Mechanisms of Copper Corrosion in Aqueous Environments

Summary Statement
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First, I do need to emphasize that the comments which follow are mine and do not represent the views of MIT or of the US Nuclear Waste Technical Review Board. I want to thank the Swedish National Council for Nuclear Waste for the invitation to take part in this important Workshop. Nuclear electric generation is an important part of the energy mix of many nations of the world and it is important that the wastes which are produced be disposed of in a reliable manner. Officials in many of those nations are considering geologic repositories as one approach to handling high-level nuclear waste and spent nuclear fuel. In some instances, as in Sweden, repositories are contemplated in rock formations that lead to reducing chemical environments and the material of choice in terms of the construction of waste packages is copper. The claims that have emerged over a period of more than two decades from the KTH research group led by Hultquist, which purport to show that copper corrodes in oxygen free water at room temperature, have generated global concern. These claims were contrary to the understanding of the thermodynamics of the copper-water system from the very beginning as they are today.

The fact that these claims have been taken seriously, as they should, by both the developer of the Swedish repository, SKB, and the Swedish regulatory body, SSM, is reflected in the Stockholm Workshop. Representatives from the parties in Sweden that have interest in this matter presented summaries of their research and/or commissioned studies, statements were made by a Panel of which I was a member, and an extended dialogue occurred among the participants. The above was well documented at the workshop, and I do not wish to repeat all of that. In the following, I have summarized my views on the work that was presented in Stockholm in the form of a series of opinions that I consider to be completely objective. In addition, I have included four recommendations for follow-up actions that I believe should be pursued as a means of resolving this matter.

(1.) The Thermodynamics

There is much to argue that from a thermodynamics perspective the reaction proposed by the KTH team does not proceed.

$$Cu + H_2O \rightarrow H_2(g) + H_xCuO_y$$

The hydrogenated copper oxide reaction product is not known in nature and, thus, this reaction is unknown in the thermodynamics of copper corrosion. I have seen no compelling data to suggest that this reaction product has been produced and identified in any of the KTH team publications.

Recommendation: If the above reaction has any merit, then it must be demonstrated that the reaction products that are proposed are indeed produced. There are a host of sophisticated surface analytical techniques that should be committed to such a demonstration.

(2.) Experimental Confirmation

There have been many episodes in the history of science in which seemingly remarkable observations have ultimately been shown to be (a) associated with an artifact of the experiement, or (b) contrary to scientific understanding at that moment in history but subsequently demonstrated by researchers around the world to be genuine. Polywater is an example of the former. The observation by Coriou and his colleagues in France that high purity water could cause intergranular stress corrosion cracking of Inconel 600 is an example of the latter that is now well known to anyone who has interest in nuclear electric generation. The fact that some researchers have attempted to confirm the findings of the KTH team without success suggests that there may be some peculiarity in the design of the KTH experiments that has escaped identification. There is a need for a clear understanding of the experimental details associated with the KTH work.

Recommendation: While scientists may debate the merits of opposing views as expressed in the literature and in public debate, the most productive approach in my view is a well-controlled experiment that is definitive. In the present case, the reactants Cu and H_2O must be completely specified and controlled. The products must be identified with certainty. This attempt at experimental confirmation should be carried out at a third-party laboratory.

The recommended research should be done to replicate as closely as possible the methodology and apparatus of the research work at KTH that has led to the present controversy. It is important that the work be done by capable individuals at an institution that is independent of the researchers and any entity with a stake in the Swedish repository project and that the funding for the research come from an independent source. The chemistry and microstructure of the copper must be well characterized. The water must be characterized, verifiably deoxygenated at the outset of the experiment and monitored for oxygen during the course of the experiment. The conductivity of the water must be measured at the outset and monitored during the experiment. Likewise, the pH of the water should be monitored: it would be expected to increase as hydrogen is evolved. Such monitoring would allow an assessment of, for example, potential leaching of ionic species from the experimental flask and whether the membranes were effectively sealed, thereby providing a barrier to oxygen ingress from the atmosphere during the term of the experiment. In short, a careful material balances must be performed. There is no indication in the KTH work that a materials balance was performed on key elements, which represents the omission of a useful diagnostic.

It is my opinion that the above research can and should be done expeditiously.

(3.) Hydrogen Embrittlement of Copper

The KTH team has claimed evidence that some of the hydrogen that is produced by copper corrosion may embrittle the copper. There appears to be no metallographic or fractographic evidenced to support this claim nor does there appear to be any systematic evaluation of the mechanical properties of cupper which has been infused with hydrogen. It is known that hydrogen will degrade the mechanical properties of copper which is not oxygen-free and that solute segregation to grain boundaries in copper may lead to intergranular failure. However, I know of no work that has identified hydrogen embrittlement as a failure mode in the case of OFHC copper.

Recommendation: The susceptibility of copper to embrittlement by absorbed hydrogen should be examined on copper tensile specimens electrolytically charged with hydrogen at cathodic current densities that correspond to the corrosion rates associated with the measurements reported by the KTH team. Once again, this research should be performed by an objective third party institution.

(4.) Implications with Respect to the Repository

The objectives of the workshop were in part to air the various data and hypotheses that have emerged regarding copper corrosion in oxygen-free water as a step along the path of resolution of the issues of the meaning and importance of the corrosion data, particularly with respect to the potential corrosion of KBS-3 copper canisters in a repository environment. I am of the opinion that the rate of transport of water through the proposed bentonite buffer that is intended to surround the emplaced copper canisters is likely to be extremely slow. Thus, even if a corrosion reaction does occur, the amount of corrosion per unit time would be very low since it is diffusion controlled. If it is determined by means of the confirming research recommended above that copper does in fact corrode in water, as unlikely as that seems to me, I would then look to an engineering solution to bound the problem of copper corrosion with those particular conditions that may have given rise to copper corrosion clearly identified so that the conditions wherein corrosion might occur could be eliminated.

Recommendation: Copper is an obvious material to consider for disposal in chemically reducing environments. If copper corrosion in anoxic environments is observed and confirmed as described in the above research, the conditions which have led to corrosion need to be clearly identified and then either controlled or engineered out of the repository environment.