

A comment on the paper, "Corrosion of Copper by Water" By P. Szakalos *et. al.* *This journal*, **10** (11) C63-C67, (2007)

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The authors report that copper reacts with liquid water, forming H₂ gas. This is contrary to expectations, because the oxidation of copper by water to form cuprite (Cu₂O), tenorite (CuO) or copper(II)hydroxide (Cu(OH)₂) is not allowed thermodynamically. The authors claim that a hitherto unknown corrosion product (H_xCuO_y) forms in the reaction. The compound is supposed to be thermodynamically very stable, explaining the decomposition of water. Thus, the authors postulate the formation of a corrosion product which is both unknown to science and more stable than the well-known copper oxides and hydroxides. However, if such a compound existed, one would have expected to find accumulations of it in the form of ores. Since the claims made in the paper are extraordinary, they require very strong experimental support. However, it will be shown here that the experimental results may be interpreted in another way that avoids counter-intuitive postulates.

In the experiment a copper foil is immersed in pure water in a glass container which is placed in a high vacuum container made of stainless steel. The steel container is sealed by a palladium foil which allows hydrogen to penetrate to the H₂ analyzer. The experiment is started by immersing copper in water in the presence of air. The system is then closed and evacuated for 3 seconds, leaving on the order of 40 mbar of air in the chamber (my estimate). The authors then observe a pressure drop (attributed to the formation of copper oxide) which ceases after a certain time. The authors argue that all O₂ present at the start of the experiment has been consumed by copper oxide formation at this point. After another 100 hours, the evolution of H₂ starts. The H₂ evolution slows down with time. The authors argue that this is because the H₂ concentration has reached its equilibrium value (about 1 mbar). The XRD analysis after the experiment showed the presence of cuprite and tenorite on the copper foil. In addition SIMS indicated the presence of hydroxide on the surface.

In the following, an alternative explanation of the observations will be attempted. First we need to consider all the relevant components of the experimental system, comprising Cu(s), H₂O(l), H₂O(g), stainless steel, Pd foil and O₂. As mentioned by the authors, copper forms copper oxide with the residual O₂. This explains the presence of cuprite and tenorite in the corrosion product. The formation of copper(II)hydroxide is also expected under the circumstances. Once all residual O₂ has been consumed, water is the only oxidant remaining. As mentioned above, the reaction of copper with water to form CuO, Cu₂O or Cu(II)hydroxide is disallowed by thermodynamics. In contrast, the stainless steel in the container wall is an alloy containing iron and chromium and both these elements readily evolve hydrogen with water. The gas in contact with the stainless steel is close to saturation with respect to water. Under these conditions a layer of adsorbed water will form on the surface with properties similar to liquid water. The stainless steel is covered by a passive film with a thickness of a few nm. Initially, the open circuit potential of the stainless steel in contact with the aqueous adlayer is expected to be relatively high due to redox reactions involving O₂ on the oxide surface. However, oxygen reduction will cease as a result of the gettering of O₂ by the copper foil. This will cause the potential of the stainless steel to move in the negative direction (towards the equilibrium potential of Fe and Cr). The lowering of the potential will then allow hydrogen evolution to proceed on the oxide surface. This explains

the interdependence of the partial pressures of O₂ and H₂ reported by the authors. According to Fig.3 in the paper, the hydrogen partial pressure is about 1mbar at the end of the exposure. With a steel surface area of about 150 cm² (my estimate) this corresponds to the formation of a 2-3 nm thick layer of oxide or hydroxide on the steel surface. This is on the order of the passive film present from the outset on stainless steel and is not easy to detect. In this view, the observed slowing down of H₂ evolution with time is caused by this thickening of the passive film. Hence, it is suggested that the hydrogen evolution observed by the authors is caused, not by the reaction of liquid water with copper but by the reaction of adsorbed water with the stainless steel walls of the vacuum container, in the absence of O₂.

The authors performed a control experiment that included all components except copper and where pO₂ was brought down to about 10⁻⁵ bar by evacuation. The fact that no H₂ was evolved in the control experiment was used to support the claim that the H₂ detected in the experiment with Cu was actually evolved by corroding copper. It is argued that this is because the control experiment did not decrease the oxygen partial pressure sufficiently to induce hydrogen evolution by the stainless steel. Gettering of O₂ by metallic copper is expected to result in oxygen partial pressures far below 10⁻⁵ bar. The authors argument would have been more convincing if supported by a control experiment including another getter for oxygen, *e.g.*, cuprite. The authors also claim that the mass gain of copper is too great in order to be explained by the residual O₂ present at the start of the experiment. The mass gain not accounted for by O₂ is then supposed to have formed by H₂ -evolving corrosion. However, it appears that the authors have not taken into account the O₂ dissolved in the liquid water. If one includes this and the fact that the product is a mixture of oxides and hydroxides, the sample mass gain is fully consistent with copper being oxidized *only* by O₂.

To conclude, I find that the claim that pure water corrodes copper under hydrogen evolution is not supported by the experimental evidence presented in the paper. Hence, there is no need to redraw the potential-pH diagram of copper or to postulate the formation of a thermodynamically stable and hitherto unknown copper oxide hydride.