Copper Corrosion in Simulated Anoxic Granitic Groundwater

Presented by

Xihua He,[1] Tae Ahn,[2] and Jude McMurry[3]

[1]Center for Nuclear Waste Regulatory Analyses (CNWRA)

Southwest Research Institute®

San Antonio, Texas, U.S.A.

[2]U.S. Nuclear Regulatory Commission (USNRC), Office of Nuclear Material Safety and Safeguards, Washington, DC, U.S.A.

[3]Retired from CNWRA

Presented for

International High-Level Radioactive Waste Management Conference 2015

Charleston, South Carolina

April 12–16, 2015

Outline

- Introduction
- Objectives
- Literature review
- Corrosion tests
  - Experimental approach
  - Results
- Summary

Introduction

- 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

Objectives

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

CNWRA
A center of excellence in earth sciences and engineering®

Literature Review — Controversy over Copper General Corrosion

U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

- 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

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

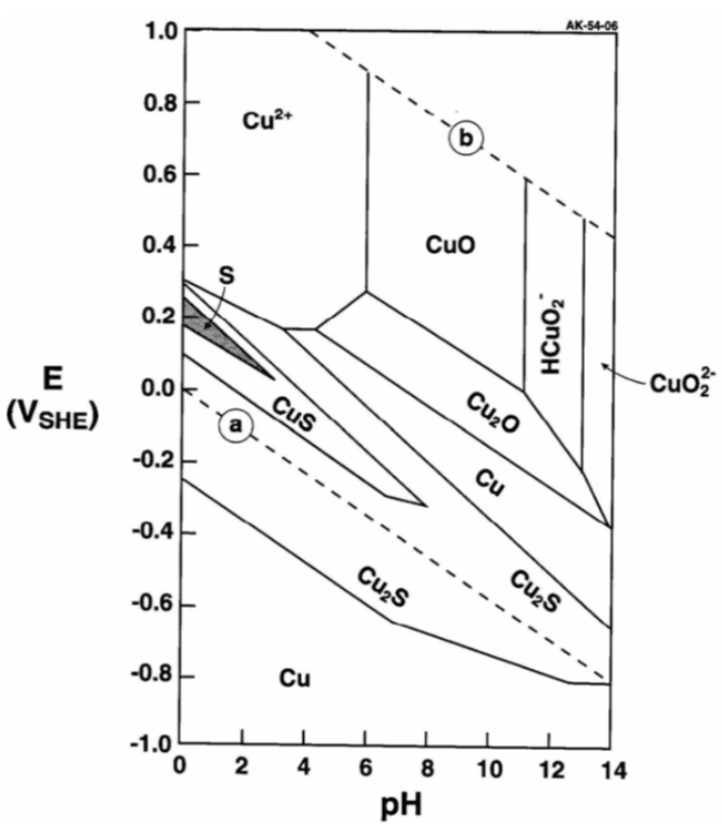
- As such, copper containers could be extremely long-lived for a wide range of host rock types
- However, Hultquist, et al. (2009) proposed a solid phase of H_xCuO_y (equivalent to CuOH for x = y = 1) as the corrosion product, which could lead to a much higher corrosion rate

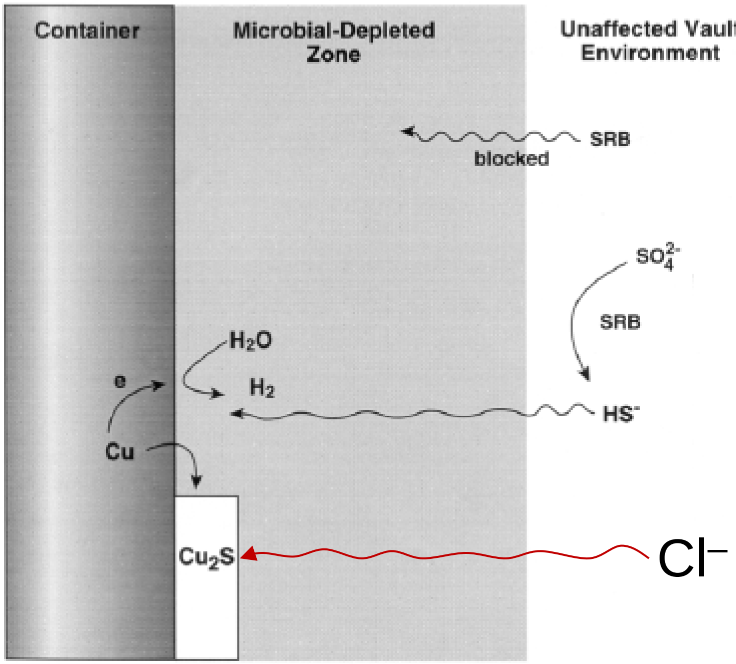
---

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

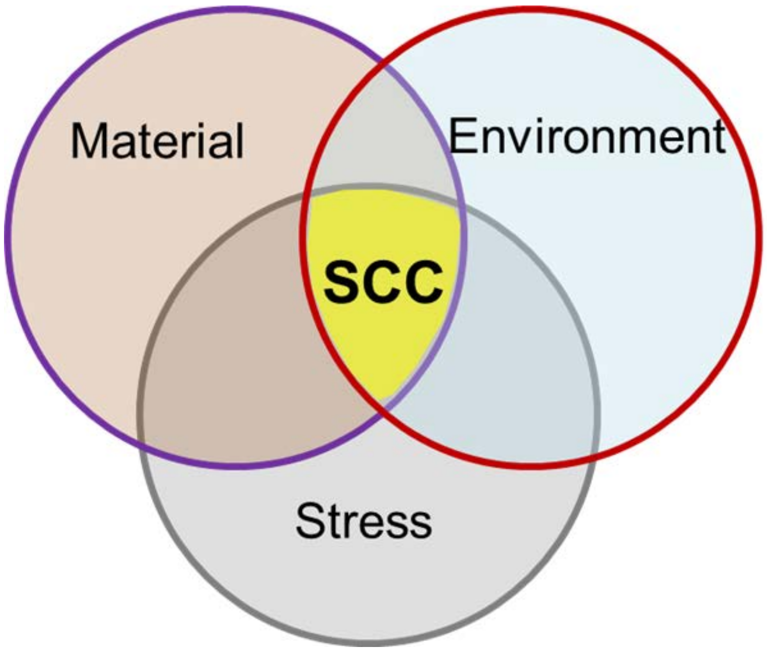




- Presence of Cl⁻ affects copper sulfide film

Literature Review — Stress Corrosion Cracking (SCC)

- 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



Technical Gaps of Copper Corrosion Observed from Literature

- 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

CNWRA
A center of excellence in earth sciences and engineering®

U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

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.**

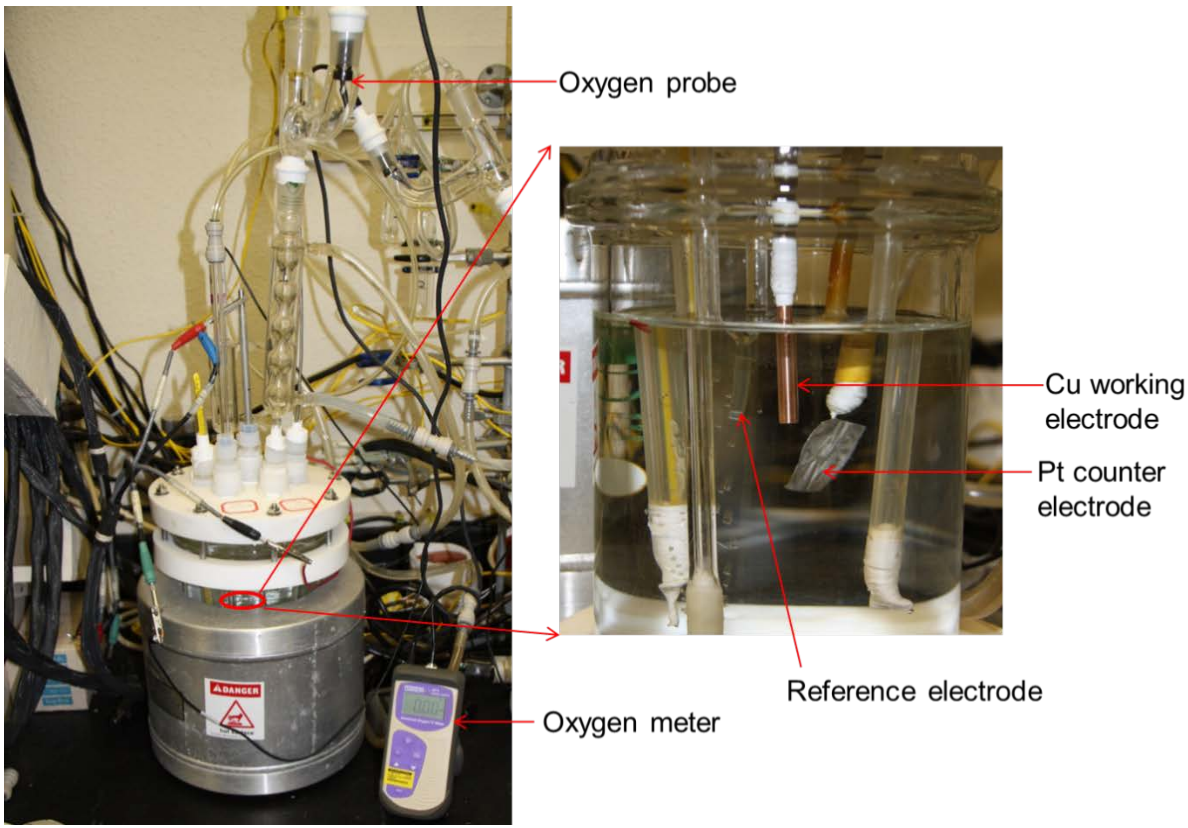
†NWMO. "Used Fuel Repository Conceptual Design and Postclosure Safety Assessment in Crystalline Rock." Pre-Project Report NWMO TR-2012-16. Toronto, Canada: Nuclear Waste Management Organization. 2012.

CNWRA
A center of excellence in earth sciences and engineering®

Corrosion Test Cell

U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

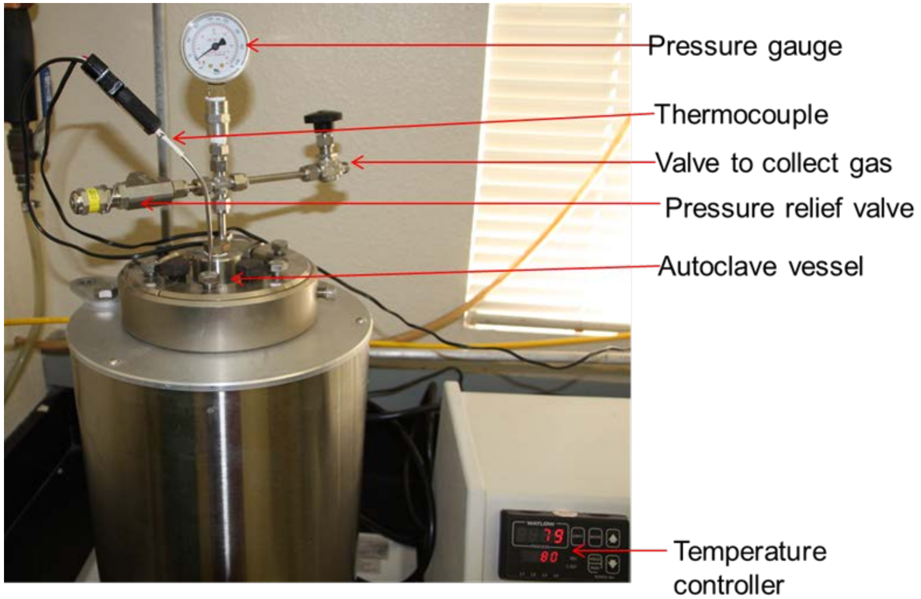
- Temperature: 50 °C and 80 °C
- Electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) used to measure corrosion rates



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

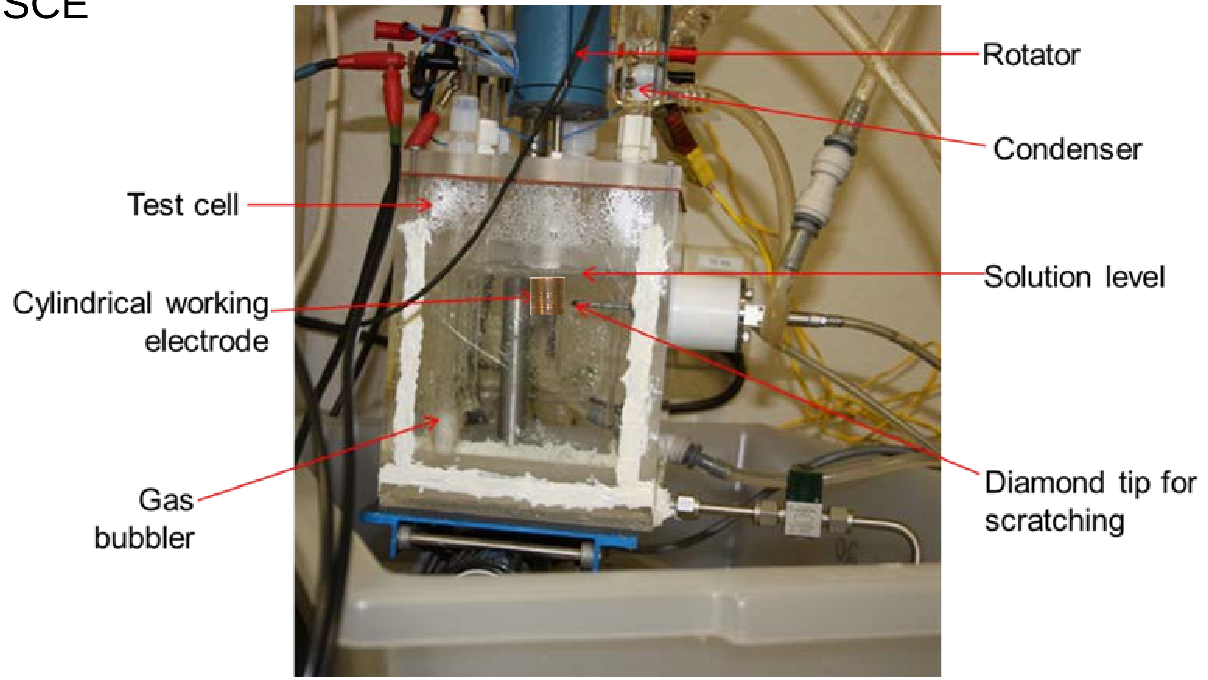
Hydrogen Generation Measurements

- 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

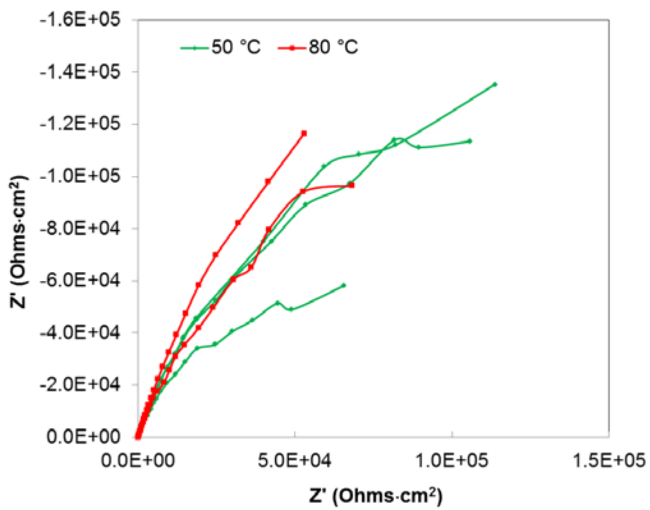


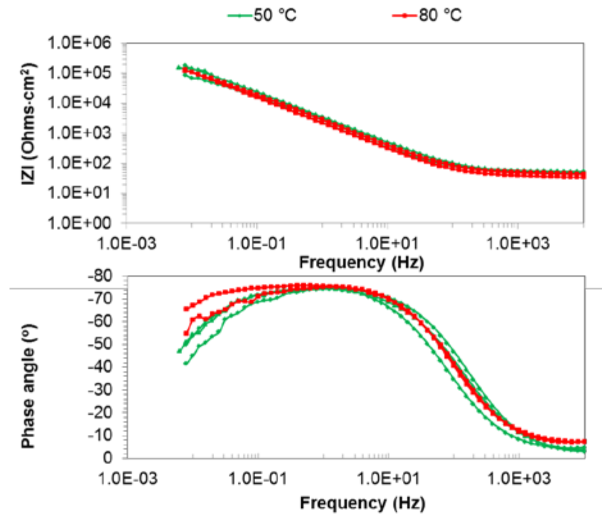
Electrochemical Impedance Spectroscopy and Linear Polarization Resistance

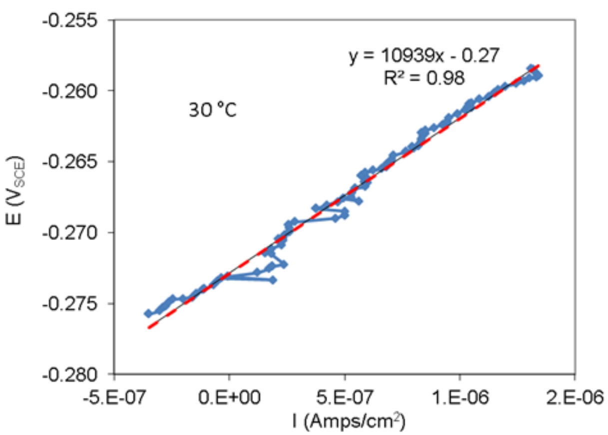
CNWRA
A center of excellence in earth sciences and engineering®

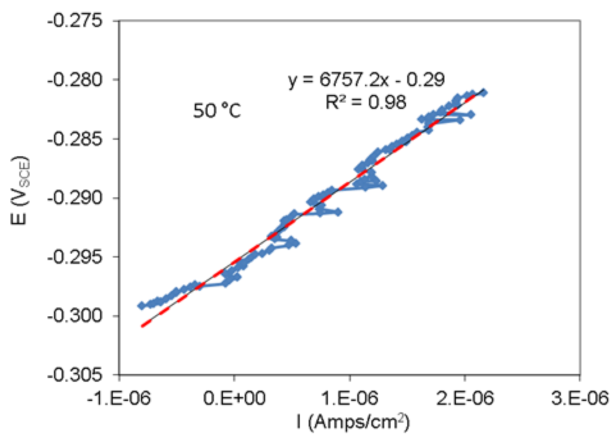
U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

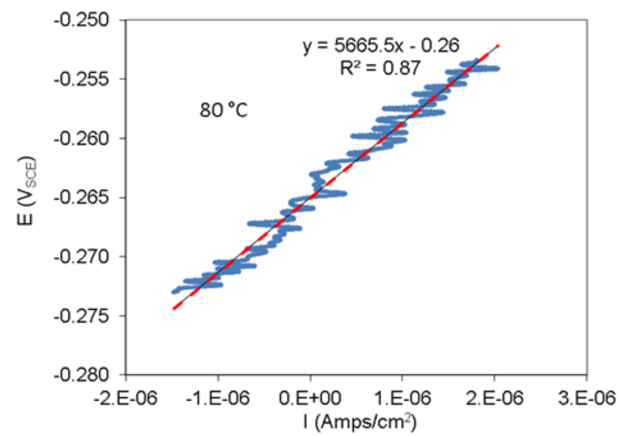
- One time-constant Randle type circuit fit for EIS and linear fit for LPR







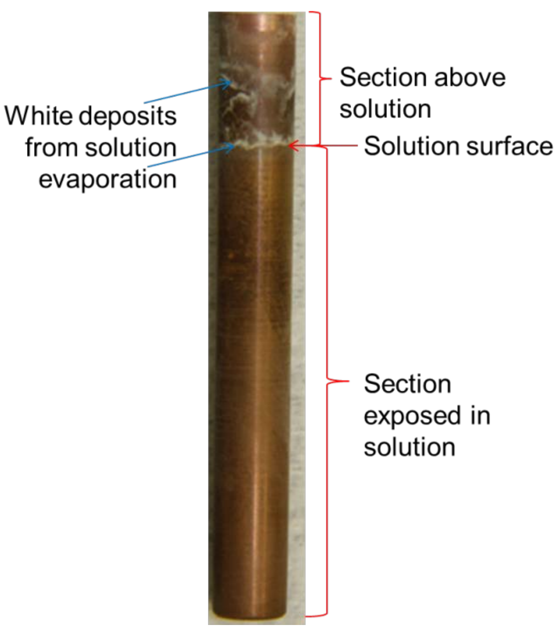




Measured Copper Corrosion Rates

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 some literature data possibly because of:

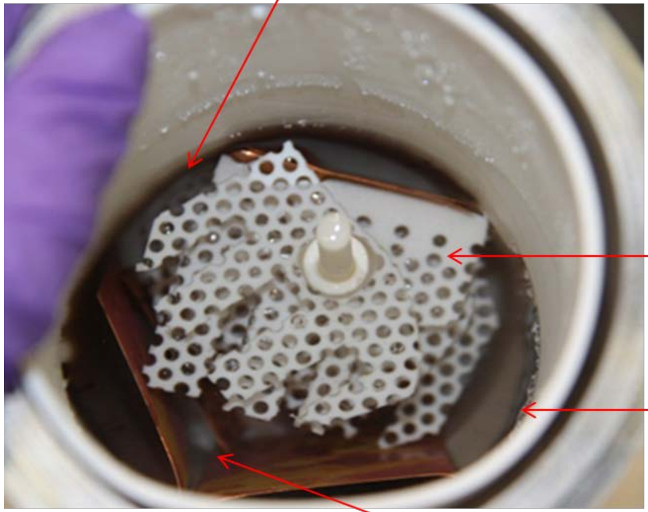
- Different methodologies
- Incomplete oxygen depletion
- Uncertainty in corrosion mechanism and corrosion process contributing to measured current

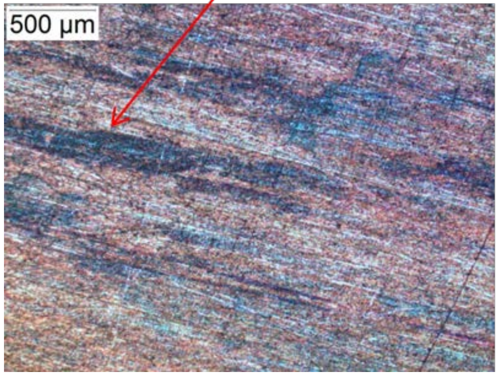
Hydrogen Generation and Post-test Solution and Copper Foils at 1 atm

CNWRA — A center of excellence in earth sciences and engineering®

U.S.NRC — United States Nuclear Regulatory Commission — Protecting People and the Environment

- 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





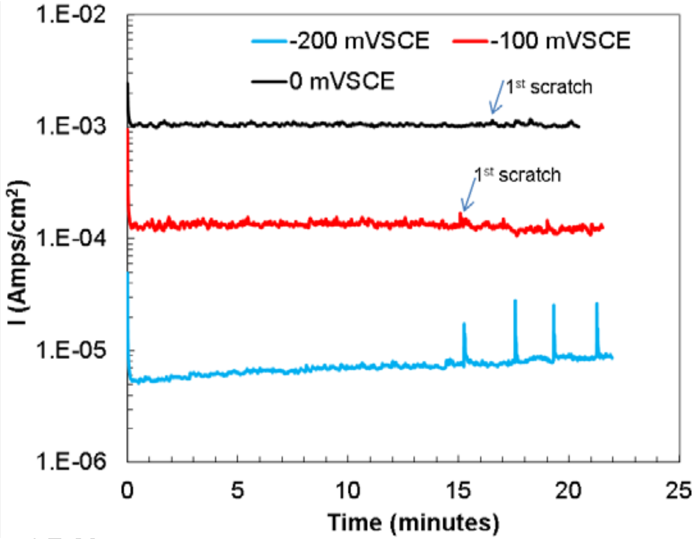
Hydrogen Generation from Test at 3 atm for 3 months

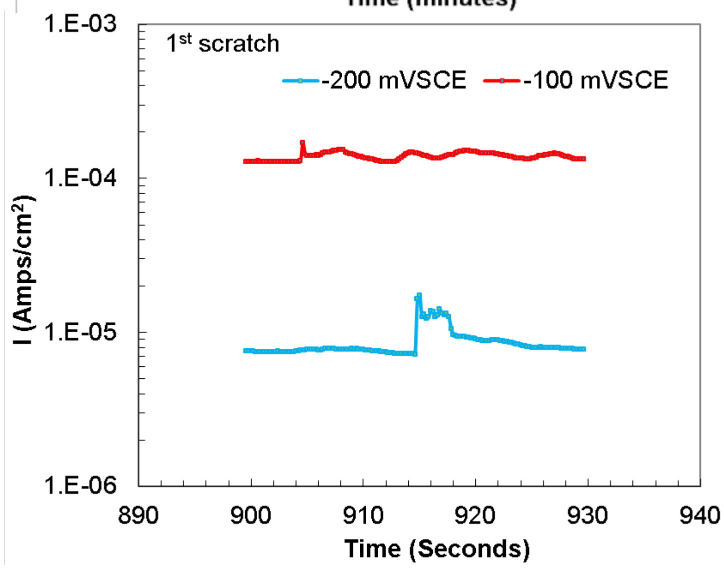
H_2 concentration from test with copper: 0.02 vol%

Control test without copper: 0.01 vol%

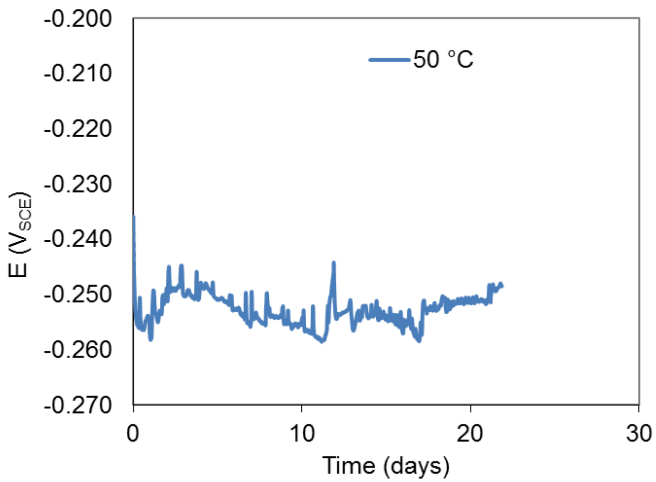
Near detection limit of 0.01 vol%

Current versus Time Transient Curves for Copper upon Scratch





Open circuit potential



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

CNWRA
A center of excellence in earth sciences and engineering®

Summary

U.S.NRC
United States Nuclear Regulatory Commission
Protecting People and the Environment

- Most of the corrosion rates measured by electrochemical methods ranged from 1—5 µm/yr, but uncertainties remain
- Measurement of hydrogen generation from copper corrosion had 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

Disclaimer

This presentation describes work performed by the CNWRA and its contractors for the NRC under Contract No. NRC–HQ–C–02–0089. The NRC staff provided technical direction and oversight to this research project. The activities reported here were performed on behalf of the NRC Office of Nuclear Material Safety and Safeguards. This presentation is an independent product of the CNWRA and does not reflect the view or regulatory position of the NRC. The NRC staff views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed or of the acceptability of any licensing action that may be under consideration at the NRC.