The Swedish National Council for Nuclear Waste (Kärnavfallsrådet)

Minutes of the discussion workshop on **Mechanisms of Copper Corrosion in Aqueous Environments**

Place: MIT, Nuclear Science and Engineering, H.H. Uhlig Corrosion Laboratory

Time: 11/04-05/2010

Present:

Dr. Fraser King, Integrity Corrosion Consulting, Canada
Prof. Digby Macdonald, Pennsylvania State University, USA
Prof. Ron Latanision, Emeritus professor, MIT, USA
Prof. Willis Forsling, Emeritus professor Luleå Universitet, The Swedish Council for Nuclear Waste, Sweden
Prof. Hannu Hänninen, Secretary, Aalto University, on sabbatical leave at MIT, Swedish Council for Nuclear Waste, Finland

Introduction

SKB is preparing a license application for the construction of a final repository for spent nuclear fuel. The copper canister provides an important corrosion-resistant barrier in the repository concept. Reliable copper corrosion data are required to support demonstrations of safety of the KBS-3 concept. Therefore full understanding of copper corrosion mechanisms and corrosion rates under repository conditions is of particular interest. Some researchers have recently questioned the conventional understanding of the copper corrosion processes under the anoxic conditions that are expected to persist in the repository in the long term (Hultquist *et al*. 2007; 2009). In particular their experimental results propose that copper can corrode spontaneously by producing hydrogen and extracting oxygen from water even under anoxic conditions, which would allow the general corrosion of copper to proceed under the long-term repository conditions. These results, however, have been a subject of several reviews and discussions (e.g., Apted *et al*., 2009; King, 2009), which have questioned the evidence for such a corrosion process on the basis of thermodynamic data and Pourbaix diagram (potential – pH diagram) for $Cu + H_2O$ system. The Swedish National Council for Nuclear Waste (Kärnavfallsrådet) arranged in November 2009 an international scientific seminar on the subject gathering almost 300 interested persons. The international experts were not able to find support for the proposed corrosion process, in general, except under highly pure water conditions. Even if the proposed mechanism could operate in certain extremely pure water conditions, it can not cause any serious effect on copper corrosion under the lifetime of the canister when calculated from the hydrogen evolution data presented (Apted *et al*., 2009). It was generally accepted that copper corrosion in oxygen-free water through hydrogen evolution under the electrochemical and pH conditions in the repository is possible, but only if the fugacity of hydrogen is very low ($f_{H2} < 10^{-11}$ atm at 25 °C) and

the cuprous ion concentration is also very low. The key parameters in copper corrosion in water systems are the fugacity of hydrogen and the activities of Cu^+ and H^+. According to the thermodynamic calculations extremely low fugacity of hydrogen and an extremely low Cu^+ activity is needed for corrosion to occur and, thus, copper is very resistant to corrosion in oxygen-free pure water. However, the situation changes radically, if sulfide ions or other unanticipated contaminants are present in the system.

The evolution of the geochemical environmental conditions in the proposed repository system is well studied and characterized (King *et al*., 2002). Initially, atmospheric O_2 trapped within the repository upon sealing, and heat from the radioactive decay creates warm, dry and oxidizing conditions. Oxygen is consumed relatively rapidly by a number of processes including corrosion of copper and reactions with microbes and other materials in the backfill (up to 200 years). Thus, the electrochemical redox conditions at the copper canister surface evolve relatively soon from warm and oxidizing to cool and anoxic as the O_2 is consumed and the heat-generating radioactivity decays. Prior to water saturation of the repository the corrosion depth of 30 μm is expected and assuming uniform corrosion maximum depth of corrosion based on the amount of oxygen available is expected to be 300 μm (King *et al*., 2002). In anoxic conditions (99…99,9% of the assessment period) corrosion is expected to cease because copper is then thermodynamically stable if the quantity $f_{H_2}^{1/2} a_{Cu^+}$ exceeds a minimum value as specified by thermodynamics. In the presence of sulfides copper is activated, because the minimum value of $f_{H_2}^{1/2} a_{Cu^+}$ is much higher, due to the activating effect of sulfide, and copper will corrode forming stable and insoluble sulfides. These findings were summarized in the Corrosion Domain Diagrams presented by Prof. Macdonald at the international workshop of The Swedish National Council for Nuclear Waste (Kärnavfallsrådet) in November 2009. The amount of corrosion depends on the potential sources of sulfides and their diffusion through the buffer material (bentonite) to the canister surface. The presence of dissolved sulfides activates copper, because it produces an equilibrium Cu/Cu_2S potential that is much more negative than that for Cu/Cu^+, thereby destroying the immunity that might have existed (at sufficiently high $f_{H_2}^{1/2} a_{Cu^+}$) in the absence of sulfide. The sulfide that forms does not (kinetically) passivate the surface. The thermodynamic activation of copper by dissolved sulfide and other sulfur-containing species (e.g., polysulfides and sulfur oxyanions) is the most important long-term corrosion process of the copper canisters and should therefore be studied and understood thoroughly. Potential sources of sulfides include pyrite (Fe_2S) and sulfates (SO_4^{2-}) in bentonite. The sulfate-reducing bacteria convert sulfates to sulfides in the repository (King, 2009).

Comments of the international panel on copper corrosion in water

Based on the presentations in the Kärnavfallsrådet's seminar "Mechanisms of Copper Corrosion in Aqueous Environments" in November 2009 the following conclusions can be drawn from the summary statements of the international panel members:

-   The general opinion of the findings of Hultquist *et al*. that copper can corrode in oxygen-free pure water at room temperature producing hydrogen was that they are controversial and contrary to the present knowledge of the thermodynamics of copper corrosion, except under exceptional circumstances of very low hydrogen fugacity and cuprous ion concentration and in the absence of activating species, such as sulfide. Water cannot be an oxidant for copper in pure water or dilute chloride solutions unless these exceptional circumstances exist. The results do not seem to be applicable to repository conditions, because the exceptional circumstances are unlikely to exist (e.g., sulfide is ubiquitous in ground water systems), and do not have implications to the lifetime of the copper canisters.

-   All trials of the other investigators have failed to show the formation of hydrogen as a corrosion product. Also the high variability of the hydrogen evolution rates measured by Hultquist *et al*. suggests that all variables are not in control in the experiments. The experimental details may have some peculiarities which have escaped identification. Therefore, research at a third-party laboratory should be done to replicate as closely as possible the methodology and the apparatus of the work that has led to the present controversy.

-   The proposed formation of a thick amorphous copper hydroxide, H_xCuO_y, was challenged as it has not been identified properly, yet. The first principles calculations based on thermodynamic properties of Cu-O-H phases have shown this phase to be unstable. The proposed reaction product is not known in nature.

-   The calculations of Prof. Macdonald (Pennsylvania State University, USA) showed, however, that the results of Hultquist *et al*. are not necessarily a violation of the known thermodynamics, if the tests were performed in extremely pure water environment, very low fugacity of hydrogen and extremely low Cu^+ content, or if the water contained some important impurities such as sulfide ions. Thus, very careful material balances are required and should be performed in the future experiments.

-   The thermodynamics of copper corrosion can be used for long-term evaluation by calculating a Corrosion Domain Diagram for copper in water (+ impurities) as a function of temperature. The diagram is divided into regions of thermodynamic immunity and corrosion in partial reaction quotient ($P = f_{H_2}^{1/2} a_{Cu^+}$, in the case of Cu in pure water) versus pH space. If, in the initial conditions corrosion is possible, the corrosion reaction proceeds and the concentration of Cu^+ and the fugacity of hydrogen at the interface will increase, thereby increasing P. With time when the limiting boundary conditions are met the corrosion will stop when P equals the equilibrium value, P^e, in a system of restricted mass transport. At equilibrium conditions the corrosion rate is determined by the transport of the activating species to and the corrosion products from the interface. The corrosion becomes controlled by the diffusion of Cu^+ and H^+/H_2 through the bentonite. The corrosion rate can be then calculated by solving the diffusion equations for Cu^+ and H^+/H_2.

- The contradictory results on copper corrosion in oxygen-free pure water, where some experiments indicate that corrosion occurs and the others indicate that copper is immune, can be explained with the corrosion domain diagrams. It is highly likely, that the poor definition and variability of the initial conditions of the experiments is the reason of controversy. In some conditions the initial concentrations of Cu^+ and H_2, and hence the value of $P = f_{H_2}^{1/2} a_{Cu^+}$ may be such that copper is immune and no corrosion takes place. Contrariwise, in the other experiments the initial Cu^+ and H_2 contents and hence $P = f_{H_2}^{1/2} a_{Cu^+}$ may be such that the system lies in the region of spontaneous corrosion as defined in the Corrosion Domain Diagrams. In this case corrosion will occur until the concentration of corrosion products (Cu^+, H_2) build-up in a closed system and stop the corrosion when $P = P_e$, where $Pe = f_{H_2}^{e,1/2} a_{Cu^+}^e$, with the superscripts designating equilibrium values. Thus, considerable care must be exercised, when designing the experiments of copper corrosion, to insure that the initial conditions are such that corrosion is thermodynamically possible.

- The ground water is far from pure water and its common contaminants are sulfide (HS^-) and other sulfur containing species as well as halides. Sulfides will activate copper giving rise to the formation of Cu_2S at electrochemical potentials that are significantly more negative than those for the formation of Cu_2O. The Corrosion Domain Diagrams show also that the immunity of copper is much more difficult to achieve in the presence of sulfides. Since already very small concentrations of sulfides result in corrosion in the copper-water system, immunity of copper in repository where significant amounts of sulfur species may be present must be engineered into the system. Corrosion rate is controlled by the mass transport of the different species in the system as well as the reaction kinetics. On the other hand, differences in the minute amounts of sulfides and other sulfur containing species such as polysulfides and sulfur oxyanions in pure water between different laboratory experiments may explain the current controversy of copper corrosion. The halides compared to the sulfides are only weakly activating and hence pose a lower threat to immunity of copper. However, considering the relatively large amounts of hydrogen formed in the experiments of Hultquist *et al.* it is important to consider in addition of impurities which are consumed in the corrosion reaction also impurities which can act as a catalyst, i.e., it is not consumed in the reaction itself, as sulfide would be.

- It was seen prudent that more well-controlled experiments, where the reactants are completely specified and controlled and the reaction products are identified with certainty, have to be performed at a third-party laboratory to (i) confirm the hydrogen evolution and measure the gas evolution rate, (ii) define the thermodynamic conditions where hydrogen is formed, (iii) examine the corrosion products further (also *in situ*), (iv) measure the corrosion rate as a function of time, (v) define the electrochemical potential, oxygen content of the water and

measure pH changes of the solution during the course of the experiment. In the beginning of the copper corrosion experiments, the Corrosion Domain Diagram calculations can be used for prediction of the result and should always be done to confirm the thermodynamic predictions. Additionally, the surface quality of the copper samples should be properly quantified.

- It has been claimed by Hultquist *et al*. that some of the hydrogen that is produced by copper corrosion is absorbed in copper and may seriously embrittle copper. However, there seems to be no evidence to support these claims and therefore a systematic evaluation is needed on hydrogen effects on the mechanical properties of Cu-OFP copper. Also the absorption, solubility, and the diffusivity of hydrogen in copper, and the possible formation of the hydride, CuH, should be studied and understood thoroughly.

- Many of the copper corrosion rate results taken from the literature and used in the corrosion rate predictions of copper canisters in the repository by Hultquist *et al*. are based on the experiments in aerated or oxic conditions and are, thus, not relevant to the anoxic long-term prediction of copper corrosion in the repository. There is plenty of evidence that low levels of dissolved oxygen (50…2000 ppb) can lead to much more extensive corrosion rates than lower or higher oxygen levels, e.g., experience from stator cooling systems of power generators. This may be also a potential explanation in the present controversy.

- The panel felt that if copper in fact corrodes in oxygen-free pure water, then the particular conditions that may give rise to copper corrosion must be clearly identified, and compared to the thermodynamic Corrosion Domain Diagram calculation. It is possible by engineering solutions to eliminate the conditions where corrosion might occur by controlling the immunity of copper and the diffusion of Cu^+ and H^+/H_2.

- Even if copper corrosion in oxygen-free pure water occurs the proposed mechanism is not significant for copper canisters in the repository, because of the differences in the environmental conditions and the corrosion would quickly be controlled by the kinetics of transport of Cu^+ and H^+/H_2 through the compacted bentonite. Thus, it cannot be expected that there is an adverse impact on the lifetime of the copper canisters by this unproven mechanism.

The above list of recommendations is considered to be very important for the follow-up actions that should be pursued as a means of resolving the present copper corrosion controversy. Especially important is the knowledge when the corrosion conditions are oxic and when they are anoxic in the long-term corrosion tests. It is impossible to interpret the corrosion data and long-term corrosion rates and to evaluate the potential risks of spent nuclear fuel disposal unless also the long-term evolution of the geochemical environment in the repository system is fully understood.

SKB's corrosion program

SKB's copper corrosion research program includes modeling studies and experiments both in the laboratory and in the repository-like environments in Äspö Hard Rock Laboratory (HRL) that are aimed to confirm that the copper canister will provide the required corrosion resistance under real repository conditions. The copper corrosion research program for understanding of the corrosion processes that is being conducted or planned by SKB includes, e.g., studies on (FUD 2010 SKB):

- copper corrosion and stress corrosion cracking in sulfide/water system;
- copper corrosion in compacted bentonite environments;
- copper corrosion in repository-like environments (LOT and MiniCan);
- copper corrosion in oxygen-free water;
- independent third-party repetition of the experiments of Hultquist *et al.*.

The long-term studies of copper corrosion in repository-like environments avoid the potential complications of the interpretation of the short-term laboratory data. Most important is knowledge of the evolution of the environmental conditions in the compacted bentonite and measurement of the corrosion rates in the repository-like environment. In the project "Long-term test of buffer material" (LOT) the primary task is to investigate bentonite buffer properties and mineral stability in a repository-like environment. However, also copper corrosion, cation diffusion and bacterial behavior are studied to find out what is the mean corrosion rate under initial oxic conditions as compared to the corrosion modeling results ($<7x10^{-6}$ m/year). Identification of possible pitting and role of corrosion products in uneven general corrosion are also of interest. In the project "Miniature canister corrosion experiment" (MiniCan) model canister experiments are performed for understanding corrosion of cast iron insert and its effects following a leak in the copper canister. Additional copper corrosion and stress corrosion experiments are involved. During the experiment, the electrochemical potential (corrosion potential of the canister and the redox potential of the environment), water content and pressure as well as canister strain on the outer surface are monitored (due to the production of iron corrosion products from the corrosion of cast iron insert). Also galvanic corrosion and crevice corrosion are studied with the experiments. The experiments are not heated, but are carried out at ambient temperature (15 ºC), and, thus, they give little temperature-related information of the real canister behavior and corrosion in the early period when canister surface temperature is elevated due to heat generation of the spent nuclear fuel radioactivity which decays under time. The model canister tests will run for a period of at least five years after which they will be withdrawn for examination.

The large number of the separate projects and the work spread across different organizations and countries can hamper the management of this ambitious but diverse program. The SKB's objectives should be clearly documented in a master plan in which clear definitions are presented regarding the questions that have to be answered and what are the critical experiments for solving the issues. This would allow the overall picture of the research strategy to become clear for the wider audience.

Conclusions

The corrosion mechanism and corrosion rate of copper in oxygen-free water environments is the key research issue at the moment. However, copper corrosion in the repository-like environments has also to be studied in order to be able to transfer the laboratory corrosion data to the real repository conditions.

In order to judge, on the evidence for copper corrosion in pure water under anoxic conditions, it is recommended that the third-party copper corrosion studies are started. In these experiments in addition to hydrogen evolution also the change of the environmental conditions has to be monitored including the corrosion potential and local pH. Hydrogen evolution may be enhanced by increasing the surface to water volume ratio and thus it is recommended to use copper powder samples in addition to the thin foils in the same laboratory. The copper powder can be pre-oxidized allowing better mechanistic understanding of the role of the copper oxide films in hydrogen evolution. Hydrogen embrittlement of copper by absorbed hydrogen has also to be clarified.

In the repository-like environments, the tests will allow the observation of corrosion in unsaturated phase of bentonite, when local corrosion cells may form. Deliquescence, evaporation and rewetting can result in localized corrosion due to non-uniform wetting and differential aeration of the canister surface. In case of compacted bentonite the access of groundwater to the canister surface is not easy and due to the variation of bentonite density the groundwater reaches the copper canister surface at different times and allows it to wet first locally. Local variation of the density of bentonite will enable also greater microbial activity at the canister surface. The conducted real-time electrochemical corrosion rate measurements in the repository-like environments give important results on the progress of the experiments, but they can be confirmed only after canister extraction.

Many of the corrosion studies consider only the pure copper surface. However, in the real canister case, the exposure is started with an oxide-covered surface and the ground water in the repository contains dissolved O_2. The consumption of O_2 by corrosion and other mechanisms will lead first to copper oxidation and then to the reduction of the oxide. In aqueous sulfide solutions transformation of the oxide to sulfide, however, is expected to proceed chemically at the oxide solution interface. However, sulfide activation does necessarily require prior oxide formation. The real copper canister has a heat transfer surface and salt contaminants as well as under deposit corrosion may result in separation of anode and cathode and pitting type of corrosion attack in the early oxic phase of the repository. From the material point of view effects of the local cold work (both from manufacturing and from handling), the weld metals and the heat-affected zones of the welds on copper corrosion have to be known.

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