



Comment on “Nanometer-Scale Corrosion of Copper in De-Aerated Deionized Water” [*J. Electrochem. Soc.*, 161, C107 (2014)]

K. Spahiu^z and I. Puigdomenech

Swedish Nuclear Fuel and Waste Management Co., SE-101 24 Stockholm, Sweden

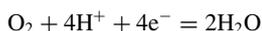
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Cleveland et al.¹ reported a study on the corrosion of copper metal in de-aerated water, stating a corrosion rate of 1 nm/day in deionized water if the O₂ concentration is on the order of, or less than, 1 ppb. (The temperature is not reported, in the following we assume it was ≈25°C.)

We claim that the trace amounts of oxygen in the experiment are sufficient to explain the derived corrosion rates. We also have concerns regarding the thermodynamic calculations and regarding the way in which the authors interpret results of thermodynamic calculations in other studies. These points are developed in the following.

Incompletely Deaerated Conditions

In the thermodynamic analysis by Cleveland et al.,¹ the oxygen line in the Pourbaix diagram (their Figure 5) represents the equilibrium:



with an equilibrium constant equal to 10^{83.2} (from the Phreeqc database²). This reaction corresponds to:

$$E_{\text{SHE}} = 1231 \text{ mV} - 59.16 \text{ pH} + 59.16 (\log p_{\text{O}_2}) / 4$$

where p_{O_2} is the equilibrium partial pressure of oxygen gas. This expression is plotted as line “b” in Figure 5 of Cleveland et al.,¹ and it shows that the redox potential depends on the logarithm of p_{O_2} . Even by assuming that by flushing with an inert gas one can decrease the partial pressure of oxygen by about eight orders of magnitude (from 0.21 atm to 1 ppb or 10⁻⁹ atm), the redox potential will only decrease by 59.16 × (-9/4) = -123 mV as compared to 1 atm O₂. Thus, the point plotted apparently at random by the authors in Fig. 5 between the points where the line pH = 7 intersects the lines “a” and “b” (read in the plot as ~+380 mV at pH 7) should instead have been plotted at ~+683 mV at pH 7 for 1 ppb O₂ in gas phase, but higher up in the region where CuO(s) and Cu(OH)₂(aq) are the more stable species of the Cu-O-H system. Even such small O₂ concentrations hence represent very oxidizing conditions for metallic copper. Additionally, in Figure 5 the label “Cu⁺” is obviously a misprint, because the stability area of Cu⁺ would be dependent on the redox potential but independent of pH.

The experimental setup used by Cleveland et al.¹ consisted of 30 mL solution purged with 99.9999% N₂ directly from the gas flask through a microporous glass filter. The oxygen content of the gas emanating from the cell was determined as 1–2 ppb oxygen in the gas phase, that is, the partial pressure of oxygen in the measuring cell was $p_{\text{O}_2} \approx (1 \text{ or } 2) \cdot 10^{-9} \text{ atm}$, given that the total ambient pressure during the measurement was ≈1 atm. Using Henry’s law constant,³ this would correspond to an oxygen concentration in solution of ≈(1.3–2.6) · 10⁻¹² M. This is equivalent to (4.2–8.3) · 10⁻⁵ ppb in the aqueous phase. In a separate experiment, the authors measured 8 to 18 ppb O₂ as an upper limit in the water with the same oxygen sensor, and the authors estimated O₂ concentrations from impedance measurements to be <6.5 ppb. It seems that either of the measurements, gas phase or water phase, are more than 5 orders of magnitude in error; alternatively the measurements are insufficiently described. Thus 6.5 ppb O₂ in the aqueous solution corresponds to ≈157 ppm (not ppb) in the gas phase.

In similar experiments, King et al.⁴ estimated the dissolved O₂ from the transport-limited O₂ reduction current (measured on a copper rotating disc electrode) to ~20 ppb. We consider that more detail on the calibration procedure for measuring such low oxygen levels would have been necessary in the paper. Also, the measures used to avoid oxygen contamination in their experimental setup, for example how diffusion of air through ground glass joints and through the gas exit was avoided etc, require a thorough description. An example of a detailed description of the experimental methodology to avoid oxygen intrusion in the measuring system may be found e.g. in Bockris and Pentland⁵ and in Grønland and Noer.⁶

We will explore the possibility that traces of oxygen introduced in the experimental vessel used by the authors can explain the copper corrosion rates that the authors derived from the interpretation of their impedance data. The reduction mechanism of O₂ on Cu has been studied in detail by King et al.^{7,8} and Vazquez et al.^{9,10} The reaction is highly irreversible and involves the reduction of O₂ to OH⁻ ions via four one electron transfer steps.

Cleveland et al.¹ state that “If oxygen were present in the experimental system, the concentration associated with the upper bound of 2.5 nm/day would have been 6.5 ppb”. We do not understand how the value 6.5 ppb was obtained. Since the O₂ measurements of the gas phase and the aqueous solution are, as explained above, in contradiction, it is not clear what O₂ concentration prevailed in the aqueous solutions used by the authors. If the concentration of dissolved O₂ was 8 ppb, as measured by the authors, this would correspond to 2.5 × 10⁻⁷ mol/L and the total amount of dissolved oxygen in the 30 cm³ of solution is 7.5 × 10⁻⁹ mol. One should compare this value with the amount of oxygen that would be needed to explain the corrosion rate. The copper electrode used by the authors is a wire 0.25 mm in diameter, with an exposed area of 4.9 × 10⁻⁴ cm². The corrosion rate (Table V, p. C113) is 3.2 × 10⁻⁵ mA/cm² from kinetic simulations and <7.9 × 10⁻⁵ mA/cm² from extrapolation of impedance measurements. By considering that each molecule of oxygen consumes 4 electrons, the larger value of the reported corrosion rates, if caused by oxygen, would require consumption of 8.7 × 10⁻¹² mol O₂/day. Thus, the amount of dissolved oxygen (7.5 × 10⁻⁹ mol) in 30 cm³ of solution containing 8 ppb dissolved O₂, is sufficient to explain the reported corrosion rate (8.7 × 10⁻¹² mol O₂/day), at least for many weeks.

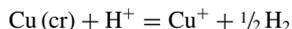
One could, however, assume a much lower O₂ concentration in the aqueous phase, since the authors report measurements of 1 to 2 ppb in the gas phase. The lowest of these values, 1 ppb, indicates that even a small flow rate (≈0.2 L/day) of the gas phase (N₂) contain enough traces of oxygen to account for the observed corrosion rate (<7.9 × 10⁻⁵ mA/cm²) from a mass-balance point of view. Considering that volumes much larger than ≈0.2 L/day would be required to maintain de-aerated conditions in the experimental vessel (perhaps 0.7 L/hour or more, by purging with ≈0.2 mL/s), also the measured O₂ concentrations in the gas phase suggest that this oxygen could cause the measured corrosion rates. As noted above, a gas phase oxygen concentration of 1 ppb represent very oxidizing conditions for metallic copper.

Relation to Study by Hultquist et al.

The authors make several references to a study by Hultquist et al.,¹¹ and to some extent compare their results to those by Hultquist

^zE-mail: kastriot.spahiu@skb.se

et al. We would like to point out that Hultquist et al. performed their experiment in a closed system where any traces of oxygen would be quickly consumed through reactions with the metallic copper in the system, thus yielding completely deaerated conditions, contrary to the case for system studied by Cleveland et al. When in contact with completely deaerated water, copper could corrode until an equilibrium concentration of H_2 in the aqueous phase is reached. The corresponding partial pressure of hydrogen in a gas phase at equilibrium with such an aqueous solution may be calculated using the equilibrium constant for the main reaction



A straightforward calculation of the equilibrium of this reaction yields very similar equilibrium concentrations as a calculation with a chemical equilibrium software such as PhreeqC², which includes all possible side redox reactions. The calculations give a partial pressure of $H_2 \approx 10^{-8.6}$ atm in the gas phase (2.5 ppb) and $\approx 4 \times 10^{-12}$ mol Cu(I)/L. This partial pressure of hydrogen gas results in a value of $P = f_{H_2}^{\frac{1}{2}} a_{Cu^+} \approx 10^{-16}$ at pH = 7, as seen also in Figure 1 of the technical report by Macdonald and Sharifi-Asl.¹² However, contrary to the statements made by Cleveland et al.,¹ these calculated H_2 fugacities are *not* consistent with the experimental observations^{11,13} made by Hultquist and co-workers of hydrogen partial pressures in the order of tenths of millibar. (Nor is this stated by Macdonald and Sharifi-Asl;¹² they only state that at sufficiently low partial pressures of hydrogen and copper ion concentrations, copper corrosion will occur to a certain extent, which is consistent with the equilibrium data given above.) Hence, whereas the results by Cleveland et al. are compatible with thermodynamic data, those by Hultquist et al. are not. (The paper by Hultquist et al. will be further commented in a Correspondence to the journal in which it was published.)

It is also illustrative to compare the corrosion rate derived by the authors from their impedance measurements, with the H_2 production rate reported by Hultquist et al.¹³ The copper corrosion rate derived by the authors from their impedance measurements ($< 7.9 \times 10^{-5}$ mA/cm²) corresponds to a production rate of $< 1.7 \times 10^{-11}$ mol H_2 /day, assuming that the formation of each H_2 molecule requires two electrons. From Table 1 in Hultquist et al.¹³ the H_2 production rate is $\approx 6.4 \times 10^{-9}$ mol H_2 /day at 23°C. The copper surface area in the experiment by Cleveland et al. is 4.9×10^{-4} cm² and that in the

experiment by Hultquist et al. is 140 cm². Normalising to unit areas, it follows that the observed corrosion rate by Cleveland et al. is around three orders of magnitude higher than the rate that may be derived from the observations published by Hultquist et al.¹³ This suggests that different processes are observed in the two experiments.

Conclusions

We conclude that the results presented by the authors¹ may not be considered to support the claim that copper will corrode in deaerated deionized water if hydrogen is removed. Instead the results may be explained by the presence of traces of oxygen in the experimental setup. The authors' conclusion regarding the relevance of their findings for e.g. nanometer scale electronics may still be correct, provided that they are applied to systems with trace amounts of oxygen. However, for the considerably more reducing conditions (Eh typically below -100 mV) expected in a final repository for nuclear waste, these findings are not relevant.

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