

Mechanisms of Copper Corrosion in Aqueous Environments

Summary Statement

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1. Based on the presentations at the workshop and the literature sent to us, I would like to make the following summary statement. The findings of Hultquist [1-3] and Szakálos [4] that copper can corrode in oxygen-free water is controversial as it appears to contradict present-day knowledge of thermodynamics that copper is inert in an oxygen-free environment. This finding, if applicable to repository conditions, has implications for the lifetime of the copper canisters to be used for the storage of spent nuclear wastes under SKB's KBS-3 concept. The workshop convened on 16 November 2009 serves to give all parties a chance to present their findings to an audience with a diverse range of background.
2. In order to be in conformance with known thermodynamics on the copper-water system, Hultquist and Szakálos have proposed the formation of an amorphous copper hydroxide H_xCuO_y . However, such a hydroxide has yet to be directly determined. The authors report that powder x-ray analyses on a number of different copper samples from the anoxic experiments showed spectra indicative of the CuO and Cu₂O with distortions.
3. In contrast to these results, experiments conducted by two other groups of investigators failed to show the presence of hydrogen. The experimental setups differed from that of Hultquist. In the study by Simpson and Schenk [5], copper specimens were immersed in 8000 mg/l chloride solutions at 50 °C and 80 °C and a flow of nitrogen was passed over the samples. A gas chromatograph was used with an assumed detection limit of 1 vppm H₂. Both weight gains and losses were measured for the copper foils but no hydrogen was detected. The authors concluded that water cannot be an oxidant for copper in pure water or dilute chloride media. Eriksen et al [6, 7] also reported no hydrogen evolution during the exposure of copper to distilled water for 61 days. However, their gas chromatograms showed the presence of oxygen in the system, which would have reacted with any hydrogen formed. The authors did note that the lack of hydrogen evolution notwithstanding, "the surface of exposed copper foils were unevenly corroded with smaller areas clearly discoloured whilst large areas were seemingly unaffected."
4. It is stated in the draft report by SKB's consultant, F. King [8], and in the presentation by C. Lilja of SKB [9] at the 16th November Workshop that an attempt by Möller in 1995 to reproduce the experiment of Hultquist showed that no visual difference in copper strips could

be discerned from Pd-and Pt-sealed vessels. However, at the same Workshop, Szakálos informed the participants that Möller was able to reproduce the experiment after contact with Hultquist on the experimental details. If true, then it is regrettable that the same observation by a third party has not been disclosed in published reports. Instead, Möller's initial findings have often been cited in support of the claim that the observations of Hultquist have not been reproduced by others.

5. In view of the claim by Hultquist and Szakálos on what seems to be a violation of known thermodynamics, it is only prudent that more experiments be carried with the aims to (i) confirm or disprove the formation of hydrogen through direct detection by mass spectrometry; (ii) study the experimental conditions of Hultquist and Szakálos under which hydrogen is formed; (iii) examine the reaction products formed on the copper by *in-situ* methods to avoid any phase transformation on exposure to atmospheric conditions; (iv) measure the strength of the exposed copper; (v) quantify the thickness of the corrosion layers as function of time, and other relevant tests. More detailed experiments have also been suggested by Professor (Emeritus) Latanision, a member of the panel.
6. There are a number of voluminous reports giving critical analyses of the work by Hultquist and Szakálos. It is my opinion that all these critiques and reports are neither helpful nor fruitful in the furtherance of our understanding on copper corrosion in aqueous environments. Without more studies on the reaction conditions leading to copper corrosion in seemingly anoxic conditions and a careful analysis of reaction products formed, any hypothesis put forth can only be speculative. In the course of such an investigation, different detection technique including that of surface science is important. Surface science studies are relevant for a fundamental understanding on how reactions occur and to be dismissive of its use based on a subjective opinion that "the fundamental conditions and the processes that operate in the gas phase are totally different from those that occur in solution" [8] would be to presume prior knowledge of the outcome.
7. A joint study involving the KTH investigators, SKB and an unbiased third party should be conducted to come to a full understanding of the observations. I suggest that Hultquist and Szakálos be involved in the investigation solely because they should be able to advise on the experimental conditions that have led them to the observations made.
8. The results obtained from such a joint investigation may or may not have implications for the final depository of nuclear waste in copper canisters but unless and until we know more, we really can say nothing (although a lot has been said already). The knowledge that can be gained from further work, whether there are some experimental artifacts that have been

overlooked or whether copper indeed corrodes under certain conditions, can only help in our understanding of the copper-water system.

9. Although this may not be in the terms of reference for the summary statement, I would like to comment on the lack of critical comments and feedback on SKB's published reports. I feel that there should be documentation of the comments/queries/feedback together with the responses by the authors of the reports. As an example, in the Posiva report (Working Report 2003-45), an attempt was made to detect hydrogen in the gas phase. As no hydrogen was found, the authors commented that this could be due to the limited sensitivity of the method, and suggested how the sensitivity of detection could be increased by decreasing the headspace volume, decreasing the initial pressure of nitrogen and/or decreasing the length of the experiment. However, there is no indication of any follow-up experiments based on the suggestions. Furthermore, when the experiment was extended from 6 to 30 days, it is stated in the report that "the analysis of the gas phase for hydrogen could not be performed because of a failure in taking the gas sample at the end of the test". As these are simple experiments which do not involve an extensive length of time, I am surprised that the experiment had not been repeated. One of the conclusions in the report was that "the corrosion of copper at room temperature virtually stops after 60-80 h due to anoxic condition established in the experiments". This is at odds with the results presented in the same report where the authors show a line with a positive slope indicating increasing resistance of the Cu-wire probe with time (i.e., continuing corrosion) (Fig. 10a of report) and also with the solution analysis for dissolved copper where the copper concentration after 30 days was higher than for 1 – 25 days. In view of such contradictions, I wonder if anyone reads the reports generated and gives critical comments.
10. I am of the opinion that there should be a mechanism in place for a critical review of the publications to ensure that meaningful experiments are conducted and repeated if necessary so that the reports published at the SKB website are scientifically sound and informative.
11. Lastly, I would like to thank the Swedish National Council for Nuclear Waste for their kind invitation to serve as a member of the panel.

References

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