

## **The corrosion of copper in water – impacts on the safety of the repository**

Three researchers (Szakálos, Hultquist, and Wikmark) at the Royal Institute of Technology (KTH, Kungliga Tekniska Högskolan) in Stockholm have published articles (Szakálos, 2007, Hultquist, 2008) on the corrosion of copper in oxygen-free water in 2007–2008.

They are suggesting that copper could corrode in oxygen-free environment by taking oxygen from water molecules. If this is true, this process would enable the continuation of general corrosion and the copper canister would not withstand the final disposal conditions.

The corrosion of copper in oxygen-free water is not a new topic as such. One of the three researchers (Hultquist) published an article (Hultquist, 1986) as early as in the 1980s on much the same lines as the more recent findings. Several research teams have attempted to replicate the experiment (SKI, 95–22, SKB TR–88–17, Simpson, 1987), but they have failed to produce similar results. The main differences are that the other teams have not observed any formation of hydrogen, and that the only corrosion product was  $\text{Cu}_2\text{O}$  – presumably produced with the oxygen trapped in the container.

### **Main findings of the Szakálos and Hultquist articles**

The first article (Szakálos, 2007) presents experiments in which the gas produced by the corrosion of copper is measured. Correspondingly, the second article (Hultquist, 2008) presents the results of an experiment in which pieces of copper have been immersed in water for 15 years. Both articles claim that copper is corroded in oxygen-free water, and that the process produces hydrogen and a previously unknown copper compound. Based on the results, the researchers are claiming that the corrosion observed during these experiments endangers the safety of the spent fuel repository, and that the hydrogen gas produced by corrosion makes copper brittle.

Posiva has examined the experimental arrangements used and the conclusions reached in the articles in collaboration with the Swedish SKB and international corrosion experts. Here are some of our findings:

- The interpretations found in the first article (Szakálos, 2007) question the fundamental knowledge of materials, and the test results have not been confirmed by any other research team. (Most of the references found in the articles of the research team refer to the publications of their fellow team members.) Claims suggesting that hydrogen gas affects the material characteristics of copper are presented vaguely, without any reference to scientific publications or textbooks dealing with the subject.
- The article (Szakálos, 2007) also elicited a response questioning the possible formation of an unknown copper compound and the scientific foundation of the corrosion process presented (Johansson, 2007).
- In the article (Szakálos, 2007), the amount of residual oxygen is reported as 0.8 mg in  $0.05 \text{ dm}^3$ , corresponding to 16 ppm of dissolved oxygen, which in turn is twice the solubility of oxygen in water at the temperature of 25 °C (at atmospheric pressure). The amount of oxygen is high considering that the researchers report that they partially emptied the equipment at the beginning of the experiment.

- The second article (Hultquist, 2008) deals with an experiment in which copper samples have been immersed in water (glass bottles) for 15 years (Figure 1)



**Figure 1:** Experimental arrangement in which copper samples have been immersed in water in a glass container for 15 years. In the container on the left, hydrogen is allowed to diffuse from the bottle through a palladium membrane. The container on the right is completely sealed (Hultquist, 2008).

The photograph is believed to indicate that copper corrodes in a container in which hydrogen gas diffuses through a Pd membrane on the lid of the bottle. Correspondingly, corrosion is not observed in the other glass container that still contains hydrogen. It is claimed that corrosion occurred in oxygen-free water. As Figure 1 shows, green spots are formed on the surface of the copper samples during the experiments. According to analyses, these spots contain oxygen and copper. This could also indicate that the samples were in contact with oxygen (air). This fact has raised doubts over the experimental arrangements: that there may have been a leak, and that the test conditions may not have been oxygen-free, and that it cannot be disregarded that oxygen could have entered the container during the 15 years. And if the container was not airtight, it must have also allowed water vapour through. Hence, the experimental arrangement could, in principle, just show how copper corrodes in air and produces the same compounds on the surfaces of the samples that are found on, for example, copper roofs.

- In the summer of 2008, the Swedish Nuclear Power Inspectorate (SKI) invited their group of experts (BRITE, Barrier Review, Integration, Tracking and Evaluation) to review the article (Szakálos, 2007) published by the KTH researchers. The BRITE group came to the conclusion that the experiment does not confirm that copper corrosion would occur by the claimed corrosion mechanisms. The expert group commented that the KTH research team exaggerates the effects of corrosion on the safety of the repository (Brite, 2008).
- The BRITE expert group also commented that the claimed  $H_xCuO_y$  phase could not be reliably verified in other studies, and that this phase has not been observed in solid form in nature. Correspondingly, there are examples of how metallic copper has been in contact with oxygen-free water for hundreds of millions of years with no evidence

of a  $H_xCuO_y$  phase or any such reactions. These natural analogies clearly demonstrate that the corrosion process proposed by the KTH researchers would not be a likely event in oxygen-free and reducible environments (Brite, 2008).

- The BRITE expert group proposed that an independent research group be set up to replicate the experiments. The experts also suggested that the test equipment and planned methods of analysis of the proposed research group should be reviewed by a panel of experts (Brite, 2008).
- In order to prove that copper corrodes in oxygen-free water, the researcher group should also exclude all other sources of hydrogen, as these factors could explain the anomalous results obtained by the KTH researchers.

### Consideration of the phenomenon in Posiva's safety argument

Posiva has selected highly pure, oxygen-free copper as the canister overpack material because of its good resistance to corrosion in reducible (oxygen-free) environments analogous to final disposal conditions. Safety arguments are intended to provide assurance of long-term safety by reviewing the possible corrosion mechanisms and corrosion speeds of copper in different circumstances. Safety arguments are updated at regular intervals to accommodate, for example, the latest research findings and measurement data. Posiva monitors continuously the results of long-term experiments on copper corrosion in environments analogous to final disposal conditions (such as experiments in the Äspö Hard Rock Laboratory). In addition studies are carried out to determine the behavior and characteristics of the copper material and how they are affected by different conditions.

The much debated views of the KTH research team are taken into account in the future work programme, and the hypothesis will be subject to further research to determine the accuracy of the hypothesis and its potential effects on the long term safety of the spent fuel repository. In autumn 2009, Posiva will launch experimental tests at VTT (the Technical Research Centre of Finland) together with SKB and others in an attempt to replicate the experiments described in the article (Hultquist, 2008) and determine if similar results can be achieved. The first results are expected to be available in the spring of 2010.

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