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Copper Corrosion in Simulated Anoxic Granitic Groundwater

Presented by

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Outline

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Introduction

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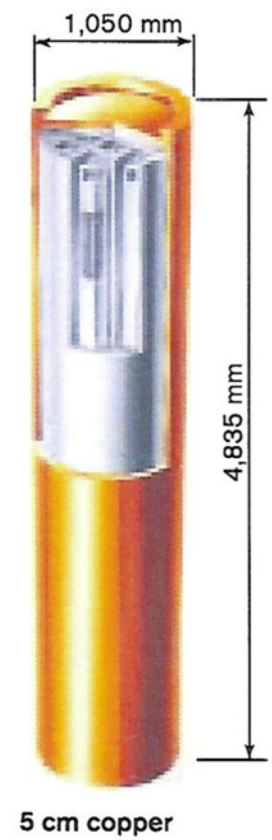
- Copper has been considered as one of the corrosion allowance waste package materials in several countries including Sweden, Canada, Japan, and others
- Several possible corrosion processes shown in the literature
  - General corrosion in aerated groundwaters
  - General corrosion in the presence of aqueous sulfide
  - Pitting in aerated saline conditions
  - Microbially influenced corrosion
  - Stress corrosion cracking



Sweden's and Finland's Adopted KBS-3 method

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Objectives

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- Literature review of copper corrosion process in anoxic repository environment
- Experiments to address important technical gaps identified from the literature

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Literature Review — Controversy over Copper General Corrosion

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- According to the copper Pourbaix (potential-pH) diagram in O_2-free environments, copper is thermodynamically stable
- Corrosion would be negligible per the following reaction

$$2Cu + H_2O \Leftrightarrow Cu_2O + H_2$$

- As such, copper containers could be extremely long-lived for a wide range of host rock types
- However, Hultquist, et al. (2009) proposed a solid phase of H_xCuO_y (equivalent to CuOH for x = y = 1) as the corrosion product, which could lead to a much higher corrosion rate

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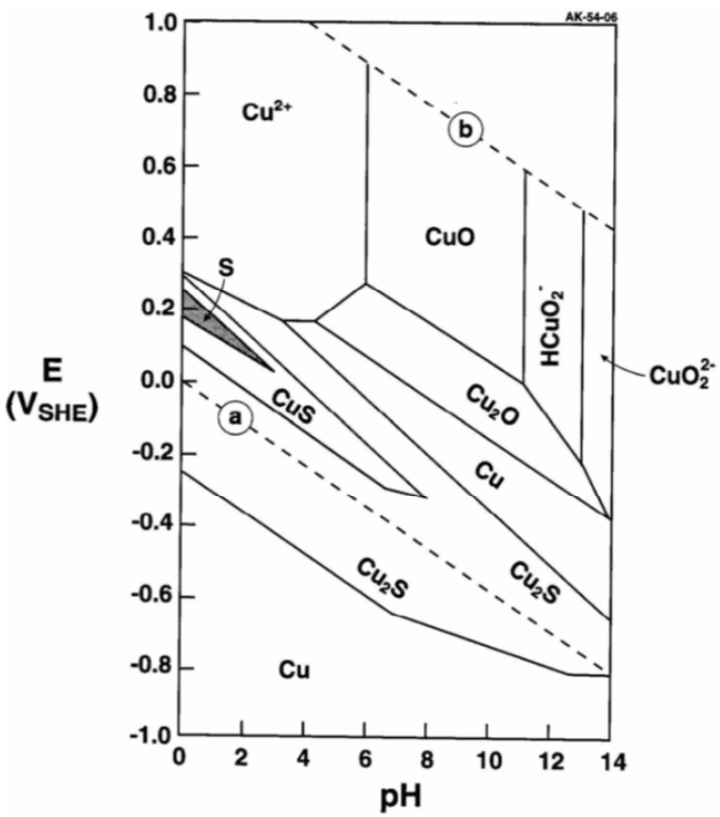
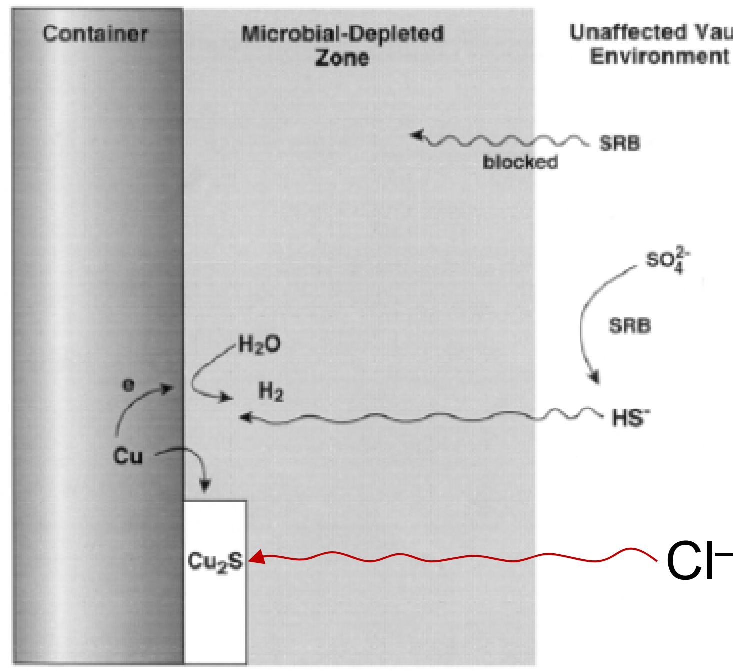
Hultquist, G., P. Szakalos, M.J. Graham, A.B. Belonoshko, G.I. Sproule, L. Grasjo, B. Danilov, T. AAstrup, G. Wilmark, G.-K. Chuah, J.-C. Eriksson, and A. Rosengren. "Water Corrodes Copper." *Catalysis Letters*. Vol. 132. pp. 311–316. 2009.

Literature Review — Remote Microbial Activity Can Produce Sulfide

- Copper is thermodynamically unstable in water in the presence of sulfide





- Presence of Cl^- affects copper sulfide film

Literature Review — Stress Corrosion Cracking (SCC)

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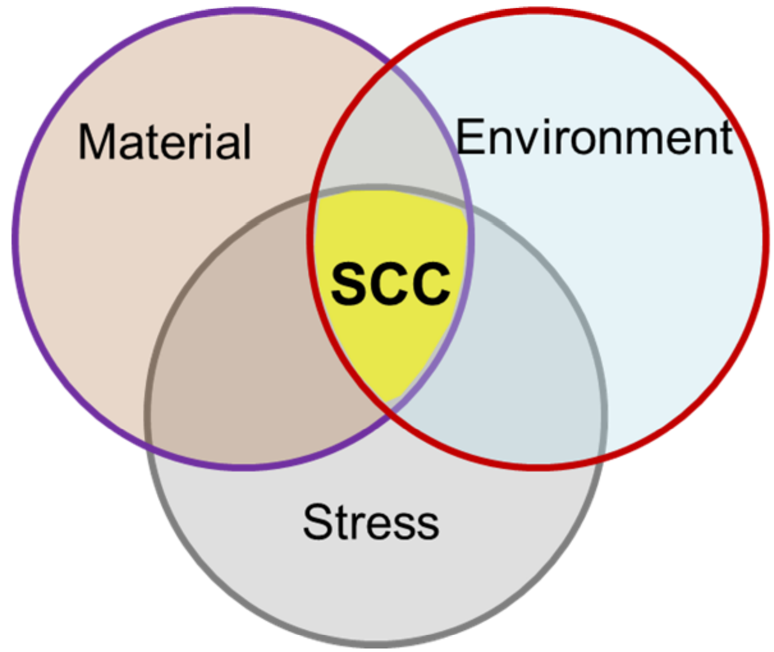
- Only a limited number of environments can sustain SCC of copper
  - Nitrite (from moist air radiolysis) and ammonia/acetate (possible products of remote microbial activity) are known to cause SCC of Cu if present in sufficient quantities
- Most likely sources of stress are those in the final closure weld
- Stress could be applied by hydrostatic, buffer swelling, and glacial loads



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Technical Gaps of Copper Corrosion Observed from Literature

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- Thermodynamic stability of copper in O_2-free pure water
- Copper sulfide film passivity in sulfide-containing environments and the effect of chloride on sulfide film

Copper Corrosion Studies in Simulated Anoxic Granitic Groundwater

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Comparison of Three Reference Groundwaters for Deep Crystalline Rocks			
Species	Concentration (M)		
	Simulated Granitic 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.

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Corrosion Test Cell

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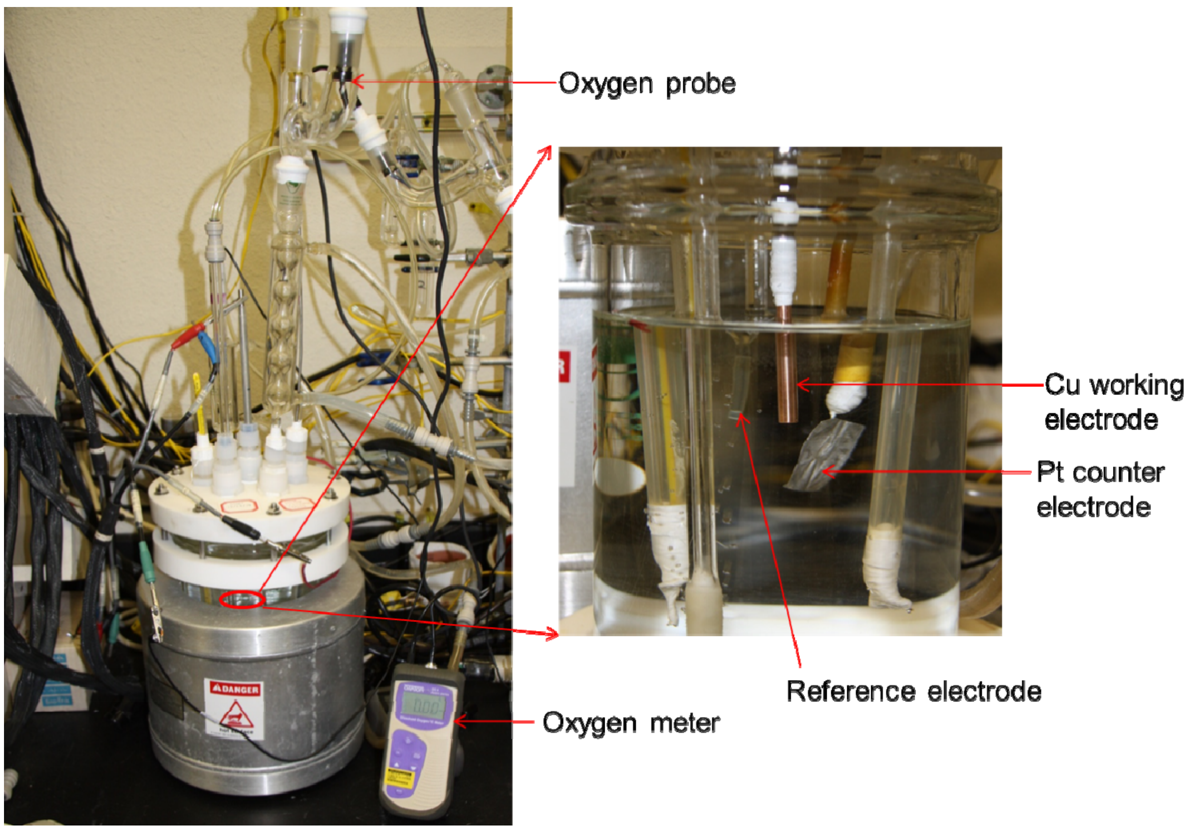
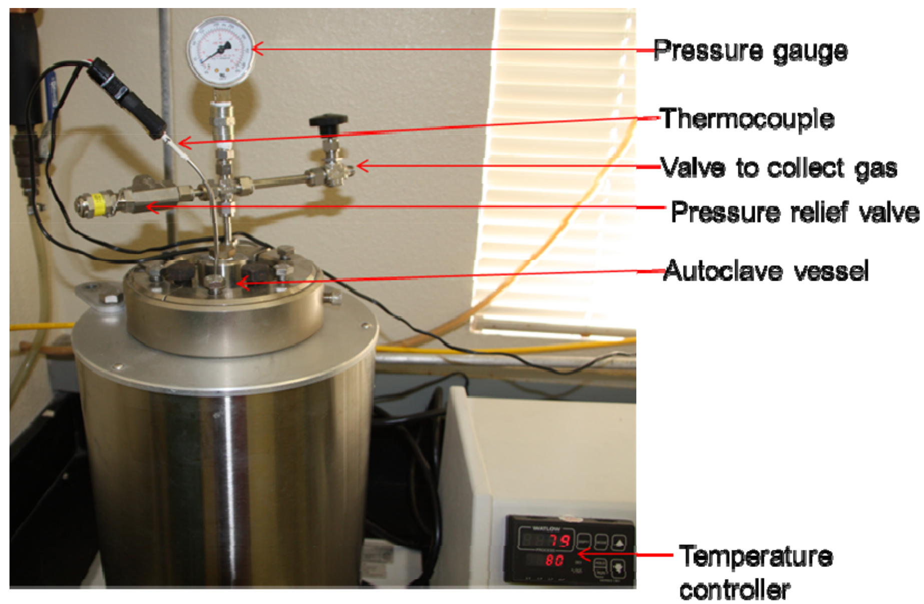
- Temperature: 50 °C and 80 °C
- Electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) used to measure corrosion rates



- O_2 concentration was monitored to ensure anoxic condition
- Oxygen free copper with a copper concentration of 99.997 percent

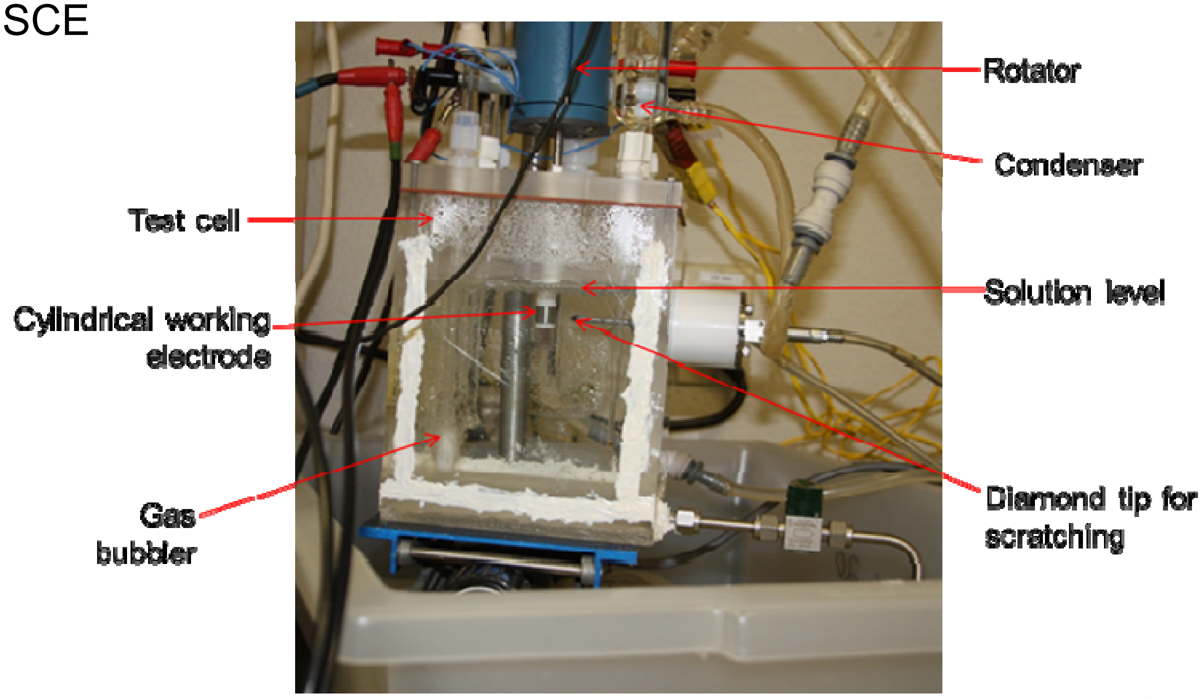
Hydrogen Generation Measurements

- Autoclave for hydrogen generation measurement
  - Immerse coupons at 80 °C under inert gas deaerated condition
  - The gas from the vapor phase was sampled at 3 and 6 months and analyzed with gas chromatography immediately after sampling
  - Conducted at two inert gas pressures: 1 and 3 atm
  - A control test without specimen was conducted at 3 atm



Scratch Repassivation Test Setup

- Rotating cylindrical electrodes exposed to anoxic granitic groundwater at 50 °C
- Surface scratch made while the electrode was polarized at −200, −100, 0 mV_{SCE}
- One scratch was one complete revolution around the surface
- 4 scratches were made at each applied potential



Electrochemical Impedance Spectroscopy and Linear Polarization Resistance

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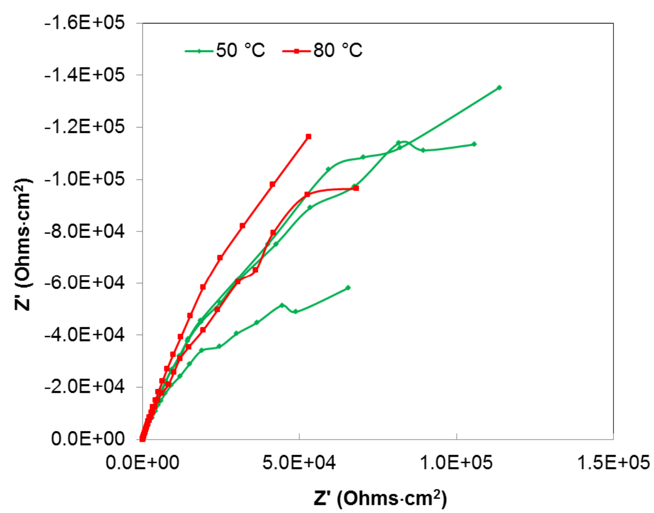
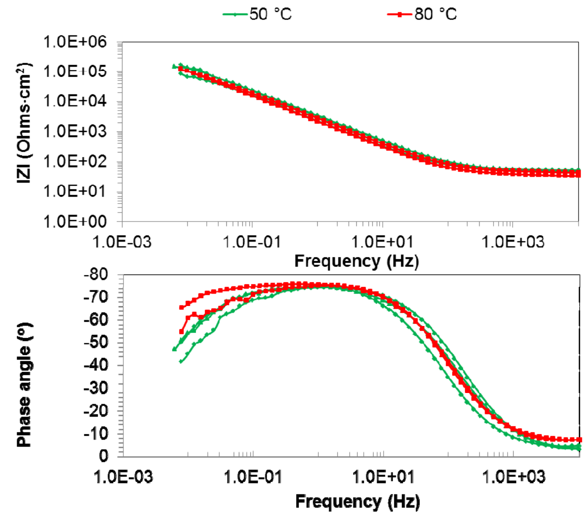
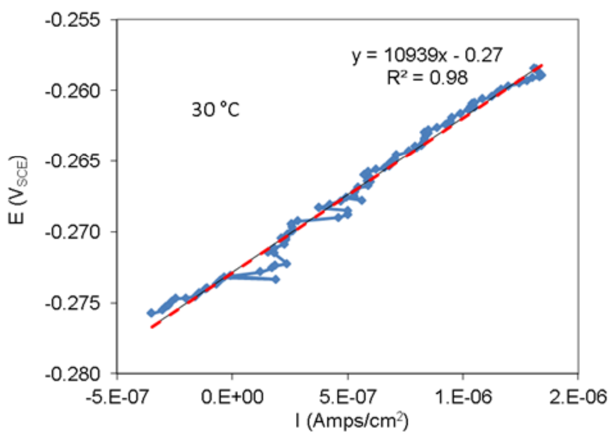
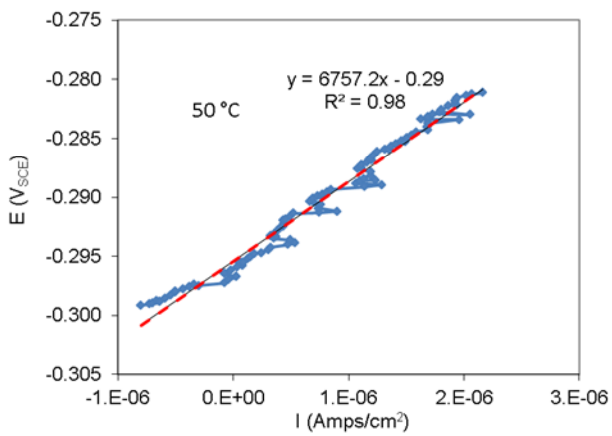
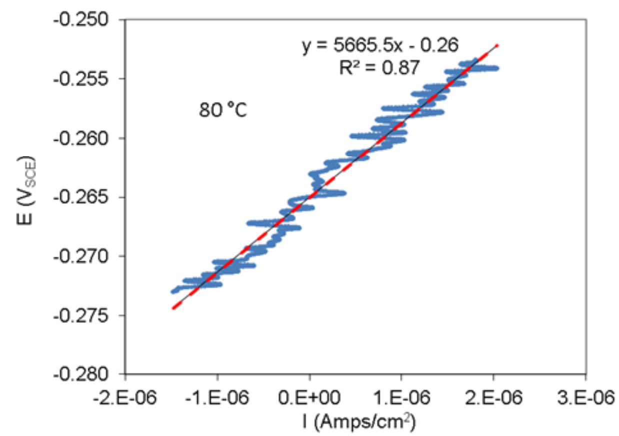
- One time-constant Randle type circuit fit for EIS and linear fit for LPR











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Measured Copper Corrosion Rates

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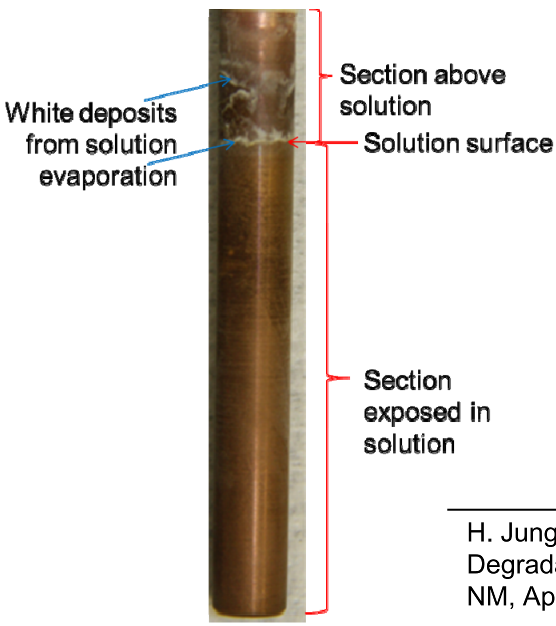
Corrosion Rates of Copper Exposed to Simulated Anoxic Granitic Groundwater								
Temperature, °C			50			80		
Corrosion rate, μm/yr	Test 1	EIS	0.83	0.95	2.4	1.0		0.48
	Test 2	EIS	5.0	3.5	3.4	3.0	3.0	4.4
		LPR	5.3	5.1	4.9	6.7		
Average corrosion rate, μm/yr			3.5 ± 1.8			3.1 ± 2.3		

Post-test specimen with black corrosion film



Higher corrosion rates than in Jung et al. (2011) (4×10^{-3} to 2×10^{-2} μm/yr) possibly because of:

- Different methodologies (electrochemical testing vs. theoretical calculation
- Incomplete oxygen depletion

H. Jung, T. Ahn and X. He, "Representation of Copper and Carbon Steel Waste Package Degradation in a Generic Performance Assessment Model," IHLRWMC 2011, Albuquerque, NM, April 10-14, 2011

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Hydrogen Generation and Post-test Solution and Copper Foils at 1 atm

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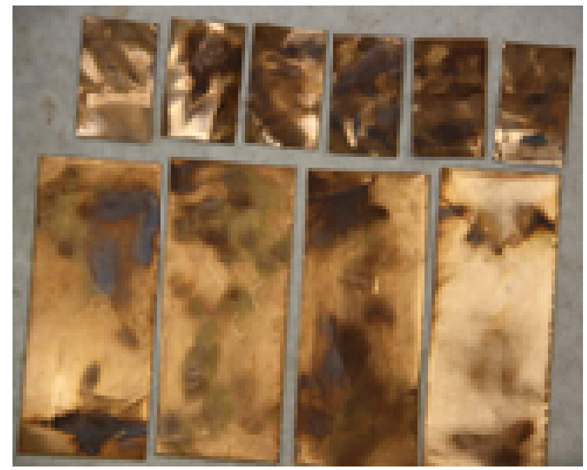
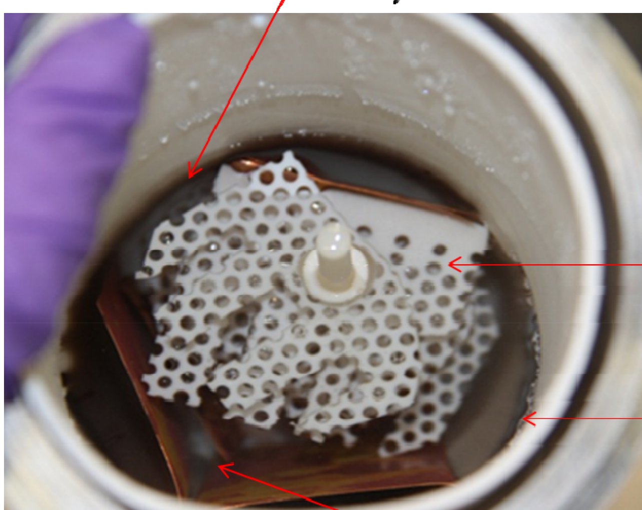
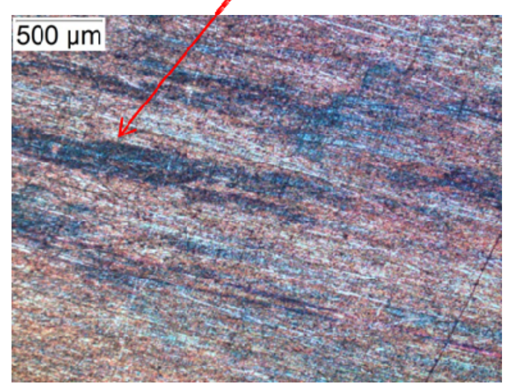
- Small amount of hydrogen was measured from vapor phase at 3 and 6 months
- Similar amount of hydrogen was measured from tested and untested copper foil







Hydrogen Generation from Test at 3 atm for 3 months

H_2 concentration from test with copper: 0.016 vol%

Control test without copper: 0.013 vol%

Near detection limit of 0.01 vol%

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Current versus Time Transient Curves for Copper upon Scratch

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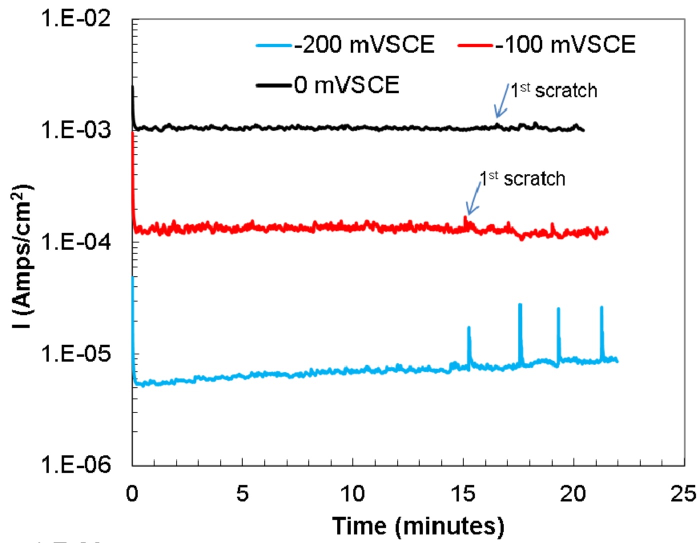
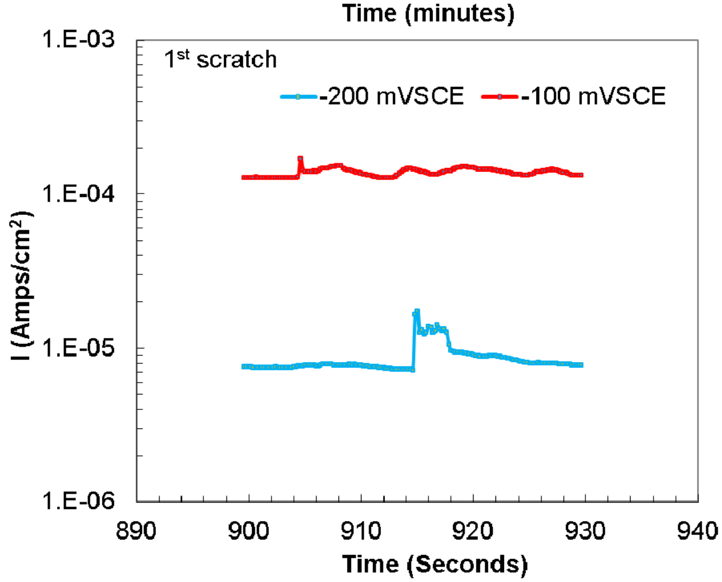
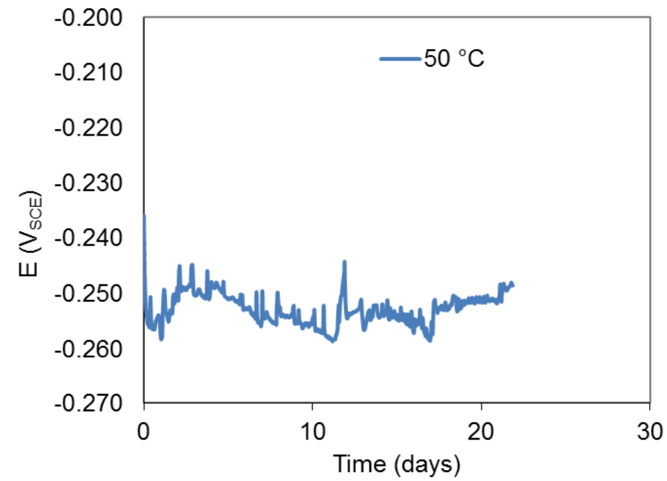




Open circuit potential



- The peak current upon the scratch was only clearly visible at −0.2 V_{SCE}

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Summary

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- Most of the corrosion rates measured by electrochemical methods ranged from 1—5 µm/yr
- Measurement of hydrogen generation from copper corrosion had high uncertainty because of
  - Very small amount which is near equipment detection limit
  - Background hydrogen from metallic test cell
  - Residual O_2 from incomplete purging
- Copper showed little to no repassivation capability upon scratch under polarization
- In all the tests including completed autoclave tests, copper was corroded with black film (predominantly CuO)
- More in-depth analyses are needed to improve understanding of copper corrosion in anoxic environments

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