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

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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 1,900 ppm K-Ca-Na-Cl-bearing water with Cu-foils. Copper rapidly degrades into chalcocite (Cu₂S) and minor covellite (CuS) in the presence of H₂S. Chalcocite growth and corrosion pit depths were measured for four different experimental runs yielding corrosion rates between 8.8-116 µm/yr. depending on duration of experiment, brine composition, and clay type (bentonite vs. Opalinus Clay). Results of this research show that nuclear waste containers act as a substrate for mineral growth in response to corrosion and that Cu canisters are a possible engineered barrier system material.

Keywords: Corrosion; copper; bentonite; hydrothermal experiment; engineered barrier; canister

1.0 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 (Börjesson et al. 2010). One idea for high-level nuclear waste repository is to pack Dual Purpose Canisters with bentonite in an underground repository (Carlsson 2008; Greenburg and Wen 2013). Dual purpose canister designs vary but most proposed canisters will be constructed from steel or stainless steel with a steel reinforced

concrete overpack (IAEA 2000). Copper cladding is added to the steel canister in several EBS design concepts (Pusch 2008). 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) (Pusch 2008; Greenburg and Wen 2013). 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 gigawatt-days per metric ton burnup can heat the host rock to 299°C within 1 meter from the waste package after 85 years (25 years ventilation; 15 m package spacing) (Greenberg and Wen 2013). 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 (King, 2007; King, et al. 2010; King and Lilja, 2011; Macdonald and Sharifi-Asl, 2011; Schwartz, 1996, 2008; Scully and Edwards, 2013). For instance, Macdonald and Sharifi-Asl (2011), King (2005), and the review of King et al. (2013) 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. Macdonald and Sharifi-Asl (2011) 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 King et al. (1992) 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 (King et al., 1992) 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.

2.0 Methods

2.1 Experimental setup

Much of the experimental setup was previously characterized in Cheshire et al. (2014), but key points are summarized here. The bentonite clay used originates from a reduced horizon in Colony, Wyoming. One experiment included Opalinus clay as a wall rock component 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), Frappe et al. 2003) 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 (King et al. 2001)) 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.

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-K α radiation. Data were collected from 2 to 70 °2 θ with a 0.02 °2 θ step-size and count times of 8 to 12 seconds per step.

Electron microscopic analyses were performed using a FEITM 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 μ m 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.

3.0 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) (Figure 1). Chalcocite formed a hexagonal morphology ranging from discrete plates to completely coalesced patches on the copper surface (Figure 2A & C). Chalcocite crystallized on the copper surfaces due to available H_2S from the decomposition of pyrite in the hydrothermal environment. It is evident that the formation of these surface bound minerals was from the direct crystallization from solution in the localized environments surrounding the metal plates.

There were minor amounts of an unknown fibrous material associated with the copper surface (Figure 2B). Corrosion seemed to take place with an initial dissolution of the copper developing dissolution features on the copper surface (Figure 2A).

3.2 Copper corrosion

The thickness of the chalcocite layer and the depth of the corrosion pits varied with both temperature profile and experiment duration. In most of the experiments the chalcocite forms a thick layer over a corroded/pitted layer. This layer is visible both in the SEM images of Cu corrosion (Figure 3) and the reflected light images (Figure 4). A notable exception to this is the Opalinus Clay run, EBS-17, where the chalcocite layer was found to be either absent or extremely thick. For the ramped temperature experiment, EBS-4, the average chalcocite thickness was $3.0(1) \mu\text{m}$. In the isothermal experiments in both bentonite (EBS-11) and Opalinus Clay (EBS-17), the layer was thicker, $8.2(4) \mu\text{m}$ and $5.6(4) \mu\text{m}$ respectively. The chalcocite layer was thinner in the six-month long-term cooling run (EBS-16) with a depth of only $2.6(1) \mu\text{m}$.

Chalcocite layer thickness generally correlated with the amount of pit corrosion the Cu foil had undergone, but also depended on the sulfur content of the system. The initial overall thicknesses of the copper foils was $\sim 63 \mu\text{m}$. For EBS-16 and EBS-17, the width of the corrosion pitting was also measured to give an approximate aspect ratio for the corrosion pits. Both the thickness of the chalcocite and the depth of the pits formed approximately normal distributions for all EBS runs, giving confidence that a random distribution was measured. The only run differing from this pattern was EBS-17, which exhibited two different corrosion environments. One averaged a corrosion pit depth of $9 \mu\text{m}$, which is in alignment with the copper corrosion measurements on other EBS runs. The other behavior resulted in significant pitting depths up to and above $25 \mu\text{m}$. For the four experiments a total of 849 measurements were made, 414 of the chalcocite layer and 445 of the pit depths. The short-term isothermal experiments in both bentonite and Opalinus Clay yielded similar average pit corrosion depths, $13.5(6) \mu\text{m}$ and $13.1(6) \mu\text{m}$ respectively. The ramped experiment (EBS-4) incurred less corrosion, having an average pit depth of only $5.7(2) \mu\text{m}$. However, the six-month experiment (EBS-16) copper foils

developed only 4.3(1) μm corrosion depths, which is similar to that of EBS-4, but sustained over a much longer period of time. Pitting corrosion was restricted to the exterior surfaces of the rolled copper foil. The surfaces within the rolled copper foil were protected from the brine and thus did not suffer significantly from either chloride or sulfide attack.

Corrosion rates (Table 4) were determined by dividing the average corrosion pit depth by the number of days in the run. Corrosion rates from the two isothermal experiments on bentonite and Opalinus Clay are within experimental error of each other and displays the highest corrosion rates measured. Copper foils from the Opalinus Clay experiments exhibited several regions of extreme corrosion (Figures 3D and 4D). These parts of the copper foil were corroded > 50% and show deep channeling in the Cu foil. The corrosion rate for the five week ramped experiment (EBS-4) was half that of the isothermal experiments, 0.16(6) $\mu\text{m}/\text{day}$ for the ramped versus $\sim$ 0.31 $\mu\text{m}/\text{day}$ for the isothermal experiments. The six-month long-term cooling experiment had a much smaller average corrosion rate of 0.024(8) $\mu\text{m}/\text{day}$. This is consistent with the reduced corrosion found in the long-term experiment.

The nature of corrosion pitting in the copper foils was similar for all experiments. The average aspect ratio of the width to the depth of the corrosion pits found in the experiment with the least corrosion, the six-month extended cooling run, was 1.4(9). The run with the most corrosion, the six week Opalinus Clay run, had a nearly identical aspect ratio of 1.3(8). The similarity of these aspect ratios indicates that although more rapid corrosion is occurring during the six-week experiment, the pit shapes are unaffected by rate and retains the same nature regardless of the amount of corrosion the copper foil has undergone. A wide variety of corrosion pit structures exist, but extremely deep corrosion pits are just as common as shallow wide ones.

4.0 Discussion

4.1 Copper interactions

Copper corrosion in a sulfide-bearing, compacted bentonite environment has been suggested to be a function of both sulfate reducing bacteria growth conditions (e.g., available carbon, sulfate concentrations, and electron donors) and geochemical parameters effecting sulfide diffusion (e.g., bentonite density, fluid content, and ferrous iron concentrations) to the copper surfaces (Pederson 2010). Overall reactions associated with sulfide-induced copper corrosion involving chalcocite (Cu_2S) formation can be written as,

One reason for listing these three reactions is to denote the importance of H_2S , HS^- , and S^{2-} on activating copper corrosion and the appearance of chalcocite ($\text{Cu}_2\text{S}_{(\text{s})}$) as the product sulfide solid (Macdonald and Sharifi-Asl, 2011). Under anoxic and high temperature repository conditions, chloride and sulfide corrosion will be the primary (non-radiolytic) mechanism affecting copper waste canisters (King et.al, 2010). Biotic sulfate reduction mechanisms probably will be minimal at high-temperature conditions; therefore the dominant sulfide source is likely from sulfide minerals associated with the original bentonite barrier material or the wall rock. The electrochemical mechanisms of copper corrosion in the case of interactions with sulfide- and chloride-bearing solutions under anaerobic conditions have been advanced by Chen et al. (2010, 2011a); Chen et al. (2011b); King (2010); King and Lilja (2011); King et al. (2013). Macdonald and Sharifi-Asl (2011) provides a comprehensive thermodynamic description of copper stability under various conditions including temperature effects. It is expected that in the presence of Cl^-

bearing pore solutions or brines, the predominant Cu aqueous complex under nominally anoxic conditions in the presence of bentonite clay and copper metal is CuCl_2^- (King et al., 2013; Schwartz, 2008). The appearance of chalcocite in copper corrosion experiments quantifying the formation of sulfide films has stimulated investigations to understand the effects of such film on the copper surface such as the influence on corrosion rates and mechanisms, and the level of protectiveness (Chen et al., 2011a). According to Chen et al. (2010, 2011a), the suggested reaction leading to the formation of chalcocite in Cu-Cl solutions can be expressed as:

The stepwise mechanism proposed by these authors involves adsorption of the Cu $(\text{HS})_{\text{ads}}$ species and its subsequent decomposition to CuCl_2^- and HS^- leading to $\text{Cu}_2\text{S}_{(s)}$ precipitation as described by reaction (2). However, other mechanisms based on the interaction with Cu-Cl solutions can potentially explain $\text{Cu}_2\text{S}_{(s)}$ film growth in the presence of Cu^+ and HS^- (e.g., $2\text{Cu}^+ + 2\text{HS}^- = \text{Cu}_2\text{S}_{(s)} + \text{H}_2\text{S}$). Chen et al. (2010) proposed a mechanism for $\text{Cu}_2\text{S}_{(s)}$ film growth with low porosity during the corrosion process. Although Chen et al. (2010) study suggest that growth of a porous $\text{Cu}_2\text{S}_{(s)}$ film can be described as diffusion-limited, the heterogeneous nature of the bentonite clay cover on the copper surface (in addition to porous $\text{Cu}_2\text{S}_{(s)}$) could allow for sufficient porosity for the transport of HS^- and copper aqueous species interacting with both $\text{Cu}_2\text{S}_{(s)}$ and copper metal interfaces. This observation is indicated by the growth habit of $\text{Cu}_2\text{S}_{(s)}$ between clay crystals identified in the current experimental work. Mitigating sulfide-induced corrosion might be achieved by maintaining a high bentonite density thereby restricting sulfide diffusion (Pederson 2010). However, given the dynamic nature of bentonite swelling, its porous nature, and moisture transport in the clay EBS such mitigation could be difficult to achieve.

The equilibria between copper metal, $\text{Cu}_2\text{S}_{(s)}$, and CuCl_2^- can be represented by the following reactions:

The Eh potential for the invariant point equilibria between copper metal, $\text{Cu}_2\text{S}_{(s)}$, and CuCl_2^- at 200 and 300 °C are depicted as Pourbaix diagrams in Figure 5 (a,b). As shown in these diagrams, the Eh potentials are relatively low at the three-phase invariant point, which decreases with increasing temperature. Moreover, the computed equilibrium pH at this invariant point shifts toward near-neutral values with increasing temperature. These diagrams were generated using the CHNOSZ software package (Dick, 2008) and associated thermodynamic database. The diagram was generated assuming activities of SO_4^{2-} , Cl^- , and Cu^+ of 1.0×10^{-6} , 0.2, and 1.0×10^{-6} , respectively. The aqueous species activities were constrained by the solute concentrations used in these experiments. Thermodynamic data for $\text{Cu}_2\text{S}_{(s)}$ in CHNOSZ is sourced to Helgeson et al. (1978).

One question regarding copper surface alteration is whether surface passivation occurs when considering in the long-term barrier material performance of a repository system. There was no substantial change in the mineral thicknesses or surface coverage on copper between the ramped and isothermal, 300°C experiments. The studies by Chen et al. (2010, 2011a) indicate similar mineral surface growth at lower temperatures. Mineral growth restrictions during experiments could possibly be from copper passivation, but can also be explained by depletion in the corrosive species or surface transport. In the case of copper, as sulfide is depleted from the system chloride (in an anoxic environment) becomes the primary corrosive agent, subsequently

altering the corrosion rate (King et al. 1992; Carlsson 2008). However, further work needs to be conducted to determine if surface passivation does develop in this system or rather a change in the chemical environment has altered the corrosion rates.

4.2 Corrosion rates

A multitude of studies have investigated copper corrosion rates. Many of these previous experiments focused on the corrosion of Cu in the air or seawater in application to industrial and naval uses (Kass 1990; Nunez et al. 2005; Sandberg et al. 2006). Copper corrosion has been studied with respect to sulfur and chlorine content in the context of both nuclear repositories and other saline industrial applications (Escobar et al. 1999; Abghari 2013; Bojnov and Makela 2003; Taniguchi and Kawasaki 2008; Chen et al. 2010, 2011a; Kumpulainen et al. 2011). Since long-term experiments on the scale of nuclear repository lifetimes are not possible, archeological findings on the wear of copper artifacts give the best long-term corrosion rates available (Demchenko et al. 2004; Hallberg 1988). The long-term corrosion rates found from these artifacts range from 0.01 to 1.51 $\mu\text{m}/\text{yr}$. The atmospheric and marine corrosion rates are even smaller than this, ranging from 0.0012 to 0.8 $\mu\text{m}/\text{yr}$. in marine water and atmosphere respectively (Nunez et al. 2005). While these rates provide a basic guideline for the corrosion of copper in the nuclear repository, these experiments are not specialized enough to give specific insight into the lifetime of the Cu canister in an EBS.

A handful of experiments have delved into the specific conditions found in repository environments: bentonite clay pack, saline groundwater and elevated temperatures/pressures. Kim et al. (2007) investigated copper corrosion in wet bentonite with synthetic and natural groundwater for 170 to 1231 days at 70°C. These long-term bentonite and saline brine experiments yielded corrosion rates an order of magnitude or more (0.18-0.87 $\mu\text{m}/\text{yr}$.) below

those found during the EBS runs in this study (8.8-116 $\mu\text{m}/\text{yr.}$). Kumpulainen et al. (2011) mixed MX-80 bentonite with 0.5 M NaCl solution for 8.2 years yielding a lower corrosion rate (0.035 $\mu\text{m}/\text{yr.}$) compared to the rates from Kim et al. (2007) and much smaller than rates determined from this study. While both Kim and Kumpulainen's experiments used materials found in an EBS, they did not implement environmental controls such as high temperature and MPa-scale pressures.

Rosborg et al. (2005; 2011) investigated copper bentonite combinations with saline ground water. Their studies yielded corrosion rates between 2.3-20 $\mu\text{m}/\text{yr.}$ for one 4.25 years experiment (range is due to measurement technique), which is in agreement with the long-term rate (EBS-16) found in this study. Rosborg et al. (2011) showed that bentonite mixed with oxic saline groundwater for 3 and 4.2 years, yielded copper corrosion rates of 0.4 and 1.6 $\mu\text{m}/\text{yr.}$, respectively. These rates are lower compared to the corrosion rates from the current study, but are of the same magnitude as the long-term (180 days) rate found in EBS-16. Taniguchi and Kawasaki (2008) studied mixtures of bentonite and sand with varying NaS_2 concentration at 80°C. As a control they also included a study of copper corrosion in a simple solution with varying NaS_2 concentration. They found corrosion rates increased with increasing NaS_2 concentrations, 15 $\mu\text{m}/\text{yr.}$ at 0.1 M NaS_2 and 0.55 $\mu\text{m}/\text{yr.}$ at 0.001 M NaS_2 . These results validate that sulfur concentrations play a major part in the corrosion process and that relatively high corrosion rates found in this study are likely influenced by the sulfur content of the brine and packing material during the run.

4.3 Factors Influencing Corrosion

Several environmental and compositional factors contribute to the higher corrosion rates found in this study. First of all, previous experimental data was collected at significantly lower

temperatures than those used in this study. For example, EBS-4 started at 25°C and increased to 300°C (573 K) before cooling. The other copper EBS runs all reached 300°C at the outset of the experiment. The highest temperature recorded in similar experiments is 80°C (353 K) used by Taniguchi and Kawasaki (2008) followed by 70°C (343 K) used by Kim et al. (2007). The experiments of Rosborg et al. (2005; 2011) did not use elevated temperatures. Elevated temperatures increase corrosion rates, especially at neutral to lower pH (Antonijevic and Petrovic 2008; Boulay and Edwards 2001). High temperatures used in this study were chosen to closely simulate a high heat load nuclear repository. The 299°C temperature estimate for a nuclear repository given by Greenberg and Wen (2013) indicate high temperatures better simulate the corrosion activity in a new repository. Other, slower, corrosion rates will only come into play as the heat dissipates over 100 year timescales. Thus, higher corrosion rates found for all EBS test cases are a representation of maximum potential corrosion in the repository scenario we developed, early failure at high temperature / high aqueous water influx due to hydrostatic pressure.

The high corrosion rates measured during this study are also influenced by pressure. The pressure during experimental runs was 15-16 MPa for all EBS runs. Few experimental studies have dealt with corrosion rates at pressures in the MPa range. A study by Betova et al. (2003) investigated the effect of saline groundwater compositions on copper corrosion with no clay included. These experiments were run at 14 MPa and 80°C, which is a good estimate for pressure within a repository if not the temperature. Nuclear waste repositories will likely be 400 to 700 m deep and have to withstand an evenly distributed load of 7 MPa hydrostatic pressure from groundwater and a 7 MPa pressure from swelling of the bentonite (King et al. 2002). Betova et al. (2003) measured corrosion rates of 5.5-17 µm/yr. over six days. These rates are within an

order of magnitude in agreement with the results from this study and indicate that elevated pressure may have more of an effect than previously estimated by King et al. (2002), who assumed the pressure effect to be ~ 10% based on theoretical estimates of equilibrium constants at pressure. Further experimental studies at pressure are needed to elucidate the effect of pressure on Cu corrosion.

The clay and brine composition also make a significant difference in corrosion rate. The brines used in the EBS 4, 11, 16 and 17 runs are listed in Table 1. The composition of the brine for the three bentonite runs (EBS 4, 11 and 16) was similar. The EBS-4 brine contained the highest concentration of Cl^- while the EBS-16 brine contained the highest concentration of sulfate. Despite the relatively sulfur and chloride rich compositions, both EBS-4 and EBS-16 underwent less corrosion than EBS-11. This effect is likely due to the differences in temperature profile and is not a sign of different corrosion behavior. The brine used in the Opalinus Clay experiment (EBS-17) was especially high in both chloride and sulfur, an order of magnitude higher in concentration. Several previous studies have concluded that increasing Cl and sulfur content increases the copper corrosion rate (Taniguchi and Kawasaki 2008; Abghari et al. 2013).

The increased corrosion in EBS-17, which shows corrosion tracks penetrating over half of the copper foil in some areas, is due to compositional differences in both brine and in clay. Added to the significant amount of Cl^- and SO_4^{2-} in the brine, these compositional differences explain the abundant corrosion of EBS-17. The corrosion of the outer copper foil of EBS-17 was uneven, leading to the interpretation that surface activation reactions by either chloride or sulfur species were inhibited or kinetically-hindered growth of $\text{Cu}_2\text{S}_{(s)}$ persisted locally throughout the foil's surface.

A final consideration for the corrosion rates measured is the duration of the experiments. A barrier system in a nuclear repository will be required to sustain for 10^5 to 10^6 years, but obviously no experiments can be run at those timescales. Extrapolation must then be used from measurements made on more human timescales in the laboratory. What timescale is best used becomes the essential question. Three experiment durations were used in this study: 5 weeks, 6 weeks and 6 months. The three 5-6 week experiments (EBS 4, 11 and 17) all yield corrosion rates between $0.16(6) - 0.32(15) \mu\text{m/day}$. EBS-16, however, has a much lower corrosion rate, only $0.024(8) \mu\text{m/day}$ or $8.8(3) \mu\text{m/year}$. A similar decrease in corrosion rate, although less dramatic, was observed by Kim et al. (2007). The wet bentonite with synthetic groundwater experiment lasting 188 days at 70°C had a corrosion rate of $0.87 \mu\text{m/year}$ while the experiment lasting 844 days yielded a corrosion rate of $0.18 \mu\text{m/year}$, an 80% reduction in rate. These results indicate that the duration of the experiment does matter and that long-term experiments are necessary to provide the best corrosion rates for extrapolation to long timescales. In addition, the reduced corrosion rate with time suggests the chalcocite layer formation does create a passivation layer that may be effective at repository timescales.

5.0 Conclusions

Mineral growth onto waste containers was influenced by the buffer material and fluid compositions, in addition to pressure and temperature conditions. Results of this research show that in the presence sulfide-bearing clay barrier, a copper waste container will act as a substrate for mineral growth in response to corrosion. It is evident from the corrosion product formed that sulfide- and chloride-activated corrosion, will take place at the canister-bentonite interface, thereby yielding harsh conditions at the interfacial regions of a bentonite-based repository

system. Nevertheless, the Cu canister can sustain low corrosion rates at the extreme conditions of novel repository concepts and is still a candidate EBS material.

These experimental runs show that passivation may occur on Cu waste canister surfaces in an EBS. Each run produced a buildup of chalcocite ($\text{Cu}_2\text{S}_{(s)}$) regardless of brine composition or clay type. The chalcocite layer was continuous, but thin in the 300° C six month run which yielded the lowest corrosion rate. Large amounts of chalcocite growth occurred in 6 week, 300° C run with Opalinus clay wall and related brine rock did not indicate effective passivation in the highly sulfur and chlorine rich environment. Nevertheless, the experiments show that passivation may occur in the long-term experiment (EBS-16) due to the limited chalcocite growth and low corrosion rate. The short time frame runs (5-6 week) showed intermediate chalcocite growth and intermediate corrosion, but had the same brine and clay composition as the 6 month run. This indicates that longer time scale experiments are needed to fully investigate the possibility of passivation on the Cu canister surface.

Corrosion rates found during these experiments are on consistent with those found in the literature for long-term experiments in a sulfide-rich environment ($\sim 10 \mu\text{m}/\text{year}$). Rates calculated from these runs are generally higher than those found in the literature, indicating that full-scale, long-term environmental experiments are needed to generate suitable corrosion rates for high load nuclear repositories. Experiments that focus on only one aspect of the corrosion process (e.g. sulfide concentration, chloride concentration, clay mixture, temperature, pressure, duration) are essential to distilling the effects of these factors on Cu corrosion, but lack the ability to accurately model the repository. These experiments combined many of these elements to yield corrosion rate and mineral growth measurements that are directly applicable to the newly envisioned nuclear repository concepts.

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	Stripa V2.1	Stripa V2.3	Stripa V2.4	Opalinus Clay
Species	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

485

486 Table 1. Synthetic groundwater compositions used in the experiments.

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	Bentonite, g	Opalinus Clay, g	Brine, g	Fe^o, g	Fe₃O₄, g	Cu, g	Run temp, °C	Run time
EBS-4	16.207		145.0	0.574	0.579	9.753	25/120/210/300/25	5 weeks
EBS-11	15.039		129.8	0.481	0.481	10.643	300	6 weeks
EBS-16	29.62		248.3	0.949	0.949	21.0	25/300/210/120/25	6 months
EBS-17	14.44	3.608	155.2	0.578	0.578	12.231	300	6 weeks

490

491 Table 2. Initial components and reaction conditions for EBS experiments. The iron components

492 were used as solid buffers.

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	EBS-4	EBS-11	EBS-16	EBS-17	495
O	0.02 (0.03)	0.04 (0.03)	0.22 (0.05)	0.23 (0.08)	496
S	21.36 (0.74)	20.70 (0.15)	20.35 (0.09)	21.03 (0.40)	497
Cu	78.78 (1.11)	80.72 (0.40)	80.11 (0.31)	78.49 (0.47)	498
Total	100.16 (0.44)	101.46 (0.45)	100.67 (0.25)	99.74 (0.42)	499
					500

501 Table 3. Electron microprobe analysis of sulfide corrosion products in EBS experiments. These
 502 are average values from a total of 80 analyses. Standard deviations in parentheses.
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	Chalcocite Thickness (um)	Pit Depth (um)	Corrosion rate (um/day)
EBS-4	3.0(0.1)	5.7(0.2)	0.16(0.6)
EBS-11	8.2(0.4)	13.5(0.6)	0.32(0.2)
EBS-16	2.6(0.1)	4.3(10.)	0.024(0.01)
EBS-17	5.6(0.4)	13.1(0.6)	0.31(0.1)

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Table 4. Chalcocite thickness, pit depth and corrosion rate. Standard deviation in parentheses.

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515 Figure 1. XRD plots for corrosion products on the copper foils used in the ramped heating (EBS-
516 4) and six week, 300°C heating (EBS-11) experiments. Chalcocite (Cu_2S) is the principal
517 corrosion phase.

518

Figure 2. SEM image (plan view) of copper surface showing corroded copper surfaces and various interface reaction products from both ramped (EBS-4) and isothermal, 300°C (EBS-8) heating profiles. A) Boundary between the corroded copper surface and chalcocite (Cu_2S) from EBS-4. B) Unknown fibers occurring on the copper surface in between chalcocite growths from EBS-4. These fibers might be a late-stage oxide or chloride corrosion product upon depletion of sulfide. C) Intergrown chalcocite from EBS-8. D) Atacamite (orthorhombic laths) resting on top of chalcocite crystals. Their growth is due to late stage scavenging of Cl from the brine.

Figure 3. SEM images from runs EBS-4 (A), EBS-11 (B), EBS-16 (C) and EBS-17(D). The overall thicknesses of the copper foils are $\sim 63 \mu\text{m}$. Surfaces within the rolled copper foil were relatively protected from sulfide attack.

Figure 4. Reflected light images of Cu corrosion. EBS-4 (A), EBS-11 (B), EBS-16 (C) and EBS-17 (D) with chalcocite layer (pale yellow). Copper color for images A and B, dark blue/black, images C and D, orange brown.

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 548 Figure 5. Eh-pH diagram for the Cu-S-Cl-H₂O system at (a) 200 and (b) 300°C (see text). Dotted
 549 lines denote the stability of H₂O. The black dot represent the invariant points for copper-Cu₂S_(s)-
 550 CuCl₂⁻ equilibrium.