

# Predicting Geologic Corrosion with Electrodes

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**E**ver since humans discovered how to separate metal from its ore mineral, preserving its metallic luster has been a driving force in the advancement of materials science. In modern times, developing materials that will contain and isolate nuclear waste has pushed corrosion science to new limits. We must now predict corrosion rates over geologic time scales, upwards of a million years. This article reviews the electrochemical basics that underpin metal and mineral corrosion and uses that to understand the case study of copper corrosion in nuclear-waste containers. Electrochemistry can also explain electron-transfer processes on mineral surfaces and so offer insight into weathering and environmentally relevant natural redox processes, such as those forming supergene metal deposits.

**KEYWORDS:** electrochemistry, corrosion, nuclear waste, analogues, geologic repository

## GEOLOGIC CORROSION

Corrosion, like death and taxes, is an unavoidable consequence of living on a watery, oxidizing planet. As geologists, we understand that corrosion processes on Earth were jump-started by the Great Oxidation Event (starting ~2.4 Ga), even though biology had developed the machinery for harvesting energy from sunlight and expelling molecular oxygen as a waste product long before (perhaps as early as 3.5 Ga) (Holland 2006). The first significant “rusts” to form on Earth’s crust, which were the result of increased levels of O<sub>2</sub> in the atmosphere, were the banded iron formations (BIFs) of the Paleoproterozoic, especially between 2.4 and 1.8 Ga (Klein 2005). In addition to the formation of BIFs, rising O<sub>2</sub> levels initiated the formation of supergene mineral deposits along reduction–oxidation (redox) boundaries at shallow crustal depths: these boundaries were, and are, a major mechanism for metal enrichment in crustal rocks. Unique examples of redox-driven processes in the Precambrian are the set of Oklo natural fission reactors in Gabon (~2 Ga), which are evidence of uranium being moved and concentrated by supergene (corrosion) processes in the uppermost crust. Between the formation of BIFs, natural nuclear reactors, and supergene deposits, redox reactions have been transforming the surface of the planet for billions of years.

## CORROSION AND SOCIETY

Most redox reactions are overwhelmingly energetically favorable. For example, the oxidation of ferrous iron (Fe<sup>2+</sup>) by O<sub>2</sub> to produce ferric iron (Fe<sup>3+</sup>) has a Gibbs free energy value of –27 kJ/mol at a pH of 2.5 (Erlich and Newman 2009). And where there was energy to be had, primitive life developed the catalytic machinery to harvest it. Within the fluids at ancient redox boundaries, aerobic and anaerobic microorganisms evolved ways to harvest the energy stored in chemical bonds.

Flash forward a few billion years and human civilization advanced along these ancient redox boundaries as well. It began between 6500 BC and 5000 BC with the smelting of silver, gold, tin, mercury, lead, and copper from their mineral ores. The energy produced in the Old World smelters and kilns went into liberating metals from their native compounds, be they oxide, sulfide, or carbonate ores. The discovery that copper alloyed with tin, which was mainly from cassiterite (SnO<sub>2</sub>) ore, produces a harder and more durable material marked the beginning of the Bronze Age around 3000 BC. The technically more difficult smelting of iron followed a millenium later, and the quality of life and the rate of technological progress would never be the same again. It was Greek philosopher and natural historian Pliny the Elder (AD 23–79) who first documented the propensity for these metals to return to their native states when he wrote, in his essay “Ferrum Corruptiar,” of the “spoiling” of iron metal. Now, we understand that the driving force for all material corrosion—be it metals, minerals, or any other material—is the lowering of a system’s Gibbs free energy (the energy available for doing work). The large amount of energy required by smelting relates to the strong thermodynamic driving force to return a metal to ore by corrosion reactions (symbolically illustrated in Fig. 1). Despite the uphill thermodynamic struggle, humans have always been consumed with trying to slow the rate of Pliny’s observed “spoiling”. Both Pliny and the Greek historian Herodotus (fifth century BC) suggested using tin to protect iron. Alchemists throughout history have played a role in advancing the knowledge of corrosion science through their attempts to transform base metals into noble metals. However, it was Michael Faraday in 1833 who established the first quantitative relationships between electric current and the amount of metal that was

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**FIGURE 1** This abandoned early 1900s copper blast furnace in the New World Mining District (Montana, USA) is symbolic of the full thermodynamic cycle: energy was once inputted to liberate Cu from its native minerals, whereas the iron furnace itself is now corroding back to its native oxides. PHOTO COURTESY OF EDWARD MEYER (DARTMOUTH COLLEGE, USA).

deposited on, or gas that was evolved at, a metal electrode. From then on, corrosion science became firmly grounded in electrochemistry.

Faraday provided the relation between the current measured at an electrode and the reaction rate by the formula

$$\text{Reaction Rate} = \frac{dN}{dt} = \frac{1}{nF} \frac{dQ}{dt} = \frac{I}{nF} \quad (1)$$

where  $N$  is the number of moles formed,  $t$  is reaction duration,  $Q$  is the electrical charge in coulombs (C),  $n$  is the number of electrons transferred,  $F$  is Faraday's constant (96,485 C/mol) and  $I$  is current in amperes (A) or in coulombs per second (C/s). Faraday's first and second laws of electrolysis became the basis for determining the corrosion rates of metals. We suspect that Pliny and Faraday would be amazed at how keenly interested our modern society is in controlling corrosion rates, particularly when the annual direct cost of corrosion to utilities, transportation, and infrastructure in the United States alone is estimated to be over US\$276 billion per year (Koch 2002).

Electrochemistry is a common language among Earth scientists and materials scientists in areas as diverse as metallurgy and corrosion, metal extraction from ore minerals, geological weathering, leaching processes, and elemental cycling. The timescales over which corrosion processes are assessed in these areas are variable. Material scientists who estimate the rates of steel corrosion and service life of, say, modern bridges are interested in a 50–100-year timescale. Geologists assess natural corrosion (or weathering) processes over timescales that can span millions of years.

There is a significant and established body of literature on the corrosion of metals and alloys by electrochemical techniques. Electrochemical studies of minerals have played an important role in developing mineral processing techniques that are used to liberate a metal from its ore. However, the use of electrochemical techniques to determine the fundamental corrosion parameters for minerals is less widely established.

This article will review the basic electrochemistry needed to understand corrosion and also discuss an area where materials scientists and Earth scientists have a mutual vested interest—the assessment of the corrosion resistance of materials designed to isolate and contain nuclear waste in long-term geologic repositories. This is an ideal

example to illustrate how models utilizing electrochemical data are employed to assess corrosion processes over geologic timescales. We intend for this review to provide a framework for how electrochemical techniques, although inherently challenging, can be applied to explain mineral weathering processes, or redox cycling, in natural or engineered environments.

## THE ELECTROCHEMICAL BASICS

The process of natural metal corrosion is driven by the coupling of two redox half-reactions occurring at the same rate. The anodic reaction, which results in oxidation, releases electrons into the metal. The cathodic reaction—in which an oxidant species such as  $O_2$ ,  $Fe^{3+}$ , or  $H^+$  is reduced—removes electrons from the metal. The two reactions can take place simultaneously on one metal or on two dissimilar metals that are in electrical contact. Mixed potential theory, established by Wagner and Traud (1938) and mathematically refined by Stern and Geary (1957), states that corrosion occurs on a metal as a result of localized anodic and cathodic reactions occurring simultaneously on the surface. For a naturally occurring corrosion process, the sum of the rate(s) of the oxidation half-reaction(s) at anodic sites must be equal to the sum of the rate(s) of the reduction half-reaction(s) at cathodic sites. That is, there should be no accumulation of charge on the metal's surface. The potential at which anodic and cathodic reaction rates are equal is called the “mixed” or “corrosion” potential,  $E_{corr}$ . At  $E_{corr}$ , the surface of the material corrodes as a consequence of the kinetic (i.e. rate) balance between anodic and cathodic reactions. The  $E_{corr}$  lies somewhere between the equilibrium potentials of the oxidation and reduction half reactions. The equilibrium potential,  $E_{eq}$ , can be determined for a given set of environmental conditions by the well-known Nernst relationship, here shown for the reduction of ferric ions:

$$E_{eq} = E^0 + \frac{2.3RT}{F} \log \left\{ \frac{(a_{Fe^{3+}})}{(a_{Fe^{2+}})} \right\} \quad (2)$$

for the reaction  $Fe^{3+} + e^- \leftrightarrow Fe^{2+}$

where  $E^0$  is the standard reduction potential,  $R$  is the molar gas constant,  $T$  is the absolute temperature,  $F$  is the Faraday constant, and  $a_{Fe^{3+}}$  and  $a_{Fe^{2+}}$  are the activities of ferric iron and ferrous iron, respectively.

Corrosion of mineral surfaces is also described by electrochemical mechanisms. For example, the overall reaction for the well-studied oxidative dissolution of pyrite ( $FeS_2$ ) is written in terms of the redox half-reactions for the oxidation of pyrite and the reduction of  $O_2$ :

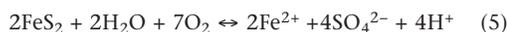
Oxidation half reaction:



Reduction half reaction:



Overall reaction:

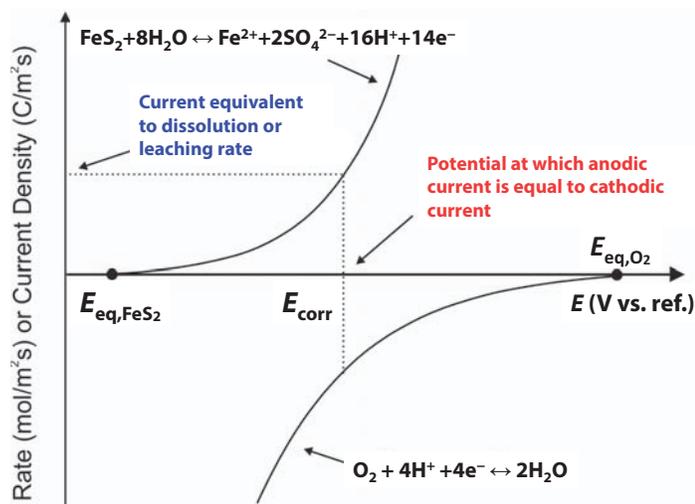


The electrochemical dissolution of pyrite by the reactions above is illustrated schematically in FIGURE 2. Validation of the electrochemical mechanism came from studies showing that oxygen in the sulfate product came from  $H_2O$ , rather than the oxidant,  $O_2$  (Bailey and Peters 1976; Taylor et al. 1984; Holmes and Crundwell 2000; Usher et al. 2004). Molecular modeling showed that the dissociation of water at Fe sites and the subsequent nucleophilic attack by hydroxyls at surface S sites was an energetically favorable pathway (Rosso et al. 1999). The rate of oxidative dissolution of pyrite is the same magnitude as either the

rate of oxidation of pyrite (to form sulfuric acid) or the rate of  $O_2$  reduction occurring at  $E_{\text{corr}}$  (FIG. 2). In natural environments, the surface of the metal or the mineral in question will dissolve and/or become covered with corrosion products, depending on environmental Eh–pH (redox and acid/basic) conditions. The  $E_{\text{corr}}$  evolves due to changes in the composition of the material surface.

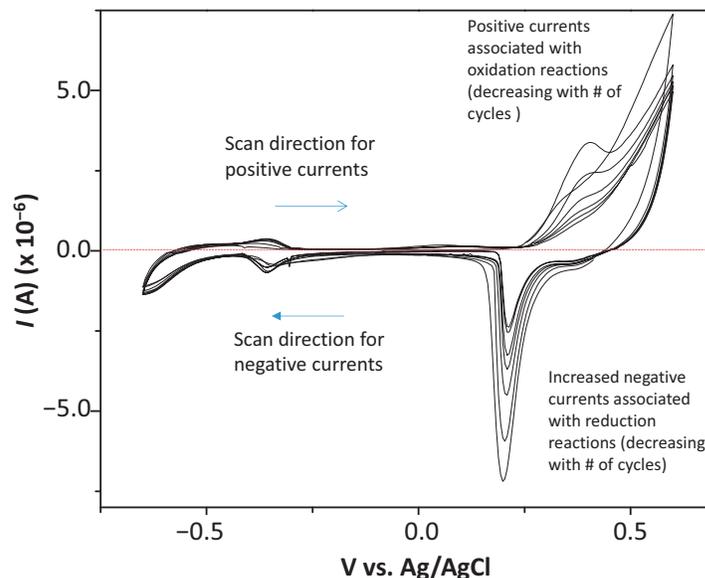
From a practical standpoint,  $E_{\text{corr}}$  can be determined by making a working electrode out of the metal or mineral of interest and measuring the potential that develops between the working electrode and a stable reference electrode (commonly a silver/silver chloride electrode, Ag/AgCl) using a high-impedance voltmeter. This type of electrochemical experiment is called a potentiometric technique. Fabricating an electrode out of a metal is straightforward; however, a mineral electrode must satisfy the condition of having either a metallic or a semiconductor degree of conductivity (e.g. sulfides and semiconducting oxides). A bulk mineral electrode is fashioned by cutting or cleaving the bulk mineral into a wafer, polishing the surface, and attaching a conductive wire. Alternatively, minerals can be evaluated by packing mineral powders into a micron-sized cavity at the tip of a Pt microelectrode (see Renock et al. 2013) or immobilizing the mineral particles on an inert electrode surface (or within a thin layer) using a conductive binder, such as graphite powder mixed with paraffin.

Metal or mineral electrodes can be polarized by making the electrode be the so-called “working electrode” in a three-electrode electrochemical cell. An instrument called a potentiostat is used to maintain the potential between the working electrode and the reference electrode. The third electrode is called the “counter electrode” and is typically made of a Pt wire mesh. These types of experiments are known generally as amperometric techniques, which involve measuring the current,  $I$ , flowing between the working electrode and the counter electrode. For example, if the working electrode potential is negatively polarized relative to  $E_{\text{corr}}$ , the rate of cathodic reaction(s) will increase at the expense of the anodic reaction(s) ( $|I_c| > |I_a|$ ) as  $E$  is polarized to the left of  $E_{\text{corr}}$  in FIG. 2), and the net current



**FIGURE 2** A schematic diagram showing the reaction rate–potential relationship for the electrochemical dissolution of pyrite. The rate of oxidation of pyrite and the rate of reduction of molecular oxygen,  $O_2$ , are both exponentially dependent on the potential at the mineral–water interface.  $E_{\text{corr}}$  takes on a value where the (sum of) cathodic and anodic rates (or currents) are equal. The thermodynamic driving force for the reaction is the potential difference between the equilibrium redox potentials for the anodic and cathodic reactions ( $E_{\text{eq, FeS}_2}$  and  $E_{\text{eq, O}_2}$ , respectively). FIGURE ADAPTED FROM HOLMES AND CRUNDWELL, (2000) WITH PERMISSION.

will be negative by convention. The current response of the working electrode is measured by the potentiostat. The various stages of oxidation and reduction can be assessed by cyclic voltammetry experiments in which the electrode potential is swept linearly between two potential limits through one or more cycles (hence “cyclic” voltammetry). Peaks in current that appear on the positive-going scan correspond to oxidation reactions and peaks that appear on the negative-going scan correspond to reduction reactions occurring on the electrode surface. An example is shown in FIGURE 3 for chalcopyrite ( $\text{CuFeS}_2$ ). Peak currents that increase or decrease over the course of multiple cycles indicate dynamic processes occurring on the surface of the working electrode. For the chalcopyrite example, decreasing currents on the positive-going scan are due to the formation of a partially protective oxide layer on the



**FIGURE 3** Cyclic voltammogram (see text for details) of chalcopyrite ( $\text{CuFeS}_2$ ) using a mineral powder microelectrode (pH 7, 25°C). Peaks in current that appear on the positive-going scan correspond to oxidation reactions and peaks that appear on the negative-going scan correspond to reduction reactions occurring on the electrode surface. By convention, anodic current is given a positive sign and cathodic current a negative sign. The # symbol means “number”.

mineral electrode that increases in thickness with subsequent cycles. In addition, the formation of a cathodic peak at low potentials (e.g. peak occurring at about  $-0.35$  V in FIG. 3) may be accompanied by the formation of an anodic peak on the subsequent cycle. This occurs when soluble redox species generated at low potentials are re-oxidized on the electrode surface during the sweep to higher potentials. Much can be learned about the energetics, kinetics, and mechanisms of corrosion and other redox processes from cyclic voltammograms, and readers are referred to the classic text by Bard and Faulkner (1980).

In terms of current,  $E_{\text{corr}}$  is the electrode potential where the anodic current,  $I_a$ , is equal and opposite in sign to the cathodic current,  $I_c$  (i.e.  $|I_a| = |I_c| = I_{\text{corr}}$  at  $E_{\text{corr}}$ ). Both  $I_a$  and  $I_c$  are equal to the sum of all currents associated with oxidation reactions and reduction reactions occurring on the electrode surface, respectively. Thus, by measuring  $I_{\text{corr}}$ , the overall corrosion rate of the material can be calculated. The corrosion scientist, armed with an electrode and Faraday’s laws, can then determine the mass loss of a material due to corrosion by

$$\frac{W}{t} = \frac{I_{\text{corr}} MW}{nF} \quad (6)$$

where  $W$  is the mass loss in grams,  $t$  is the duration of corrosion, and  $MW$  is the molecular weight of the corroding material. The mass loss can be converted into a value that is more useful, like the rate of penetration into the surface (e.g. millimeters per year), if the density and surface area of the material is known. However, the practical application of Equation (6) is not straightforward. Accurate determination of  $I_{\text{corr}}$  is technically challenging, though several methods can be employed in this regard (e.g. Tafel extrapolation, linear polarization resistance measurements, and impedance spectroscopy measurements). Bard and Faulkner (1980) is an excellent resource for understanding the different methods that are used to estimate  $I_{\text{corr}}$ .

It should be noted that determining redox kinetics using these methods has limitations when applied to semiconductor mineral electrodes. Charge depletion in semiconductor surface electronic states during polarization can affect the kinetic values obtained for redox reactions on the surface. Thus, care should be taken before assessing the kinetics of oxide and sulfide electrodes (Xu and Schoonen 2000; Meitl et al. 2009; Renock et al. 2013).

## ELECTROCHEMISTRY TO STUDY NUCLEAR WASTE DISPOSAL

The main issue with radioactive waste disposal is that the waste remains a risk to environmental and human health for, potentially, millions of years. For many repository risk assessments, the target life of the waste canisters ranges from tens of thousands of years to one million years; this ensures that the radioactivity of the waste has decayed to levels below acceptable risk should the containment fail (NWTRB 2009). Repository design proposals vary from country to country based on the composition of the spent fuel and the geologic (and geochemical) conditions of the repository site. The spent fuel itself consists of a matrix of irradiated uranium dioxide ( $\text{UO}_2$ ) containing fission products and activation products from the reactor. Due to the uncertainties inherent in the repository environment, the corrosion resistance of the waste package itself (i.e. spent fuel + metal package enclosing the spent fuel) is a significant focus for ensuring overall repository performance (Ewing and Macfarlane 2006). Radionuclide release into the environment may occur when the waste package is breached because of corrosion of the metallic canister and subsequent corrosion of the enclosed  $\text{UO}_2$  fuel matrix. Therefore, the waste-package design must account for biogeochemical attack from oxidants within the near-field environment of the waste package.

The environmental conditions of repositories are classified based on the chemistry of the groundwater that may come into contact with the enclosed nuclear waste. Whether the repository conditions are expected to be oxidizing (e.g. due to emplacement above the water table) or reducing, will dictate the possible corrosion mechanism(s) and, thus, the waste-package design. Most repository designs, except for the proposed (and now tabled) United States repository at Yucca Mountain in Nevada, call for emplacement of the waste package in reducing conditions. For example, Canadian, Finnish, and Swedish design concepts for the waste package assume predominantly reducing conditions during the service life of the repository deep underground (> 400 m deep) in granitic rocks (NWTRB 2009). For our case study, we will focus on a proposed, but not yet active, Swedish and Finnish repository design developed using Cu metal waste canisters.

An important feature of the Swedish and Finnish design is that the waste containers will be emplaced within boreholes in crystalline rock and then surrounded by compacted

bentonite clay, which has a low hydraulic permeability (KBS 1978; SBK 2012). Initially, the water in the repository is expected to be oxidizing due to trapped  $\text{O}_2$  in the tight pore spaces of the clay backfill. Over time,  $\text{O}_2$  will be consumed in reactions with oxidizable material within the repository, and the redox potential (or Eh) will drop. After the initial oxidizing interval, the groundwater that penetrates the clay buffer is expected to be predominantly anoxic (low Eh). Groundwater may also be saline (up to 15,000 mg/L  $\text{Cl}^-$ ), and contain sulfides ( $10^{-7}$ – $10^{-4}$  mol/L) with the primary oxidant being  $\text{H}^+/\text{H}_2\text{O}$  in the presence of sulfide (King et al. 2013). The Eh of the repository environment can be calculated from thermodynamic modeling of the redox species that are expected to be present in the groundwater over the service life of the repository. However, it is the  $E_{\text{corr}}$  value of the Cu containment material that determines the corrosion rate as illustrated by the corrosion current density  $I_{\text{corr}}$  versus  $E_{\text{corr}}$  relationship in FIGURE 2.

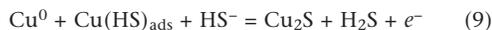
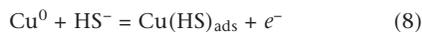
The time dependence of  $E_{\text{corr}}$  and  $I_{\text{corr}}$  over the service life of the repository can be predicted from reactive transport models that utilize electrochemical data. Briefly, reactive transport equations that take into account the diffusion of oxidants and soluble redox species to and from the waste package are solved using finite-difference methods subject to a set of initial and boundary conditions. These boundary conditions are defined by electrochemical rate expressions for all of the possible anodic and cathodic reactions that are expected to occur at the surface of the waste container. Rate constants and reaction orders for each kinetic expression come from extensive electrochemical studies done under experimental conditions that best represent the geochemical environment of the repository. In addition, a condition is imposed that the sum of the rates of the anodic reactions must equal the sum of the rates of the cathodic reactions, and this serves as the basis for a mixed potential model (reviewed in Shoesmith et al. 2003, 2004; King et al. 2011, 2013). Ultimately, predicting the time dependence of  $E_{\text{corr}}$  and  $I_{\text{corr}}$  allows for the estimation of the extent of corrosion (e.g. penetration into metal) over time by a relationship such as Equation (6).

### Copper as a Waste Container and its Resistance to Corrosion

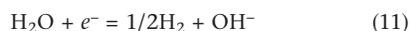
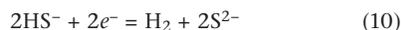
In 1978, the Swedish Corrosion Institute first proposed copper metal as a nuclear waste container material. Containers sheathed in Cu metal were predicted to exceed the 100,000 year service lifetime criteria (KBS 1978). Generally, copper metal is known to be particularly resistant to corrosion in underground environments because it is shielded by supergene minerals that form on the exposed surface. For example, you may have noticed the formation of brightly colored solids forming on the surface of exposed Cu pipes: reddish-brown cuprous oxide ( $\text{Cu}_2\text{O}$ ), green copper carbonates, green sulfates or oxychlorides, or black copper sulfides. Evidence of copper's exceptional corrosion resistance in oxidizing environments also comes from many archeological analogues. For example, underground copper pipes that carried water in Egypt nearly 5,000 years ago are still in existence (Schweitzer 1996). Furthermore, copper is one of the few metals that exist on Earth in its natural (native) form. Modern electrochemical studies using Cu electrodes, an analogue of sorts, predict that the rate of corrosion during the initial oxidizing condition in a repository is limited by the availability and rate of supply of  $\text{O}_2$  to the container, as shown in FIGURE 4A (King et al. 2013). Both the clay backfill and mineral passivation layers on the pure  $\text{Cu}^0$  act as diffusion barriers that limit the transport of  $\text{O}_2$  to electroactive sites on the  $\text{Cu}^0$  surface. In addition, mass transport of redox products away from the corroded surface must also be considered. For

example,  $\text{Cl}^-$  from saline pore water in the surrounding clay backfill enhances corrosion rates via the formation of soluble anions, such as  $\text{CuCl}_2^-$ , that can diffuse away from the container. Under these conditions, diffusion of  $\text{CuCl}_2^-$  away from the surface is rate limiting, as shown in FIGURE 4B.

After all of the  $\text{O}_2$  in the repository is consumed (about 200 years according to some models; King et al. 2013), corrosion will be controlled by hydrogen sulfide,  $\text{HS}^-$ , which may diffuse to the container surface from anaerobic dissolution of sulfides present in the surrounding clay or from possible microbial sulfate reduction. The anodic reactions that occur in the presence of hydrogen sulfide include:



and result in the precipitation of a chalcocite ( $\text{Cu}_2\text{S}$ ) layer on the  $\text{Cu}^0$  surface. The cathodic reactions probably include:



The rate of corrosion of  $\text{Cu}^0$  is not limited by the kinetics of the half reactions but by diffusion of  $\text{HS}^-$  through the  $\text{Cu}_2\text{S}$  layer (Chen et al. 2011, 2014; King and Lilja 2011). Because diffusion of  $\text{HS}^-$  through the surrounding clay barrier is orders of magnitude smaller than diffusion through the porous passivation layers formed on the  $\text{Cu}^0$ , the rate of corrosion of a copper canister in the repository will ultimately be limited by the rate of transport of  $\text{HS}^-$  through the clay barrier (Fig. 4C).

Reactive transport models that incorporate the conditions present during the relatively brief oxic period, as well as the anoxic period, have predicted  $E_{\text{corr}}$  of the canister to drop from  $\sim -0.2$  V to  $\sim -1.0$  V (vs Ag/AgCl) after a few hundred years, and, after depleting the initially trapped  $\text{O}_2$ , remain at these extremely low potentials for  $10^6$  years (King et al. 2011). A brief interval in between the oxic and anoxic periods with an undefined  $E_{\text{corr}}$  indicates a period in which the waste canister heats up to temperatures that dry out the

surrounding clays and effectively shut down aqueous corrosion. Integration of  $I_{\text{corr}}$  over time gives the charge density, which can then be used to determine the depth of corrosion (King et al. 2011). Models generally show  $< 1$  mm of uniform penetration into the Cu after  $10^6$  years suggesting a service lifetime well within the established criteria (King et al. 2013). Model predictions like this are cited as evidence of copper's suitability for nuclear-waste containment designs.

### The Debate about Anaerobic Corrosion Mechanisms

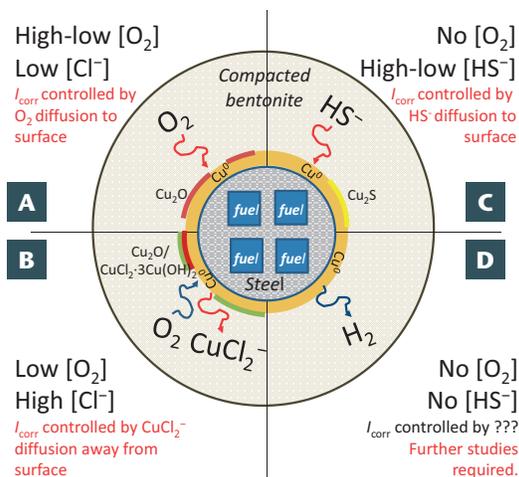
Despite the hopeful predictions above, there remains a question as to whether  $\text{Cu}^0$  will anaerobically corrode by a reaction mechanism(s) that is not considered in the mixed potential models. Specifically, experimental studies have demonstrated the production of  $\text{H}_2$  gas from  $\text{Cu}^0$  that has been immersed in pure anoxic water that does not contain  $\text{HS}^-$  (Hultquist 1986). Though no experimentally verifiable corrosion mechanism has been put forward to explain the production of  $\text{H}_2$ , Åkermark (2013) suggests that these findings are sufficiently provocative to warrant further study (see Fig. 4D). A lack of a comprehensive understanding of all the possible mechanisms of  $\text{Cu}^0$  corrosion would have implications for moving forward with present designs because it could mean the difference between corrosion rates on the order of nanometers per year versus rates as high as micrometers per year (King et al. 2011; Åkermark 2013). Though the debate remains unresolved, both sides agree that more fundamental electrochemical experiments are required to explore all possible mechanisms of  $\text{Cu}^0$  corrosion in anaerobic environments.

### CONCLUSIONS

Corrosion is a fundamental and integral process to the geology that controls the geochemical makeup of the Earth. Corrosion processes have likely played a central role in the origin of life, have been a major factor in the migration and spread of civilization, and will certainly help society (both through the natural production of supergene metal deposits and man's own understanding of corrosive processes) to technologically advance. Electrochemical methods enable geologists and materials scientists to better understand the fundamentals of corrosion and redox reactions through the determination of two fundamental parameters: the corrosion potential, and the corrosion current. Mixed potential models that predict how the corrosion current and corrosion potential vary over geologic time have been applied to  $\text{Cu}^0$  metal proposed to be used in containing and isolating spent nuclear fuel from the environment. This nuclear-waste containment case study, which details  $\text{Cu}^0$  corrosion, provides a framework for understanding how fundamental electrochemical methods and mixed potential models can be used to assess the dissolution of minerals. Electrochemical methods, in combination with surface-sensitive spectroscopy and microscopy techniques, as well as molecular modeling of redox reactions, will help us understand and improve hydrometallurgical processing of minerals and could potentially be used to assess geologic processes involved in the formation and long-term corrosion (weathering) of minerals themselves.

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**FIGURE 4** Schematic showing four generalized examples (A–D) of geochemical conditions that a Cu waste container may experience over the lifetime of a geologic nuclear-waste repository, where the corrosion rate-limiting mechanisms change depending on the evolution of the conditions within the repository. (A) For high-low  $[\text{O}_2]$  and low  $[\text{Cl}^-]$  conditions, the rate-limiting process is  $\text{O}_2$  diffusion through a  $\text{Cu}_2\text{O}$  layer to the metal surface. (B) For low  $[\text{O}_2]$  and high  $[\text{Cl}^-]$  conditions, the rate-limiting process is  $\text{CuCl}_2^-$  diffusion from surface. (C) For no  $[\text{O}_2]$  and high-low  $[\text{HS}^-]$ , the rate-limiting process is  $\text{HS}^-$  diffusion through a  $\text{Cu}_2\text{S}$  layer to the metal surface. (D) Further studies are necessary to confirm the corrosion rate-limiting process(es) in the absence of both  $[\text{O}_2]$  and  $[\text{HS}^-]$ .

## REFERENCES

- Åkermark T (2013) Some scientific considerations on the article: 'Scientific basis for corrosion of copper in water and implications for canister lifetimes' published by F. King and C. Lilja. *Corrosion Engineering, Science and Technology* 48: 475-476
- Bailey LK, Peters E (1976) Decomposition of pyrite in acids by pressure leaching and anodization: the case for an electrochemical mechanism. *Canadian Metallurgical Quarterly* 15: 333-344
- Bard AJ, Faulkner LR (1980) *Electrochemical Methods: Fundamentals and Applications*. John Wiley & Sons, New York, 864 pp
- Chen J, Qin Z, Shoesmith DW (2011) Rate controlling reactions for copper corrosion in anaerobic aqueous sulphide solutions. *Corrosion Engineering, Science and Technology* 46: 138-141
- Chen J, Qin Z, Wu L, Noël JJ, Shoesmith DW (2014) The influence of sulphide transport on the growth and properties of copper sulphide films on copper. *Corrosion Science* 87: 233-238
- Ehrlich HL, Newman DK (2009) *Geomicrobiology*. CRC Press, Boca Raton, 628 pp
- Holland HD (2006) The oxygenation of the atmosphere and oceans. *Philosophical Transactions of the Royal Society B - Biological Sciences* 361: 903-915
- Holmes PR, Crundwell FK (2000) The kinetics of the oxidation of pyrite by ferric ions and dissolved oxygen: an electrochemical study. *Geochimica et Cosmochimica Acta* 64: 263-274
- Hultquist G (1986) Hydrogen evolution in corrosion of copper in pure water. *Corrosion Science* 26: 173-177
- KBS (1978) Copper as canister material for unprocessed nuclear waste - evaluation with respect to corrosion. KBS Teknisk Rapport 90, Final Report 1978-03-31 of the Swedish Corrosion Institute. *Kärn-Bränsle-Säkerhet*, Stockholm, 296 pp
- King F, Lilja C (2011) Scientific basis for corrosion of copper in water and implications for canister lifetimes. *Energy Materials* 6: 153-158
- King F, Kolar M, Vähänen M, Lilja C (2011) Modelling long term corrosion behaviour of copper canisters in KBS-3 repository. *Corrosion Engineering, Science and Technology* 46: 217-222
- King F, Lilja C, Vähänen M (2013) Progress in the understanding of the long-term corrosion behaviour of copper canisters. *Journal of Nuclear Materials* 438: 228-237
- Klein C (2005) Some Precambrian banded iron-formations (BIFs) from around the world: Their age, geologic setting, mineralogy, metamorphism, geochemistry, and origin. *American Mineralogist* 90: 1473-1499
- Koch GH and 5 coauthors (2002) *Corrosion Costs and Preventative Strategies in the United States*. Report number FHWA-RD-01-156, NACE International, Houston, 12 pp
- Meitl LA and 5 coauthors (2009) Electrochemical interaction of *Shewanella oneidensis* MR-1 and its outer membrane cytochromes OmcA and MtrC with hematite electrodes. *Geochimica et Cosmochimica Acta* 73: 5292-5307
- NWTRB (2009) *Survey of National Programs for Managing High-Level Radioactive Waste and Spent Nuclear Fuel*. A Report to Congress and the Secretary of Energy. United States Nuclear Waste Technical Review Board, Arlington, 76 pp
- Renock D, Mueller M, Yuan K, Ewing RC, Becker U (2013) The energetics and kinetics of uranyl reduction on pyrite, hematite, and magnetite surfaces: A powder microelectrode study. *Geochimica et Cosmochimica Acta* 118: 56-71
- Rosso KM, Becker U, Hochella MF Jr (1999) The interaction of pyrite {100} surfaces with O<sub>2</sub> and H<sub>2</sub>O: Fundamental oxidation mechanisms. *American Mineralogist* 84: 1549-1561
- Schweitzer PA (1996) *Corrosion Engineering Handbook*. Marcel Dekker, Inc., New York, NY
- Shoesmith DW (2006) Waste package corrosion. In: Macfarlane AM, Ewing RC (eds) *Uncertainty Underground: Yucca Mountain and the Nation's High-Level Nuclear Waste*. MIT Press, Cambridge, pp 287-299
- Shoesmith DW, Kolar M, King F (2003) A mixed-potential model to predict fuel (uranium dioxide) corrosion within a failed nuclear waste container. *Corrosion* 59: 802-816
- Shoesmith DW, Noël JJ, Gatisto F (2004). An experimental basis for a mixed potential model for nuclear fuel corrosion within a failed waste container. In: Hanchar JM, Stroes-Gascoyne S, Browning L (eds), *Scientific Basis for Nuclear Waste Management XXVIII, Symposium Proceedings*. Materials Research Society, pp 81-87
- SKB (2012) *Long-term safety for the final repository for spent nuclear fuel at Forsmark: Main report of the SR-Site project*. Volumes 1-3, Report SKB TR-11-01. Svensk Kärnbränslehantering AB, Stockholm, 276 pp
- Stern M, Geary AL (1957) Electrochemical polarization. 1. A theoretical analysis of the shape of polarization curves. *Journal of the Electrochemical Society* 104: 56-63
- Taylor BE, Wheeler MC, Nordstrom DK (1984) Stable isotope geochemistry of acid mine drainage: experimental oxidation of pyrite. *Geochimica et Cosmochimica Acta* 48: 2669-2678
- Usher CR, Cleveland CA Jr, Strongin DR, Schoonen MA (2004) Origin of oxygen in sulfate during pyrite oxidation with water and dissolved oxygen: an in situ horizontal attenuated total reflectance infrared spectroscopy isotope study. *Environmental Science & Technology* 38: 5604-5606
- Wagner C, Traud WE (1938) The analysis of corrosion procedures through the interaction of electrochemical partial procedures and on the potential difference of mixed electrodes. *Zeitschrift Für Elektrochemie und Angewandte Physikalische Chemie* 44: 391-402
- Xu Y, Schoonen MAA (2000) The absolute energy positions of conduction and valence bands of selected semiconducting minerals. *American Mineralogist* 85: 543-556

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A crude crystal of djurleite on natrolite and crossite matrix with minor benitoite from the Gem Mine, San Benito Co., California. Image by Dr. J. Weissman from *Excalibur's Photographic Guide to Mineral Species CD*.

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