

COPPER CORROSION IN SIMULATED ANOXIC GRANITIC GROUNDWATER

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Copper is considered as candidate material for waste packages in geological disposal systems for high-level radioactive waste. This paper reports independent analyses of copper as a potential waste package material based on literature review and experimental studies. Experimental tests of general corrosion, hydrogen generation, and scratch repassivation for copper samples were conducted under anoxic conditions using a synthetic saline groundwater based on reference compositions for deep groundwaters in crystalline rocks of the Canadian Shield. Results indicate that the copper corrosion rates in anoxic waters (less than 10 ppb of O₂), measured by electrochemical methods, could be higher than those reported in the literature at this O₂ level. Corrosion products were observed after the tests. This observation differs from statements in the literature that copper would experience little to no corrosion in a reducing environment. Hydrogen also was found to be generated by the corrosion process, albeit in very small amounts. Scratch repassivation tests show the film formed on copper exposed to this anoxic groundwater had very weak repassivation capability under polarization. More in-depth analyses are needed to improve understanding of copper corrosion in anoxic environments.

I. INTRODUCTION

Engineered barriers are typically designed to work with natural barriers to ensure isolation of high-level radioactive waste (HLW) from the biosphere. Waste packages are an important part of the engineered barrier system. Waste package materials could undergo chemical degradation (i.e., corrosion) when contacted by groundwater liquid and vapor phases. Long service lifetimes for waste packages help to limit radionuclide release to the biosphere, making corrosion of waste packages an important technical issue in HLW disposal.

Various factors determine the selection of waste package materials, including the corrosion behavior in the expected disposal environment. Worldwide, many proposed underground disposal repositories are to be located in the saturated zone far below the water table, at

depths where reducing groundwater chemistries are likely and the amount of dissolved O₂ available for corrosion is limited. Moreover, small amounts of dissolved O₂ either in the groundwater or introduced by repository operations would be relatively quickly depleted in a repository by a combination of waste package corrosion, aerobic microbial activity, and the oxidation of certain redox-sensitive minerals. The duration of an initial period of oxidizing conditions is broadly estimated to range from 1 to 1,000 years,¹ until the groundwater chemistry evolves to anoxic, reducing conditions. Various metal alloys, including those of copper, carbon steel and cast iron, stainless steels, and titanium have been considered as candidate waste package materials for saturated repositories². This paper focuses on copper corrosion in simulated anoxic granitic groundwater.

II. LITERATURE REVIEW

Copper has been proposed for use as a waste package material in a number of repository programs including those in Switzerland, Sweden, Finland, Japan, and Canada². Copper tends to corrode uniformly in Cl⁻ containing environments with little tendency to experience localized corrosion or stress corrosion cracking, giving copper an important advantage over other materials. The thermodynamic stability of copper in an O₂-free environment based on Pourbaix diagrams indicates copper is not reactive with water in this environment. This implies that copper could have extremely long container lifetimes in a wide range of host rock types. However, partly because of its susceptibility to microbially influenced corrosion, repository designs typically call for copper to be used in conjunction with a buffer material. Jung et al.³ examined literature data of copper corrosion in both oxic and anoxic environments for the development of a generic performance assessment model for a variety of potential HLW geological disposal systems^{4,5}. The constant corrosion rates for copper in anoxic environments were estimated to be 4×10^{-3} to 2×10^{-2} $\mu\text{m}/\text{yr}$ [2×10^{-4} to 8×10^{-4} mils/yr], with a pitting enhancement factor of 1, which means that pitting

³Retired

corrosion is assumed to occur at the same rate as general corrosion, under this environment.³

Copper is the material of choice for the waste container in the Swedish Nuclear Fuel and Waste Management Company (SKB)'s license application for long-term disposal of spent nuclear fuel.⁶ The SKB corrosion rate data are based on modeling (e.g., Pourbaix diagrams and thermodynamic data) and is expected to be very low. According to the low corrosion rate, copper waste containers with a 5 cm [2 in] thickness are predicted to maintain their integrity for nuclear waste containment for at least 100,000 years. In contrast, Hultquist et al.⁷ proposed, based on a different corrosion mechanism, that a copper container thickness of more than 1 m [39 in] might be required to achieve a durability of 100,000 years. Scully and Hicks⁸ conducted an independent review for the Swedish Radiation Safety Authority and recommended further work to resolve the controversy over the corrosion mechanisms in O₂-free water. However, King² commented that the difference on the extent of corrosion associated with the controversy over the different corrosion mechanisms is small because if copper corrosion proceeds via the copper corrosion mechanism proposed by Hultquist et al.⁷, the corrosion rate will eventually be limited by a separate process, the accumulation of hydrogen in contacting water.

Overall, although there has been considerable work on the corrosion behaviors of copper relevant to repository environments, two main issues are still actively being investigated:

1. Thermodynamic stability of copper in O₂-free pure water
2. Copper sulfide film passivity in sulfide-containing environments and the effect of chloride on sulfide film⁹

III. EXPERIMENTAL APPROACHES

III.A. Simulated Granitic Groundwater for Copper Corrosion Tests

Groundwaters worldwide in crystalline rocks are generally characterized by reducing conditions and by increased salinity with depth¹⁰. At a nominal repository depth {e.g., 500 m [1,640 ft]}, groundwaters may be at or near thermodynamic equilibrium with secondary mineral phases such as calcite (calcium carbonate) or gypsum (calcium sulfate), though dissolved carbonate and sulfate concentrations typically are variable but low. For example, SO₄²⁻ concentrations in Swedish groundwater samples from a nominal repository depth range from near 0 to values approaching 600 mg/L¹¹.

Designs for a repository constructed in a granitic host rock call for an engineered barrier such as Na-bentonite, a swelling clay material, to reduce the likelihood of advective transport near the waste containers. As groundwater saturates and reacts with the bentonite, dissolution and ion exchange reactions initially will alter the composition of near-field water contacting the container and, if the container fails, that of the water contacting the spent fuel waste form. For example, ion exchange reactions between Na-bentonite and the contacting Ca-rich water are likely to increase the dissolved Na concentration and decrease the dissolved Ca concentration. If the bentonite also contains some gypsum (CaSO₄·2H₂O), its dissolution will tend to increase the concentration of sulfate ions in the contacting water. These effects are the most pronounced in the early stages of saturation of the bentonite. As additional pore volumes of groundwater move through the bentonite over time, the near-field water chemistry will gradually evolve to a composition more similar to that of the surrounding groundwater.

For the copper corrosion experiments reported here, a solution composition was selected to be representative of a deep groundwater chemistry that is likely to occur at nominal repository depth in a massive crystalline bedrock such as granite¹². The solution composition is based on reference Canadian Shield groundwater compositions identified by nuclear waste management research programs^{13,14}, particularly the reference synthetic groundwater WN-1m, initially developed for use in sorption experiments from groundwater data collected over depths between 350 and 800 m [1,148 and 2,624 ft] below the surface in crystalline rocks of the Canadian Shield¹³. Its composition is in the mid-range of concentration values for analyzed Canadian Shield groundwaters at depth¹⁵, and it is at or near equilibrium with calcite. The simulated groundwater composition for this study and similar compositions in Gascoyne¹³ and NWMO¹⁴ are listed in Table 1.

Chemical reagents NaCl, KCl, Na₂SO₄, CaCl₂, MgCl₂·6H₂O, and NaHCO₃ were used to prepare this simulated groundwater. The pH was measured to be 6.65 at ambient temperature and pressure.

III.B. Open Circuit Potential and Corrosion Rate Measurement

Open circuit potential (OCP) was measured with the copper electrodes immersed in the granitic groundwater at 50 and 80 °C [122 and 176 °F], respectively. Electrochemical impedance spectroscopy (EIS) and linear

TABLE 1. Comparison of Three Reference Groundwaters for Deep Crystalline Rocks

Species	Concentration (M)		
	Reference Simulated Groundwater (This Study)	Synthetic Groundwater WN-1m*	Reference Deep Groundwater CR-10†
Na ⁺	8.0×10^{-2}	8.0×10^{-2}	8.0×10^{-2}
Ca ²⁺	1.0×10^{-2}	5.0×10^{-2}	5.0×10^{-2}
Mg ²⁺	3.0×10^{-3}	3.0×10^{-3}	2.5×10^{-3}
K ⁺	4.0×10^{-4}	4.0×10^{-4}	3.8×10^{-4}
Cl ⁻	9.2×10^{-2}	2.0×10^{-1}	2.0×10^{-1}
SO ₄ ²⁻	7.0×10^{-3}	9.0×10^{-3}	1.0×10^{-2}
HCO ₃ ⁻	8.9×10^{-4}	1.0×10^{-3}	1.1×10^{-3}

*Gascoyne, M. "Reference Groundwater Composition for a Depth of 500 m in the Whiteshell Research Area—Comparison With Synthetic Groundwater WN-1." Report AECL TR-463. Pinawa, Canada: Atomic Energy of Canada Limited. 1988.
 †NWMO. "Used Fuel Repository Conceptual Design and Postclosure Safety Assessment in Crystalline Rock." Pre-Project Report NWMO TR-2012-16. Toronto, Canada: Nuclear Waste Management Organization. 2012.

polarization resistance (LPR) were used to measure corrosion rates of copper exposed to deaerated solutions at 50 and 80 °C [122 and 176 °F]. OCP also was monitored during the tests while EIS and LPR were not conducted. Cylindrical electrodes of 6.4 mm [0.25 in] diameter and 50 mm [2 in] length machined from oxygen-free high conductivity pure copper rods were used as working electrodes in the tests. A 2-L [0.53-gal] glass cell equipped with a gas bubbler for deaerating, a condenser, a saturated calomel reference electrode (SCE), a platinum counter electrode, and a thermo well was used in the test. Fig. 1(a) shows an image of the test cell. The solution was deaerated with ultrahigh purity (UHP) argon before and during the test to achieve an anoxic condition. An oxygen meter with detection limit of 10 ppb was set at the exit of the argon gas from the solution to monitor oxygen concentration. The meter indicated that the oxygen concentration is below the detection limit after deaerating the solution for several hours. Daily monitoring shows the oxygen concentration was maintained below the detection limit of the oxygen sensor.

EIS was conducted at the OCP, using an alternating current voltage amplitude of 10 mV. The EIS data were fit to an equivalent electric circuit to obtain polarization resistance, R_p . LPR was performed between -10 to 10 mV versus OCP. The LPR data were fit linearly to obtain R_p . The corrosion rate was calculated in

accordance with ASTM G102 from R_p measured from both EIS and LPR¹⁶ assuming that (i) the current distributes uniformly across the surface area exposed to solution, (ii) both the anodic and cathodic Beta Tafel Constants are 120 mV/decade (i.e. the Stern-Geary constant is 0.027 V/decade), and (iii) the valence of the copper after oxidation in the corrosion process is 2+.

III.C. Hydrogen Generation Measurement

Hydrogen generated from the corrosion process was collected from a sealed autoclave and the concentration was quantified to determine the extent of hydrogen production. Copper foil was used in the test. The foil was 0.25 mm [0.01 in] thick, oxygen free, and had a copper concentration of 99.997 percent.

The autoclave cylinder and head were made from Hastelloy[®] (one nickel-based super alloy) and Type 316 stainless steel, respectively. A Teflon liner was set inside the cylinder to avoid direct solution contact with the nickel alloy. The volume of the autoclave was 2.1 L [0.55 gal] and the solution amount was 1.2 L [0.32 gal]. Before immersing the materials in solution, the solution was deaerated with UHP argon gas in a UHP nitrogen gas purged glove box. In the process of deaeration, the oxygen concentration was measured with the same type of oxygen meter used above. After both the oxygen concentration in the solution and the glove box reached 0, the autoclave was sealed in the glove box to achieve anoxic condition. The pressure vessel lid was fit with a thermo well and a calibrated pressure gauge for temperature and pressure monitoring. A needle valve for gas sampling and a pressure relief valve were connected to the autoclave. Fig. 1(b) shows an image of the autoclave with the vessel in the heater to achieve the desired temperature.

The gas from the vapor phase was sampled at 3 and 6 months using Tedlar[®] gas sampling bags and analyzed with gas chromatography immediately after sampling. The gas chromatography instrument used has a hydrogen detection limit of 0.01 volume percent. Some of the post-test copper foils were analyzed for hydrogen in the metal using Inert Gas Fusion method with detection limit of 0.1 ppb.

III.D. Scratch Repassivation Tests

A scratch repassivation test was used to investigate the repassivation capability of material film when it was

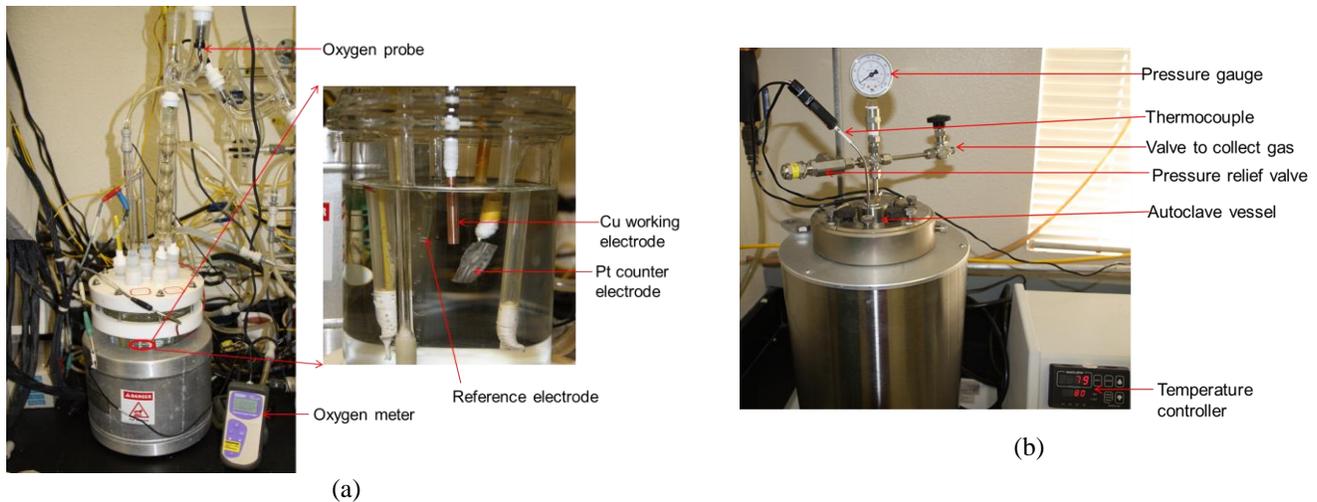


Fig. 1. Corrosion test cells (a) open circuit potential and electrochemical impedance spectroscopy measurement cell, (b) autoclave for hydrogen generation measurement

mechanically disrupted. The working electrode was a hollow cylindrical shaped specimen, machined from oxygen-free high conductivity pure copper rod with outer diameter of 9.52 mm [0.375 in] and height of 10 mm [0.4 in]. The scratch was scribed by impinging a diamond tip loaded on a stainless steel rod into a working electrode rotating at 30 revolutions per minute for 2 seconds; as such, one scratch was one complete revolution around the surface. Two minutes after the first scratch was scribed, another scratch was scribed at the same location. This process was repeated at another location on the same sample by shifting the sample vertically for each test specimen. At each scratch, the electrode was held at fixed potentials and the current was measured. All the tests were conducted at 50 °C [122 °F] in deaerated solutions.

IV. RESULTS AND DISCUSSION

IV.A. Open Circuit Potential and General Corrosion Rates at 50 and 80 °C [122 and 176 °F]

The OCP data at 50 and 80 °C [122 and 176 °F] are shown in Fig. 2. At both temperatures, OCP stabilized at $-0.26 \text{ V}_{\text{SCE}}$, but fluctuated during the entire testing process.

The first test for general corrosion rates measurement using EIS started at 50 °C [122 °F], then the temperature was elevated to 80 °C [176 °F]. In the second test, the test was repeated with both EIS and LPR measurements. The test duration at each temperature was 1 month with EIS and LPR measured every 10 days. The EIS data for the first test, shown in Fig. 3, had similar features, with one time constant in the measurement frequency range.

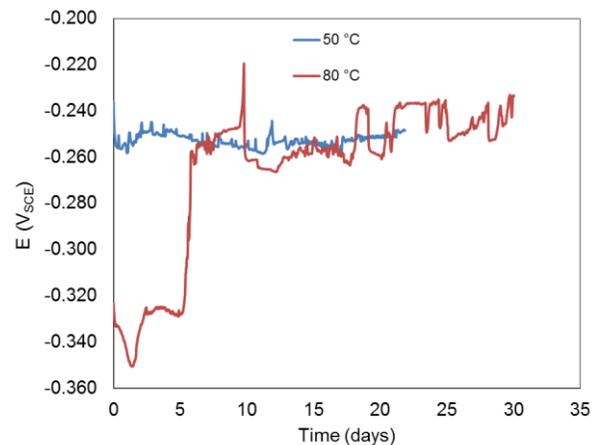


Fig. 2. OCP of copper exposed to simulated anoxic granitic groundwater at 50 and 80 °C [122 and 176 °F]

The data were fit with a one time-constant Randle-type circuit. Corrosion rates summarized in Table 2 were calculated from the polarization resistance using copper density, 8.94 g/cm^3 [0.32 lb/in³], and equivalent weight as 31.8 g [0.0701 lb]. The estimated corrosion rates are several $\mu\text{m/yr}$ [several hundredths of a mil/yr]. Considering the data uncertainty, there is no clear trend on temperature dependence of the corrosion rates.

In the second test, LPR measurement was performed after EIS. Over the small polarization range, the current response is near linear, which allows the data to be fit with a straight line to determine the polarization resistance. The corrosion rates calculated from the linear polarization curves also are included in Table 2. They

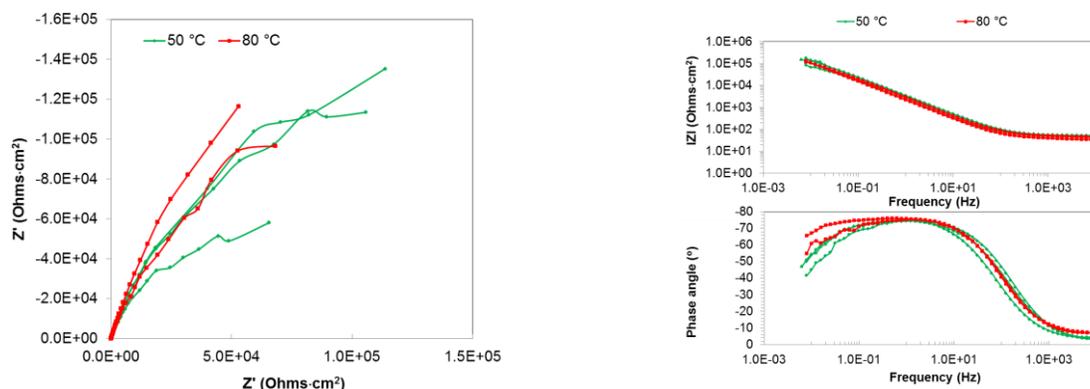


Fig. 3. Nyquist and bode plots of EIS of copper exposed to simulated anoxic granitic groundwater at 50 and 80 °C [122 and 176 °F]

TABLE 2. Corrosion Rates of Copper Exposed to Simulated Anoxic Granitic Groundwater

Temperature, °C [°F]		50 [122]			80 [176]		
Corrosion rate, $\mu\text{m/yr}$	Test 1	EIS	0.83	0.95	2.4	1.0	0.48
	Test 2	EIS	5.0	3.5	3.4	3.0	3.0
		LPR	5.3	5.1	4.9	6.7	
Average corrosion rate, $\mu\text{m/yr}$		3.5 ± 1.8			3.1 ± 2.3		

were very close to those measured using EIS, which provides further confidence on the measured corrosion rate data using EIS. One posttest specimen is shown in Fig. 4, as an example. The surface was tarnished with a black film in some areas, which could be CuO formed from the corrosion process. There were some white deposits on the specimen above the solution, which was due to the solution evaporation at elevated temperatures. Examination under optical microscope shows some localized features, but those features are too shallow to be characterized as pits.

IV.B. Analysis of Hydrogen Generated at 80 °C [176 °F]

The copper corrosion test duration in simulated anoxic granitic groundwater in an autoclave was 6 months. As the autoclave heated, the internal pressure increased. After the autoclave temperature stabilized at 80 °C [176 °F], the pressure remained steady at 0.48 atm [7.0 psi]. The pressure increase corresponding to the temperature is primarily from two sources: (i) the pressure of the nitrogen gas contained in the autoclave originally at 1 atm [14.7 psi] increased and (ii) water evaporated with increasing temperature. Using ideal gas law and the 0.9 L [0.24 gal] head space, the pressure increase from 20 to 80 °C [68 to 176 °F] is 0.20 atm [2.9 psi], which is lower than the total pressure increase. This means that water also evaporated into the head space at this temperature, which led to pressure increase of 0.28 atm [4.1 psi]. The relative humidity in the autoclave

was calculated to be 57 percent using water vapor partial pressure of 0.28 atm [4.1 psi]¹⁷ at the test temperature. At this relative humidity, the stainless steel head and the nickel alloy vessel corrosion should be negligible and does not contribute to any hydrogen generation.

Gas was sampled at 3 and 6 months for composition analysis. Hydrogen was detected in both samples. The hydrogen concentrations were 0.18 percent and 0.20 percent, respectively. Assuming corrosion of 1 mole of copper released 1 mole of electrons (i.e. generated 0.5 mole of hydrogen), the corrosion rates were calculated to be 0.076 and 0.084 $\mu\text{m/yr}$ [0.0030 and 0.0032 mils/yr], respectively.

The corrosion rates calculated from generated hydrogen are almost two orders of magnitude lower than that measured using EIS and LPR (shown in Table 2). This could be because the corrosion rates determined from hydrogen generation were at open circuit condition, but the corrosion rates measured from EIS and LPR were under small polarization condition. In addition, the generated hydrogen was not measured *in-situ* and chemical reaction (1) may not actually represent the actual copper corrosion mechanism, which could also lead to discrepancy of the corrosion rate. A small amount of hydrogen could have escaped during the test from the autoclave or during sampling and transfer process, which could lead to underestimating the corrosion rate. For the current test condition, 10 ml [0.34 oz] leakage of

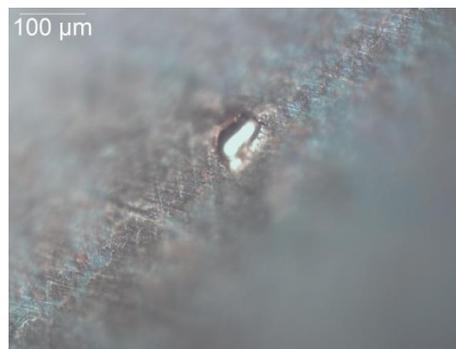
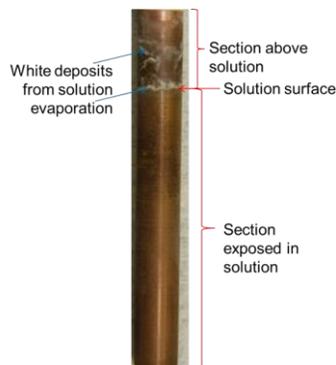


Fig. 4. Example of posttest copper electrodes after exposing to simulated anoxic granitic groundwater

hydrogen under standard conditions leads to a corrosion rate underestimate of $0.2 \mu\text{m}/\text{yr}$ [$0.01 \text{ mils}/\text{yr}$].

The test was stopped at 6 months. The post-test solution in the autoclave and the specimens are shown in Fig 5. The solution was still clear, but there was black powder at the bottom of the cell. The copper foil also was tarnished with a black film in some areas, which is consistent with observations shown in Fig. 4. Three post-test copper foils were analyzed for hydrogen content along with one base specimen. The tested specimens had hydrogen contents of 3, 3, and 5 ppm, but the untested specimen had a hydrogen content of 6 ppm. This indicates the hydrogen detected in the tested specimen may not all be from the corrosion process. Further analysis is needed to understand if hydrogen was absorbed by the copper during corrosion.

IV.C. Copper Scratch Repassivation at $50 \text{ }^\circ\text{C}$ [$122 \text{ }^\circ\text{F}$]

Scratches were scribed at potentials slightly above the OCP shown in Fig. 2. Fig. 6(a) shows the current versus time transient curves for copper when four successive scratches were made at two locations on the surface of the rotating working electrodes at applied potentials of -0.2 , -0.1 , and 0 V_{SCE} in deaerated simulated granitic groundwater at $50 \text{ }^\circ\text{C}$ [$122 \text{ }^\circ\text{F}$]. The current increased with the polarization potential. The peak current upon scratch was only clearly visible at $-0.2 \text{ V}_{\text{SCE}}$. At the other two higher potentials, the peak current was masked by the larger current. Fig. 6(b) is the expanded view of the first transient at -0.2 and $-0.1 \text{ V}_{\text{SCE}}$. The material only showed partial repassivation at $-0.2 \text{ V}_{\text{SCE}}$, with the base current increased after scratch. This test suggests the repassivation tendency for copper in the test environment is very weak. At higher potentials, there is no repassivation.

V. CONCLUSIONS

This study investigated copper corrosion in simulated anoxic granitic groundwater. General corrosion rate, hydrogen generation, and repassivation capability were studied using electrochemical methods. Specific conclusions follow:

Most of the corrosion rates of copper measured by electrochemical methods in O_2 -free simulated granitic groundwaters (O_2 less than 10 ppb) ranged from $1\text{--}5 \mu\text{m}/\text{yr}$ [$0.039\text{--}0.2 \text{ mils}/\text{yr}$]. At this O_2 level the rates are higher than the general corrosion rate ranges of 4×10^{-3} to $2 \times 10^{-2} \mu\text{m}/\text{yr}$ [2×10^{-4} to $8 \times 10^{-4} \text{ mils}/\text{yr}$] in the literature³ for reducing environments. These significantly higher copper corrosion rates are at odds with some arguments in the literature that copper would experience little to no corrosion in a reducing environment, but they agree with other literature statements that copper corrosion rates could be higher under such environments. The differences among reported corrosion rates could be related to factors such as differing methodologies or experimental solutions.

Hydrogen from copper immersion in the same O_2 -free simulated granitic groundwaters was detected from the vapor phase, but not in the metal. The corrosion rates calculated from generated hydrogen are two orders of magnitude lower than those measured using EIS and LPR, shown in Table 2. This could be because the corrosion rate determined from hydrogen generation is at open circuit condition, whereas the corrosion rates measured from EIS and LPR are under small polarization conditions. In addition, loss of small amounts of hydrogen could underestimate the corrosion rate. Copper showed little to no repassivation capability upon scratch under polarization. In all the tests, copper was corroded with black film covering the surface. More in-depth analyses are needed to improve understanding of copper corrosion in anoxic environments.

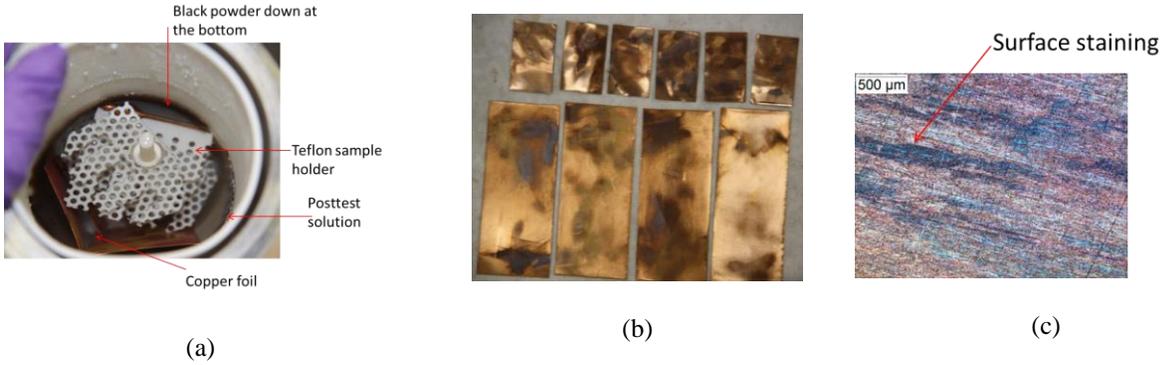


Fig. 5. Post-test solution and copper foils after exposure to simulated anoxic granitic groundwater at 80 °C [176 °F] for 6 months (a) copper foil in pressure vessel, (b) copper foil, (c) high magnification photo of copper

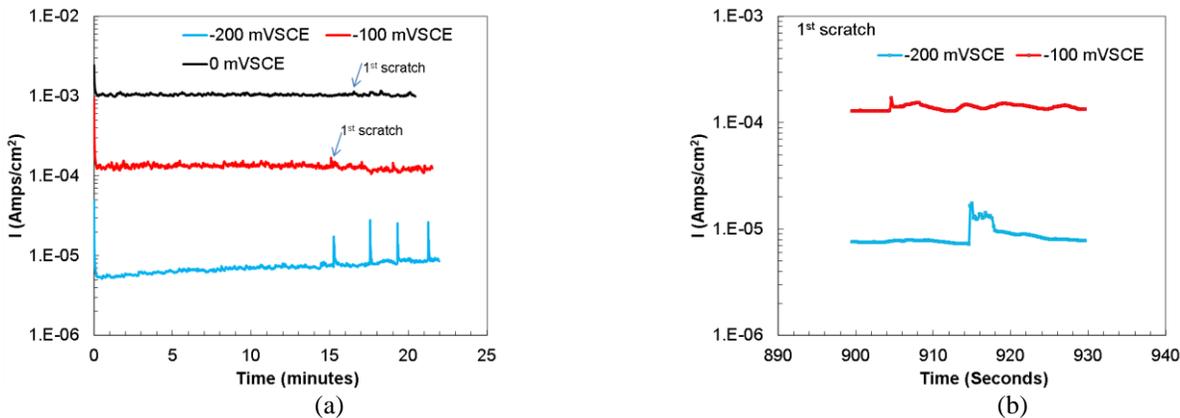


Fig. 6. Current versus time transient curves for copper when four successive scratches were made at two locations on the V_{SCE} in deaerated simulated granitic groundwater at 50 °C [122 °F] (a) entire test duration (b) 1st scratch

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