

Is Copper Immune to Corrosion When in Contact With Water?

Digby D. Macdonald
Center for Electrochemical Science and Technology
Department of Materials Science and Engineering
Pennsylvania State University
University Park, PA 16802
Tel: (814) 863-7772; E-mail: ddm2@psu.edu.

Sweden's SKB-III plan for the disposal of high level nuclear waste (HLNW) is predicated upon the condition that copper, the material from which the canisters will be fabricated, is thermodynamically immune to corrosion when in contact with pure water. In the immune state, corrosion cannot occur because any oxidation process of the copper is characterized by a positive change in the Gibbs energy, rather than a negative change, as demanded by the Second Law of Thermodynamics for a spontaneous process. Accordingly, "immunity" is a thermodynamic state that must be characterized upon the basis of thermodynamic arguments.

Consider the lowest corrosion reaction in the copper/water system:



The change in Gibbs energy for this reaction can be written as

$$\Delta G = \Delta G^0 + 2.303RT \log \left(f_{\text{H}_2}^{1/2} a_{\text{Cu}^+} / a_{\text{H}^+} \right) \quad (2)$$

which, upon rearrangement yields

$$\log \left(f_{\text{H}_2}^{1/2} a_{\text{Cu}^+} \right) = \frac{\Delta G - \Delta G^0}{2.303RT} - pH \quad (3)$$

where ΔG^0 is the change in standard Gibbs energy; i.e., the change in Gibbs energy when all components of the reaction are in their standard state with the fugacity of hydrogen, f_{H_2} , and the activity of cuprous ion, a_{Cu^+} , being equal to one. At equilibrium, $\Delta G = 0$, and designating the equilibrium values of f_{H_2} and a_{Cu^+} with superscripts "e" we may write

$$f_{\text{H}_2}^{e,1/2} a_{\text{Cu}^+}^e = 10^{-\left(\frac{\Delta G^0}{2.303RT} + pH\right)} \quad (4)$$

We now define two quantities, P and P^e , as follows

$$P = f_{\text{H}_2}^{1/2} a_{\text{Cu}^+} \quad (5)$$

and

$$P^e = f_{\text{H}_2}^{e,1/2} a_{\text{Cu}^+}^e \quad (6)$$

The condition for spontaneity of Reaction (1) then becomes $P < P^e$ and immunity is indicated by $P > P^e$.

The quantity P^e has been calculated for Reaction (1) using Equation (4) and is plotted as a function of pH in Figure 1. These plots divide the P versus pH domain into regions of immunity (upper region) and corrosion (lower region). Accordingly, P^e versus pH divides the domain into regions of thermodynamic immunity (upper region) and corrosion (lower region). These plots clearly demonstrate that whether copper is immune (thermodynamically stable) depends sensitively upon the value of P and hence upon the initial conditions in the system. Thus, if P is small (e.g., at Point a, Figure 1), $P < P^e$ and the corrosion of copper is spontaneous as written in Equation (1). On the other hand, if the system is located at Point (b), Figure 1), $P > P^e$ and corrosion is not possible, thermodynamically, and hence the metal is “immune”. Returning now to the case described by Point a, we note that as the corrosion reaction proceeds, the concentration of Cu^+ and the fugacity of hydrogen at the interface will increase, particularly in a medium of restricted mass transport, such that P will steadily increase with time until it meets the value of P^e at the corresponding temperature. At this point, the metal may be classified as being “quasi-immune”; “quasi” only because transport of Cu^+ and H_2 away from the canister surface, through the bentonite overpack must be matched by corrosion, in order to maintain $P = P^e$ at the metal surface. Accordingly, the corrosion rate ultimately becomes controlled by the diffusion of Cu^+ and H_2 through the adjacent bentonite overpack. Thus, we conclude that, for any system starting at a point below the P^e versus pH for the relevant temperature, copper metal is not thermodynamically immune and will corrode in the repository at a rate that is governed by the rate of transport of the corrosion products away from the metal surface. Of course, this rate is readily predicted by solving the diffusion equation, if the diffusivities of Cu^+ and H_2 in bentonite are known.

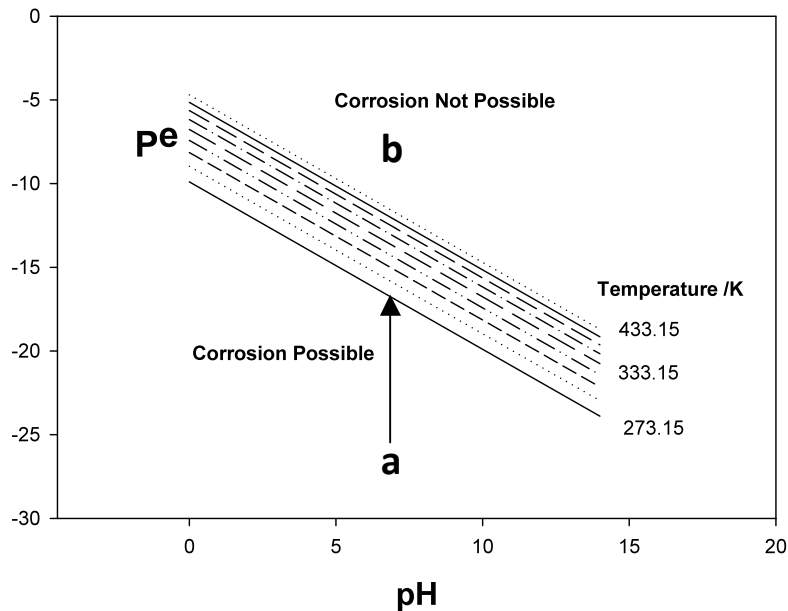


Figure 1: Corrosion domain diagram for copper in water as a function of temperature.

As noted above, for any system whose initial conditions (value of P) lie above the relevant P^e versus pH line, copper is unequivocally immune and corrosion cannot occur as it would violate the Second Law of Thermodynamics. It is evident, that the conditions for immunity may be engineered in

advance by doping the bentonite with a $Cu(I)$ salt and a suitable reducing agent to simulate hydrogen, such that the initial conditions lie above P^e versus pH. It is suggested that cuprous sulfite, Cu_2SO_3 , might be a suitable material. Of course, the dopant will slowly diffuse out of the bentonite and into the external environment, but it might be sufficiently slow that the conditions of immunity may be maintained for a considerable period. Thus, in a “back-of-the-envelope” calculation,

$$t = L^2/D \quad (7)$$

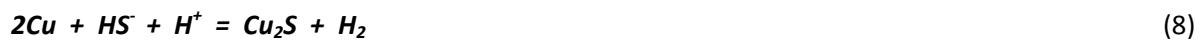
we choose $L = 10$ cm and $D = 10^{-9}$ cm²/s to yield a diffusion time of 10^{11} seconds or 316,456 years. At a time of this order, the value of P at the canister surface will have been reduced to P^e and corrosion will have initiated at a rate that is determined by the transport of Cu^+ and H_2 through the bentonite overpack. It is important to note that the above calculation is only a rough estimate and that a more accurate value can be obtained by solving the diffusion equation with experimentally determined values for the diffusivities of Cu^+ and H_2 . The important point is that immunity may be maintained for a sufficiently long period that the more active components of the HLNW will have decayed away.

Table 1: Prediction of copper corrosion in pure water as a function of solution composition at 273.15 K and at pH = 7. Activity coefficients assumed to be one. $\text{Log}(P^e) = -16.895$.

Case	a_{Cu^+}	ppb _{Cu⁺}	f_{H_2}	ppb _{H₂}	Log(P)	Corrosion possible?
1	10^{-6}	63	10^{-6}	0.002	-9	No
2	10^{-6}	63	10^{-12}	2×10^{-9}	-12	No
3	10^{-6}	63	10^{-18}	2×10^{-15}	-15	No
4	10^{-6}	63	10^{-24}	2×10^{-21}	-18	Yes
5	10^{-6}	63	10^{-30}	2×10^{-27}	-21	Yes
6	10^{-6}	63	10^{-18}	2×10^{-15}	-15	No
7	10^{-12}	63×10^{-6}	10^{-18}	2×10^{-15}	-21	Yes
8	10^{-18}	63×10^{-12}	10^{-18}	2×10^{-15}	-27	Yes
9	10^{-24}	63×10^{-18}	10^{-18}	2×10^{-15}	-33	Yes
10	10^{-30}	63×10^{-24}	10^{-18}	2×10^{-15}	-39	Yes

To complete the discussion with regards to copper immunity, when in contact with pure water, we give in Table 1 various combinations of the fugacity of hydrogen, f_{H_2} , and the activity of cuprous ion, a_{Cu^+} , and the calculated values of P , together with a judgment on whether corrosion is possible or whether immunity should prevail. As can be seen from the values contained in Table 1, the values of $P^e = [Cu^+].p_{H_2}^{1/2}$, for equilibrium, assuming unit activity and fugacity coefficients, are very low and hence it should be relatively easy to ensure immunity by doping as indicated above. However, it is also noted that experiments that have been performed to detect the corrosion of copper in contact with pure water have yielded contradictory results, with some experiments indicating that corrosion occurs while others indicate that copper is immune. It is suggested by the present author that this unsatisfactory state of affairs stems from a poor definition of the initial conditions of the experiment, and in some cases the concentration of Cu^+ and H_2 may be such that P exceeds the equilibrium P^e versus pH correlation and hence the system pre-exists in the immune condition. In this case, no corrosion would be expected to occur as the metal is thermodynamically immune. On the other hand, in other experiments, the initial $[Cu^+]$ and p_{H_2} may be such that the system is characterized by a P value that lies below the P^e versus pH correlation shown in Figure 1, indicating that corrosion is spontaneous. In this instance, corrosion will occur until the concentrations of corrosion products build-up in a closed system to render $P = P^e$. At that point, corrosion will cease. Clearly, considerable care must be exercised, when designing experiments to demonstrate the corrosion of copper, to ensure that corrosion is spontaneous upon initiation of the experiment.

The analysis presented above is restricted to the corrosion of copper in contact with pure water. However, ground water is far from pure and a common contaminant is bisulfide ion, HS^- . This species arises from dissolution of sulfide minerals in the host rock of the repository, from dissolution of pyrite in the bentonite, and even from the decomposition of organic (plant) material. It is fair to conclude that bisulfide, and other sulfur-containing species are ubiquitous in groundwater environment at concentration ranging up to a few ppm, at least. It is also well-known that sulfide, including bisulfide, activates copper by giving rise to the formation of Cu_2S at potentials that are significantly more negative than the potential for the formation of Cu_2O . Thus, in the presence of bisulfide, the lowest corrosion reaction of copper may be written as



for which the change in Gibbs energy is written as

$$\Delta G = \Delta G^0 + 2.303RT \log \left(f_{H_2}^{1/2} / a_{HS^-} \cdot a_{H^+} \right) \quad (9)$$

As before, we define an equilibrium value of P as

$$P^e = f_{H_2}^{e,1/2} / a_{HS^-}^e \quad (10)$$

where

$$f_{H_2}^{e,1/2} / a_{HS^-}^e = 10^{-\left(\frac{\Delta G^0}{2.303RT} + pH\right)} \quad (11)$$

Values of P^e versus pH are plotted in Figure 2 as a function of temperature for temperatures ranging from 0 °C to 160 °C in steps of 20 °C. Again, P^e versus pH divides the diagram into two regions corresponding to spontaneous corrosion (lower region) and immunity (upper region). The reader will note that the P^e values for the lines are more positive than those for the Cu – pure water case by a factor of about 10^{27} , demonstrating that immunity is much more difficult to achieve in the presence of bisulfide.

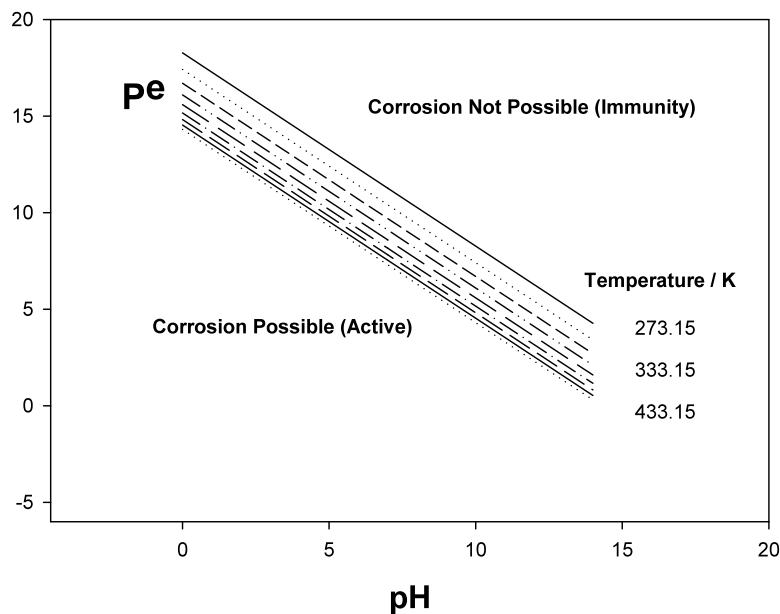


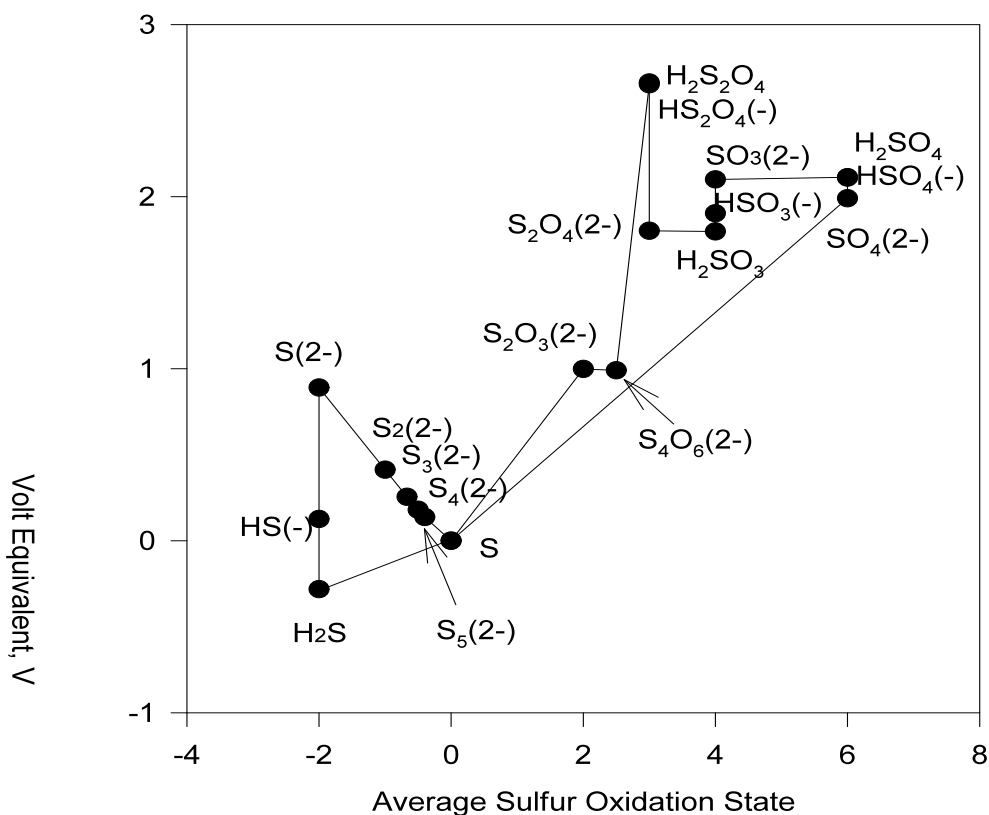
Figure 2: Corrosion domain diagram for copper in water + HS⁻ as a function of temperature.

In order to illustrate the difficulties posed by small amounts of bisulfide in the environment, different combinations of the fugacity of hydrogen, f_{H_2} , and the activity of cuprous ion, a_{Cu^+} , together with the corresponding value of P^e for $T = 273.15$ K and $pH = 7$ are given in Table 2. Noting again that immunity is achieved only if $P > P^e$, it is evident that the desired immune condition could only be achieved by having extraordinarily low concentration of HS⁻ and/or an extraordinarily high partial pressure of hydrogen. For example, the two conditions that are listed in Table 2 that are predicted to yield immunity are Cases 4 and 9, which have [HS⁻] and p_{H_2} combinations of 3.3×10^{-10} ppm and 10^{-6} atm and 0.033 ppm and 10^{10} atm, respectively. In the first case, the concentration of HS⁻ is orders of magnitude lower than the sulfide concentration in ground water (a few ppb to a few ppm), particularly in the presence of bentonite, which commonly contains pyrite, FeS₂. In the second case, the required partial pressure of hydrogen (10^{10} atm) is impossibly high to be achieved and maintained practically in the repository. Accordingly, the prospects for achieving immunity of copper in a repository in which the ground water contains a significant concentration of bisulfide must be judged as being remote. Of

course, these predictions can be easily checked by experiment and experiments to do so should be performed at the earliest opportunity.

Table 2: Prediction of copper corrosion in pure water containing bisulfide ion as a function of solution composition at 273.15 K. Activity coefficients assumed to be one. $\text{Log}(P^e) = 10.21$.

Case	$a_{\text{HS}^-} / \text{m}$	ppm_{HS^-}	$f_{\text{H}_2} / \text{atm}$	ppb_{H_2}	$\text{Log}(P)$	Corrosion possible?
1	10^{-4}	3.3	10^{-6}	0.002	1	Yes
2	10^{-6}	0.033	10^{-6}	0.002	3	Yes
3	10^{-8}	0.00033	10^{-6}	0.002	5	Yes
4	10^{-10}	0.0000033	10^{-6}	0.002	7	Yes
5	10^{-12}	3.3×10^{-8}	10^{-6}	0.02	9	Yes
6	10^{-14}	3.3×10^{-10}	10^{-6}	0.02	11	No
5	10^{-6}	0.033	10^{-4}	0.2	4	Yes
6	10^{-6}	0.033	10^{-2}	20	5	Yes
7	10^{-6}	0.033	1	2000	6	Yes
8	10^{-6}	0.033	10^2	2×10^5	7	Yes
9	10^{-6}	0.033	10^4	2×10^7	8	Yes
10	10^{-6}	0.033	10^6	2×10^9	9	Yes
11	10^{-6}	0.033	10^8	2×10^{11}	10	Yes
12	10^{-6}	0.033	10^{10}	2×10^{13}	11	No



Volt Equivalent Diagram for S/H₂O System at pH=0 and at 25 C

Figure 3: Volt-Equivalent diagram for the S/H₂O system at 25°C, pH = 0.

As noted above, the calculations presented above are of a “back-of-the-envelope” nature and a much more detailed analysis is warranted to fully define the conditions over which immunity of copper might be expected. The analysis should involve the following activities:

1. The analysis should entail the full range of sulfur species, as defined in the volt-Equivalent diagram (e.g., Figure 3). All of the species plotted in this diagram, except sulfite and sulfate, can donate atomic sulfur to the copper surface and hence, potentially, are strong activators of the metal, thereby making immunity harder to achieve. Other activating species should be included in the analysis, including chloride, bromide, and other anions. It is important to note that the sulfur species used to construct the Volt-Equivalent Diagrams are very labile and hence readily change from one to the other as conditions change in the system. Accordingly, a prime objective will be to ascertain which of the species are the most effective at destroying immunity on copper. This can only be done by comparing the Corrosion Domain Diagrams (e.g., Figures 1 and 2) for the reaction of copper with each of the sulfur species.

2. The system should be modeled along the corrosion evolutionary path, which is defined by the variation of temperature, pH, $[HS^-]$, and p_{H_2} as the repository ages; note that these four quantities are the primary independent variables for Reactions (1) and (8). The time dependences of pH, $[HS^-]$, and p_{H_2} must be modeled by solving the transport equations for the transfer of H^+ , HS^- , and H_2 across the bentonite layer, recognizing the existence of a source term for bisulfide in the bentonite (dissolution of FeS_2). Solution of the thermal diffusion equation will yield the temperature as a function of distance from the copper surface and time. Because the diffusivities of H^+ , HS^- , and H_2 are temperature-dependent, as is the rate constant for FeS_2 dissolution, the system of equations that will describe the evolution of the repository and hence that will indicate whether and under what conditions immunity may be achieved, will be highly non-linear and must be solved numerically.
3. The possibility of doping the bentonite with a $Cu(I)$ salt, such as Cu_2SO_3 , should be explored to determine whether immunity might be maintained over extended periods. Thus, the “back-of-the-envelope” calculations reported above suggest that immunity might be maintained over periods of several hundreds of thousands of years. Given that the performance horizon of the repository is 10,000 years, it may well be possible to impose immunity on the system over the entire, planned storage period. Practically, this issue could be explored by inserting source terms in the model outlined in 2 above for Cu^+ and SO_3^{2-} from the bentonite overpack.