	7.50
Experiment	**EBS 4**	**EBS 11**	**EBS 16**	**EBS 17**

2.2. Solids characterization

2.2.1. Mineral compositions of the pre- and post-reactant materials were determined using three methods

X-ray diffraction (XRD) analyses of experimental materials determined mineral compositions. Metal plates after hydrothermal reactions were mounted to an open aluminum holder and analyzed as is to capture the undamaged corrosion products. XRD measurements were conducted with a Siemens D500 diffractometer using Cu-Kα radiation. Data were collected from 2 to 70 °2θ with a 0.02 °2θ step-size and count times of 8—12 s per step.

Electron microscopic analyses were performed using a FEI™ Inspect F scanning electron microscope (SEM). All samples were Au-coated prior to SEM analysis. Imaging with the SEM was performed using a 5.0 kV accelerating voltage and 1.5 spot size. Energy dispersive X-ray spectroscopy (EDX) was performed at 30 kV and a 3.0 spot size.

Electron microprobe analyses were performed at the University of Oklahoma using a Cameca SX50 electron microprobe equipped with five wavelength-dispersive spectrometers and PGT PRISM 2000 energy-dispersive X-ray detector. Chemical analysis was performed using 20 kV accelerating voltage, 20 nA beam current, and 2 μm spot size (Table 3).

2.2.2. Corrosion rate determination

Post-reaction copper foils were mounted in epoxy then polished exposing the cross-sectioned surfaces. These foil mounts were then imaged using two different methods; SEM and reflected light microscopy. For each EBS run 17 to 25 images were taken for each method. These image locations were mapped and chosen to give a random distribution of the corrosion in the foils. All images were saved and analyzed in Photoshop. Each image had 7-20 data points extracted from it. The thickness of the chalcocite layer and the depth of the corrosion pitting were measured and then labeled for future analysis. Corrosion rates were determined by dividing the average corrosion pit depth by the number of days in the run.

3. Results

3.1. Copper reaction with bentonite

The primary corrosion product for all experiments was chalcocite (Cu_2S) with minor covellite (CuS) appearing in some runs (EBS-17) (Fig. 1). Other copper sulfide phases such as djurleite, anilite, and digenite were not detected in the run products. Djurleite and anilite are expected to be unstable at the temperature conditions of these experiments Sato 1992.

Chalcocite formed a hexagonal morphology ranging from discrete plates to completely coalesced patches on the copper