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Comments on E. Huttunen-Saarivirta et al., "Kinetic Properties of the Passive Film on Copper in the Presence of Sulfate-Reducing Bacteria" [*J. Electrochem. Soc.*, 165, C450 (2018)]

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In their recent journal article,[1] E. Huttunen-Saarivirta et al. have reported experiments involving 10 months' exposure of Cu specimens in simulated groundwater containing sulfate-reducing bacteria (SRB), in which electrochemical impedance spectroscopy (EIS) was used to characterize the corrosion process of these Cu specimens in situ as a function of exposure time. The EIS spectra were then interpreted using the point defect model (PDM), resulting in a claim by the authors that the Cu had been passivated. However, they also stated that the thickness of the barrier layer (passive Cu_2S film determined by XRD) was only ~ 4 nm, 0.3% of the whole thickness of the Cu_2S corrosion deposit (1.4 μm, determined by weight loss measurements), with the remaining (at least) 99.7% of the thickness being due to a porous outer Cu_2S layer. This claim raises the spectre that a passive Cu_2S film will form on the surfaces of Cu containers for nuclear fuel waste under deep geologic repository conditions, such as those anticipated in Sweden,, Finland, and Canada, and hence leaves open the question of whether or not pitting will be possible, since passivity is a pre-requisite for pitting corrosion. If this is indeed the case, then the commonly adopted specification of a corrosion allowance for nuclear waste containers in lifetime prediction models in Sweden, Finland and Canada[2–4] should be re-examined.

In this review, we offer comments about selected aspects of the paper by Huttunen-Saarivirta et al.,[1] considering the published literature and our own recent experimental results, and based on their results and those of their coworkers regarding the issue of whether or not Cu passivity is possible in deaerated sulfide solutions.

Critical Reflections

The article published by E. Huttunen-Saarivirta et al.[1] purports to demonstrate that Cu is passive in simulated groundwater in the presence of microbes (i.e., SRB), even though, in the reported experiments, it was covered with a ~ 1.4 μm-thick Cu_2S corrosion deposit and no pitting corrosion was observed after 10 months' exposure. The authors also misrepresented previous conclusions drawn by us,[5] stating that we "suggest that pitting may only occur at high sulfide concentrations".[1] However, our paper[5] states that a passive copper sulfide film would only grow under high SH^- concentration and flux conditions, an environment not anticipated in a deep geological repository (DGR). Even under such extreme conditions, the experiments presented in our paper[5] showed no evidence of pitting corrosion.

The cyclic voltammetry (CV) data presented in the Huttunen-Saarivirta et al. study[1] are misinterpreted. In the case of the cyclic anodic polarization curves (Figure 2a in Ref. 1), the authors claim that the plateau in the potentiodynamic scan at t = 10 months indicates the growth of a passive film. However, upon scan reversal, the current is retraceable for most of the scan. Such behavior should not be observed for any passive material;[6–8] instead the current should be much closer to zero on the reverse scan than on the positive-going scan. That it is not suggests that any film formed on the positive-going scan does not impede further copper oxidation and film formation from occurring on the reverse scan. This would signify the growth of a porous film, not a passive one. As well, based on the evolution of the corrosion potential (E_{CORR}) of oxygen-free phosphorous-doped copper (Cu-OFP) with the exposure time (Figure 2b in Ref. 1), the authors attributed the initial drop in the E_{CORR} to the formation of the passive film and the subsequent stabilization of the E_{CORR} to the achievement of Cu passivity, which is not convincing and lacks experimental support. More generally, for most metals the opposite is observed; an increase in the E_{CORR} is the common signature of passivity. The reasonable explanation for the E_{CORR} changes is that the conversion of the air-formed oxides on the Cu-OFP surface into sulfides[9] and the adsorption of sulfides[10–15] lead to a negative shift in the $E_{CORR.}$ The subsequent growth of a sulfide film in sulfide-sustained solutions[10,11,14] then stabilizes the E_{CORR} at some value (i.e., ~ −590 V/SHE in Ref. 1).

Interestingly, the breakdown of a passive Cu_2S film was not observed in the Huttunen-Saarivirta et al. study.[1] The authors claimed that pitting did not occur, due to a shift of the breakdown potential to more positive potentials, outside the window of the polarization scan. They stated that the breakdown potential shifts due to three factors: chloride concentration, polarization scan rate, and temperature. However, the same factors cause changes to the potential at which Cl^- will interact with metallic Cu to begin anodic dissolution of the surface. These effects, in the absence of SH^-, are shown in new data measured by us and presented here as Figures 1–3. Both the temperature (Figure 1) and the chloride concentration (Figure 2) have a marked effect, while the scan rate (Figure 3) appears to have little effect on the onset potential for the anodic current increase. Huttunen-Saarivirta et al.[1] argue that pitting (a breakdown potential) was not observed in their experiments due to the influence of these factors, but neglected to acknowledge that the same factors also shift the potential for Cl^--induced anodic dissolution such that it would not be observed in the potential range they employed. An alternative explanation for the anodic current rise, rather than the breakdown of a passive film, is anodic dissolution of the Cu surface, due to copper oxidation and formation of the soluble $CuCl_2^-$ species. We have previously shown[16] that the breakdown potential claimed by Mao et al.[17] is, in fact, the onset potential of active Cu dissolution, accelerated by Cl^- complexation in the pores of a Cu_2S film. Moreover, such a current rise is observed both in the presence and in the absence of SH^-. There is an abundance of literature[7,18–26] demonstrating that the active dissolution of Cu in Cl^--containing solutions occurs in the same potential region in which the so-called breakdown potential is observed. Huttunen-Saarivirta et al.[1] dismissed this explanation on the basis that very little Cu was found in the groundwater after the test was completed. Given

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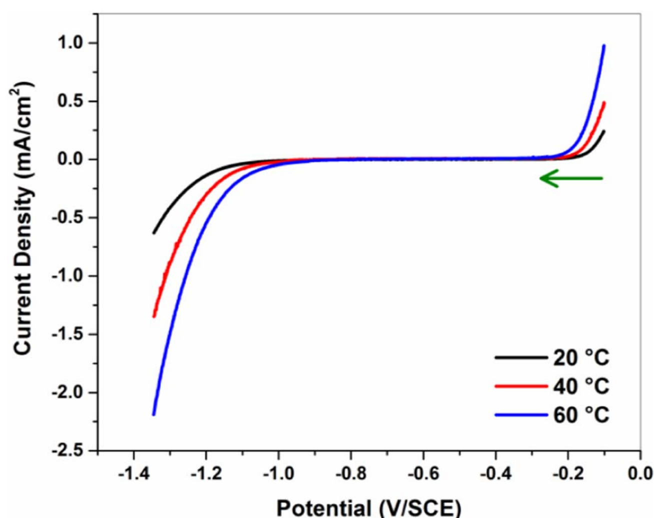

Figure 1. Potentiodynamic polarization curves recorded on copper in 0.1 M NaCl at a scan rate of 2 mV/s at an electrode rotation rate of 500 RPM at various temperatures as indicated. The green arrow emphasizes that the onset potential for anodic current increase becomes more negative with increasing temperature.

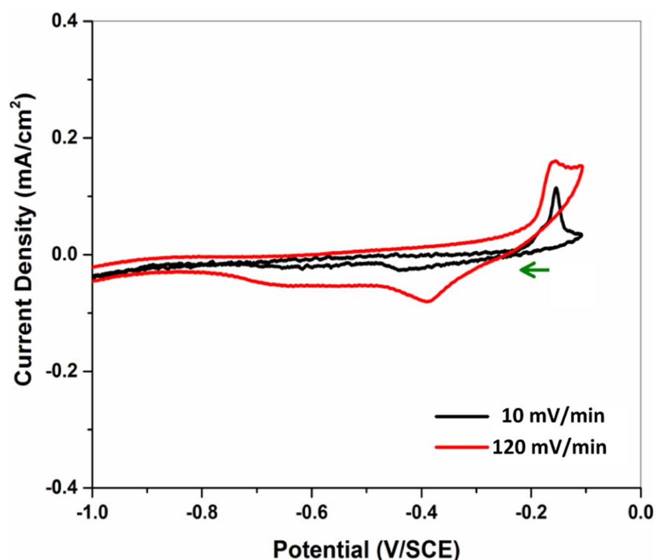

Figure 3. CVs on copper in a 0.1 M NaCl (pH 7) solution at an electrode rotation rate of 2000 RPM recorded at two different scan rates. The green arrow emphasizes the small effect of a substantial increase in scan rate on the onset potential for anodic current increase.

the extensive body of evidence for simple anodic dissolution of Cu, their rejection of the formation of a soluble $CuCl_2^-$ complex as the explanation for the sharp increase in anodic current in favor of what they call a "breakdown potential" is not valid.

There is no convincing evidence in the Huttunen-Saarivirta et al. paper[1] that a passive film was present. To suggest that a passive layer is present because the original polishing lines on the surface are visible is meaningless. The only evidence presented that a Cu_2S sulfide deposit was formed is based on XRD; however, according to the model calculations, the barrier layer film would be only 3.4-4 nm thick, making it undetectable by normal XRD. The supporting claim that the initial decrease in the E_{CORR} is evidence of passive film formation is, at best, dubious. An alternative explanation for the changes in the E_{CORR} has been addressed above.

Huttunen-Saarivirta et al.[1] propose that a thin passive Cu_2S film developed within the first 3 days of exposure, however in the final conclusions they state that the barrier layer was only 0.3% of the 1.4 μm-thick Cu_2S film, with the remaining 99.7% of the film composed of an outer porous layer. For such a layer to grow, the "barrier" layer must have been no barrier at all; i.e., the passive film was unimportant in impeding further corrosion from occurring. This again implies that a barrier layer did not actually exist, and is consistent with our observations and our evidence that any attempt to form a barrier layer under these conditions will be unsuccessful.[5] In fact, the SEM micrograph in Figure 3a of Huttunen-Saarivirta et al.[1] clearly demonstrates that the film growth led to scattered deposits, which would be detectable by XRD. Film growth in this manner (i.e., by aqueous Cu^+ transport and deposition) is consistent with our observations of Cu corrosion in solutions with low sulfide concentrations.[27] The absence of a cross-sectional analysis is a major deficiency of this paper.

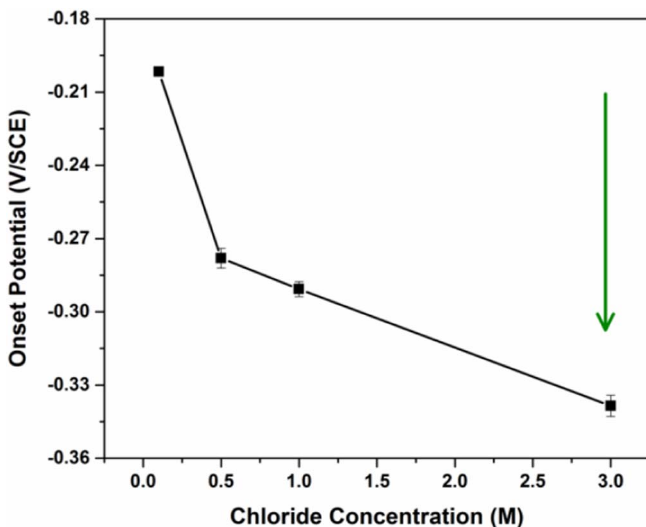

Figure 2. Onset potential for anodic current increase as a function of $[Cl^-]$ extracted from CVs recorded in 0.2 M borate–buffered solution (pH 9) at an electrode rotation rate of 2000 RPM at 20°C. The green arrow emphasizes that the onset potential for anodic current increase becomes more negative with increasing $[Cl^-]$.

Our argument is not that a barrier layer does not form, but that it is unstable, due to the extremely high Pilling-Bedworth ratio,[5] and hence rapidly fractures or develops porosity. Once that occurs, film growth leading to a thick outer deposit is free to proceed, as observed by us and in Huttunen-Saarivirta et al.[1] What is described in the Huttunen-Saarivirta et al. work as cation vacancy transport,[1] we have shown to be due to aqueous Cu^+ transport through pores and to involve a combination of soluble and nano-particulate species.[28,29] The claim in Huttunen-Saarivirta et al.[1] that Cu transport could involve migration as well as diffusion is not inconsistent with our results. At low ionic strengths, which the authors argue could have prevailed under biofilms, we have evidence for migration.[30]

Support for the argument made by Huttunen-Saarivirta et al. in favor of the existence of a passive film[1] comes from the fitting of the impedance data. However, the impedance model is predicated on the equivalent circuit assumed, and given this starting point the conclusions are inevitable. The equivalent circuit used contains an unwarranted number of time constants, given the system and impedance spectra presented. It is also important to note that the constant phase element used to represent Z_{cg}, the geometric capacitance resulting from the storage of electronic charge at the two interfaces separated by a dielectric barrier layer, was fit with exponent n values < 0.8, therefore the impedance values obtained from the fitting were not truly representative of a capacitor.

An interesting feature of the values extracted from the fitting is that none of the parameter values changed over the subsequent 10 months. Later in the paper, Huttunen-Saarivirta et al.[1] argued that the electro-

chemical behavior of the Cu was controlled by the biofilm properties. If so, then the overall conclusion should have been that the presence of a biofilm protects Cu from corrosion. An argument that the overall interfacial resistance was controlled by the presence of a biofilm appears to be a more reasonable explanation than passivation by sulfide.

According to the PDM, as applied by Huttunen-Saarivirta et al.,[1] the growth of the Cu_2S in the simulated groundwater was limited by the transport of Cu cation vacancies. This process is expressed as a Warburg impedance element in Figure 4,[1] indicating that Cu cation vacancies generated at the barrier layer/outer layer (bl/ol) interface are transported through the film and annihilated by Cu oxidation at the metal/barrier layer (m/bl) interface. The Cu flux, J_{Cu}, to the Cu_2S/solution interface to support film growth and Cu dissolution in solution must therefore be equal to the flux of Cu cation vacancies, $J_{V_{Cu}}$.

$$J_{Cu} = J_{V_{Cu}} \qquad [1]$$

In the growth of the Cu_2S film, the steady-state flux of Cu cation vacancies diffusing across the Cu/Cu_2S interface can be expressed using Fick's first law,

$$J_{V_{Cu}} = -D\frac{\partial C}{\partial x} = D\frac{C_{bl/ol} - C_{m/bl}}{\delta} \qquad [2]$$

where D is the diffusion coefficient of Cu cation vacancies (4.2×10^{-13} cm^2/s in the Huttunen-Saarivirta et al. work[1]), $C_{bl/ol}$ the Cu cation vacancy concentration at the bl/ol interface (1×10^4 mol/cm^2 in the Huttunen-Saarivirta et al. work[1]), $C_{m/bl}$ the Cu cation vacancy concentration at the m/bl interface (1×10^{-4} mol/cm^2 in the Huttunen-Saarivirta et al. work[1]), and δ the thickness of the barrier layer (4 nm in the Huttunen-Saarivirta et al. work[1]).

The Cu cation vacancy concentration values above come from Figure 8 of Huttunen-Saarivirta et al.,[1] and the authors describe calculating these concentrations using their Equation 3. These values indicate a major problem with the calculations in the Huttunen-Saarivirta et al. paper.[1] The surface concentration of copper atoms on a pure copper surface is on the order of 10^{15} $atoms{\cdot}cm^{-2}$, which, in the units used in the Huttunen-Saarivirta et al. paper, corresponds to a value of the order 10^{-8} $mol{\cdot}cm^{-2}$. When one considers that the concentration of copper lattice positions on a Cu_2S surface should be lower than that on the surface of metallic copper, and that only some fraction of these positions will correspond to vacancies, it is clear that the values of $C_{m/bl}$ are at least 4 orders of magnitude greater than what is physically possible, and the values of $C_{bl/ol}$ exceed the physically possible limit by at least 12 orders of magnitude. Therefore, all calculations based on these values are completely meaningless, and the validity of Equation 3, or that of the input data to Equation 3, is doubtful. For example, if one was to use these surface concentration values, along with a Cu_2S monolayer thickness of 3.89 Å[31] to convert the surface concentration to a volumetric concentration, Fick's law would yield a Cu vacancy flux of 2.70×10^5 $mol{\cdot}cm^{-2}{\cdot}s^{-1}$, composed of two parts: the Cu flux supporting film growth and that leading to Cu dissolution,

$$J_{Cu} = \frac{1}{A_e}\cdot\frac{dm}{dt} = \frac{1}{A_e}\cdot\frac{\Delta\left(\frac{2m_f}{M_{Cu_2S}} + \frac{m_{sol}}{M_{Cu^+}}\right)}{\Delta t} = \frac{1}{A_e}\cdot\frac{\Delta\left(\frac{2\rho d A_e}{M_{Cu_2S}} + \frac{C_{sol}V_{sol}}{M_{Cu^+}}\right)}{\Delta t} \qquad [3]$$

where A_e is the electrode surface area (17.5 cm^2[1]), ρ the density of the Cu_2S deposit (5.6 g/cm^3), d the thickness of the Cu_2S film (the film is treated as a compact film), M_{Cu_2S} the molar mass of the Cu_2S film (160 g/mol), C_{sol} the concentration of soluble Cu^+ detected in the solution (3.2 ppb after 10 months[1]), V_{sol} the solution volume (12 L[1]), M_{Cu^+} the molar weight of the Cu^+ film (64 g/mol), and t the immersion time (10 months[1]). Therefore, based on the PDM fitting data, the thickness of the Cu_2S film formed on the Cu surface (treated as a dense layer) after 10 months of immersion in the simulated groundwater would be 1.01×10^{14} cm (i.e., 1 billion kilometres, a distance greater than that from the Sun to Jupiter), which is far more than that based on the weight loss measurement, 1.4 μm. Therefore, the EIS fitting using the PDM is not valid in the work presented by Huttunen-Saarivirta et al.[1]

Additionally, Mao et al.[17] calculated the flux of Cu vacancies using,

$$J_{V_{Cu}} = \frac{I_{SS}^{bd} N_A}{\chi F} \qquad [4]$$

where I_{SS}^{bd} is the passive current density at the point of breakdown (2×10^{-5} A/cm^2[17]), N_A Avogadro's number, F Faraday's constant and $\chi = 1$ for the Cu_2S film. The Cu vacancy flux determined by this method is 2.07×10^{-10} $mol{\cdot}cm^{-2}{\cdot}s^{-1}$, which is also far less than that resulting from EIS fitting using the PDM (2.70×10^5 $mol{\cdot}cm^{-2}{\cdot}s^{-1}$) in Huttunen-Saarivirta et al.[1] This, again, suggests that the EIS fitting using the PDM is not valid and that the Cu_2S film in Huttunen-Saarivirta et al.[1] is not a passive film.

Even using the much smaller Cu vacancy flux value of Mao et al.[17] does not resolve the enormous overestimation of the corrosion rate of the supposedly passive surface in Huttunen-Saarivirta et al.[1] Combining Equations 3 and 4 above and using the vacancy flux reported by Mao et al.,[17] one can calculate that the thickness of the Cu_2S film formed on the Cu surface (treated as a dense layer) after 10 months immersion in the simulated groundwater would be 767.6 μm, which is still 548 times larger than the 1.4 μm inferred by Huttunen-Saarivirta et al.[1] based on the weight loss measurement. This outcome seems to be just another demonstration that, as stated above, either Equation 3,[1] or the input data to Equation 3, are invalid.

We have obtained impedance spectra similar to those of Huttunen-Saarivirta et al. in solutions containing low sulfide concentrations,[11] although in the absence of a bio-layer. The equivalent circuit fit was comprised of just three time constants, including a Warburg impedance element. We demonstrated that, for a $[SH^-]$ of 5×10^{-5} M, corrosion proceeded via the formation of a cellular, non-protective Cu_2S film, which led to the depletion of SH^- at the Cu surface, with film growth continuing at a constant rate. We concluded that the film growth rate was partially controlled by SH^- diffusion within the pores of the Cu_2S film and in the bulk solution. Additional similarities between the two studies (Chen et al.[11] and Huttunen-Saarivirta et al.[1]) include the structure of the corrosion product and the corrosion potential value. The Cu_2S was porous in nature and grew thicker with immersion time, much like the film in the present study. The E_{CORR}, which is dependent on the $[SH^-]$, was similar (−800 mV/SCE); however, this was for a $[SH^-]$ lower than 2.4×10^{-4} M. This comparison raises questions about the actual $[SH^-]$ present in the study by Huttunen-Saarivirta et al.[1] and points out a failure to address the previous literature when they attempted to fit their impedance data.

The case made for pitting (page C458 in Huttunen-Saarivirta et al.[1]) is misguided, and Huttunen-Saarivirta et al. misrepresent our arguments about the influence of chloride. As we have shown,[16] the current increase that is claimed to be chloride-induced breakdown of a sulfide film is, in fact, due to the anodic dissolution of copper as a chloride complex in pores and fractures in the sulfide film. We have much more evidence of this to be presented from experiments in which we carefully duplicated the experiments of Mao et al.[17] and demonstrated that the so-called breakdown potentials actually arise from the commencement of active anodic dissolution, and are observed even when no sulfide is present. The observation that no anodic current appears at very positive potentials under the conditions used in the published work[1] cannot, as claimed, be attributed to an enhanced durability of a copper sulfide film. The arguments offered (page C458[1]) are an unsuccessful attempt to explain why pitting was NOT observed in the Huttunen-Saarivirta et al. study.

Summary

The Huttunen-Saarivirta et al. study[1] offers no undisputed evidence regarding the presence of a passive Cu_2S film. The authors misinterpreted both electrochemical and surface analysis data, ignoring the abundance of literature that concludes that Cu_2S films grown under similar conditions are in fact porous in nature. Using vacancy concentration values generated by their Equation 3 without considering that they were many orders of magnitude beyond what is physically pos-

sible led to a nonsensical output from the calculations. The majority of the argument regarding the barrier layer lies within the impedance data analysis, for which the conclusion about passivity is, a priori, made inescapable by applying the PDM.

Considering the previous literature and the critical examination presented here, we posit that the Cu_2S films analyzed by Huttunen-Saarivirta et al.[1] were porous in nature and the susceptibility of Cu to localized corrosion processes, such as SH^--induced pitting, under the investigated conditions is of low probability.

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