

1 **Comment on “Nanometer-scale corrosion of copper in de-aerated deionized**
2 **water” [J. Electrochem. Soc., 161, C107 (2014)]**

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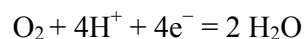
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5 Cleveland et al.¹ reported a study on the corrosion of copper metal in de-aerated water, stating
6 a corrosion rate of 1 nm/day in deionized water if the O₂ concentration is on the order of, or
7 less than, 1 ppb. (The temperature is not reported,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

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

12 **Incompletely deaerated conditions**

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



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

18
$$E_{\text{SHE}} = 1231 \text{ mV} - 59.16 \text{ pH} + 59.16 (\log p_{\text{O}_2})/4$$

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

31 The experimental setup used by Cleveland et al.¹ consisted of 30 mL solution purged with
32 99.9999 % N₂ directly from the gas flask through a microporous glass filter. The oxygen
33 content of the gas emanating from the cell was determined as 1-2 ppb oxygen in the gas
34 phase, that is, the partial pressure of oxygen in the measuring cell was $p_{\text{O}_2} \approx (1 \text{ or } 2) 10^{-9}$ atm,
35 given that the total ambient pressure during the measurement was ≈1 atm. Using Henry’s law
36 constant³, this would correspond to an oxygen concentration in solution of ≈ (1.3 – 2.6) 10⁻¹²
37 M. This is equivalent to (4.2 – 8.3) 10⁻⁵ ppb in the aqueous phase. In a separate experiment,

38 the authors measured 8 to 18 ppb O₂ as an upper limit in the water with the same oxygen
39 sensor, and the authors estimated O₂ concentrations from impedance measurements to be
40 < 6.5 ppb. It seems that either of the measurements, gas phase or water phase, are more than 5
41 orders of magnitude in error; alternatively the measurements are insufficiently described.
42 Thus 6.5 ppb O₂ in the aqueous solution corresponds to ≈157 ppm (not ppb) in the gas phase.
43 In similar experiments, King et al.⁴ estimated the dissolved O₂ from the transport-limited O₂
44 reduction current (measured on a copper rotating disc electrode) to ~20 ppb. We consider that
45 more detail on the calibration procedure for measuring such low oxygen levels would have
46 been necessary in the paper. Also, the measures used to avoid oxygen contamination in their
47 experimental setup, for example how diffusion of air through ground glass joints and through
48 the gas exit was avoided etc, require a thorough description. An example of a detailed
49 description of the experimental methodology to avoid oxygen intrusion in the measuring
50 system may be found e.g. in Bockris and Pentland⁵ and in Grønlund and Noer⁶.

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

56 Cleveland et al.¹ state that “If oxygen were present in the experimental system, the
57 concentration associated with the upper bound of 2.5 nm/day would have been 6.5 ppb”. We
58 do not understand how the value 6.5 ppb was obtained. Since the O₂ measurements of the gas
59 phase and the aqueous solution are, as explained above, in contradiction, it is not clear what
60 O₂ concentration prevailed in the aqueous solutions used by the authors. If the concentration
61 of dissolved O₂ was 8 ppb, as measured by the authors, this would correspond to 2.5×10^{-7}
62 mol/L and the total amount of dissolved oxygen in the 30 cm³ of solution is 7.5×10^{-9} mol.
63 One should compare this value with the amount of oxygen that would be needed to explain
64 the corrosion rate. The copper electrode used by the authors is a wire 0.25 mm in diameter,
65 with an exposed area of 4.9×10^{-4} cm². The corrosion rate (Table V, p. C113) is 3.2×10^{-5}
66 mA/cm² from kinetic simulations and $< 7.9 \times 10^{-5}$ mA/cm² from extrapolation of impedance
67 measurements. By considering that each molecule of oxygen consumes 4 electrons, the larger
68 value of the reported corrosion rates, if caused by oxygen, would require consumption of
69 8.7×10^{-12} mol O₂/day. Thus, the amount of dissolved oxygen (7.5×10^{-9} mol) in 30 cm³ of
70 solution containing 8 ppb dissolved O₂, is sufficient to explain the reported corrosion rate
71 (8.7×10^{-12} mol O₂/day), at least for many weeks.

72 One could, however, assume a much lower O₂ concentration in the aqueous phase, since the
73 authors report measurements of 1 to 2 ppb in the gas phase. The lowest of these values, 1 ppb,
74 indicates that even a small flow rate (≈0.2 L/day) of the gas phase (N₂) contain enough traces
75 of oxygen to account for the observed corrosion rate ($< 7.9 \times 10^{-5}$ mA/cm²) from a mass-
76 balance point of view. Considering that volumes much larger than ≈0.2 L/day would be
77 required to maintain de-aerated conditions in the experimental vessel (perhaps 0.7 L/hour or
78 more, by purging with ≈0.2 mL/s), also the measured O₂ concentrations in the gas phase

79 suggest that this oxygen could cause the measured corrosion rates. As noted above, a gas
80 phase oxygen concentration of 1 ppb represent very oxidizing conditions for metallic copper.

81 **Relation to study by Hultquist et al.**

82 The authors make several references to a study by Hultquist et al.¹¹, and to some extent
83 compare their results to those by Hultquist et al. We would like to point out that Hultquist et
84 al. performed their experiment in a closed system where any traces of oxygen would be
85 quickly consumed through reactions with the metallic copper in the system, thus yielding
86 completely deaerated conditions, contrary to the case for system studied by Cleveland et al.
87 When in contact with completely deaerated water, copper could corrode until an equilibrium
88 concentration of H₂ in the aqueous phase is reached. The corresponding partial pressure of
89 hydrogen in a gas phase at equilibrium with such an aqueous solution may be calculated using
90 the equilibrium constant for the main reaction



92 A straightforward calculation of the equilibrium of this reaction yields very similar
93 equilibrium concentrations as a calculation with a chemical equilibrium software such as
94 PhreeqC², which includes all possible side redox reactions. The calculations give a partial
95 pressure of H₂ $\approx 10^{-8.6}$ atm in the gas phase (2.5 ppb) and $\approx 4 \times 10^{-12}$ mol Cu(I)/L. This partial
96 pressure of hydrogen gas results in a value of $P = f_{\text{H}_2}^{1/2} a_{\text{Cu}^+} \approx 10^{-16}$ at pH = 7, as seen also in
97 Figure 1 of the technical report by Macdonald and Sharifi-Asl¹². However, contrary to the
98 statements made by Cleveland et al.¹, these calculated H₂ fugacities are *not* consistent with the
99 experimental observations^{11,13} made by Hultquist and co-workers of hydrogen partial
100 pressures in the order of tenths of millibar. (Nor is this stated by Macdonald and Sharifi-Asl¹²;
101 they only state that at sufficiently low partial pressures of hydrogen and copper ion
102 concentrations, copper corrosion will occur to a certain extent, which is consistent with the
103 equilibrium data given above.) Hence, whereas the results by Cleveland et al. are compatible
104 with thermodynamic data, those by Hultquist et al. are not. (The paper by Hultquist et al. will
105 be further commented in a Correspondence to the journal in which it was published.)

106 It is also illustrative to compare the corrosion rate derived by the authors from their
107 impedance measurements, with the H₂ production rate reported by Hultquist et al.¹³. The
108 copper corrosion rate derived by the authors from their impedance measurements ($< 7.9 \times 10^{-5}$
109 mA/cm²) corresponds to a production rate of $< 1.7 \times 10^{-11}$ mol H₂/day, assuming that the
110 formation of each H₂ molecule requires two electrons. From Table 1 in Hultquist et al.¹³ the
111 H₂ production rate is $\approx 6.4 \times 10^{-9}$ mol H₂/day at 23°C. The copper surface area in the
112 experiment by Cleveland et al. is 4.9×10^{-4} cm² and that in the experiment by Hultquist et al. is
113 140 cm². Normalising to unit areas, it follows that the observed corrosion rate by Cleveland et
114 al. is around three orders of magnitude higher than the rate that may be derived from the
115 observations published by Hultquist et al.¹³ This suggests that different processes are observed
116 in the two experiments.

117 **Conclusions**

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

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