Report 2009:4e from the Swedish National Council for Nuclear Waste

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Mechanisms of Copper Corrosion in Aqueous Environments

A report from the Swedish National Council for Nuclear Waste's scientific workshop,
on November 16, 2009

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Mechanisms of Copper Corrosion in Aqueous Environments

The Swedish National Council
for Nuclear Waste Report

SWEDISH GOVERNMENT
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Report 2009:4

Scientific workshop on

Mechanisms of Copper Corrosion in Aqueous Environments

November 16, 2009, Conference Center of the Confederation of Swedish Enterprise (Näringslivets hus), Stockholm.

Introduction

In 2010 the Swedish Nuclear Fuel and Waste Management Company, SKB, plans to submit an application for a final repository for spent nuclear fuel. The proposed method is called KBS and involves depositing the nuclear waste deep down in the bedrock in the municipality of Östhammar on the Swedish east coast. It is based on three protective barriers: copper canisters encapsulating the spent nuclear fuel, bentonite clay surrounding the copper canisters, and finally the rock itself.

The geological environment surrounding the copper canisters will be nearly oxygen-free, and one of the premises on which the KBS-3 rests is the assumption that copper cannot corrode in such an environment. The scientific findings of a small group of researchers at KTH (the Royal Institute of Technology) in Stockholm have therefore been met with widespread interest and debate. Their findings are in short that copper actually can corrode in pure water, free from oxygen as well as from complexing ions.

Since the release of the KTH findings, the long-term safety of the KBS-3 method has been questioned. SKB has, however, refuted the findings, and the matters were thoroughly discussed at a scientific workshop in Stockholm on November 16, 2009. The workshop was organized around two main themes:

1. A fundamental enquiry into the corrosion characteristics of copper in oxygen-free environments.
2. What additional information is needed to confirm this specific corrosion process and to assess the importance of the process for the final repository?

The workshop was hosted by the Swedish National Council for Nuclear Waste, with a panel of internationally recognized experts from the fields of chemistry and materials science and engineering, chosen by SKB, KTH, the Swedish Radiation Safety Authority, and the Swedish National Council for Nuclear Waste.

The purpose of this report is to explain the controversy and present the outcome of the workshop. The report is primarily aimed at experts in the field of nuclear waste management, such as officials at regulatory authorities and people in the nuclear industry and scientific councils.

We would also like to refer to the newsletter published on the website of the Swedish National Council for Nuclear Waste (www.karnavfallsradet.se). We would also like to refer to the publication *Nuclear Waste State of the Art Report 2010 – challenges for the final repository programme* (SOU 2010:6e).

For those readers who would like a more detailed scientific discussion of the various topics raised in this report, we would like to refer to the bibliography at the end of the report.

The report is structured in the following way:

- Executive summary: A general overview of the issue, intended for anyone interested in the management of nuclear waste disposal.
- Topic 1: A fundamental understanding of the corrosion characteristics of copper in oxygen-free environments – a scientific guide to the controversy of copper corrosion in oxygen free environments.
- Topic 2: What additional information is needed to confirm this specific corrosion process and to assess the importance of the process for the final repository? – a summary of recommendations from the members of the expert panel at the scientific workshop on November 16, 2009.

- Written statements by the panel members: A publication of the written statements prepared by the panel members after the scientific workshop.
- Edited Transcripts (# sv. redigerade utskrifter) from the scientific workshop.

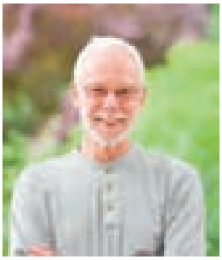
The members of the expert panel:

Dr. Ron Latanision
Dr. Latanision is Corporate Vice President and Director of Exponent's Mechanics and Materials Practice. He is a member of the National Academy of Engineering and an elected Fellow of ASM International, NACE International, and the American Academy of Arts and Sciences. Dr. Latanision is a member of the International Corrosion Council and serves as a Co-Editor-in-Chief of *Corrosion Reviews*.

Dr. Gaik Khuan Chuah
Dr. Chuah earned her PhD in Chemistry from Texas A&M University, USA. She holds a position at the National University of Singapore where she teaches and supervises students in the area of heterogeneous catalysis. Dr. Chuah has various responsibilities as the chairperson for safety in the Chemistry Department at NUS, and as a member of the Faculty of Science Safety.

Prof. Digby D. Macdonald

Dr. MacDonald earned his PhD in Chemistry from the University of Calgary in Canada. He is Distinguished Professor of Materials Science and Engineering at Pennsylvania State University. Professor MacDonald is an elected fellow of NACE International, the Electrochemical Society, the Royal Society of Canada, the Royal Society of New Zealand, ASM International, the World Innovation Foundation, the Institute of Corrosion, and the International Society of Electrochemistry.



Prof. David Shoesmith

Dr. Shoesmith is a Professor in the Department of Chemistry at the University of Western Ontario. He specializes in research on the electrochemistry of materials and corrosion science. Professor Shoesmith holds the Natural Sciences and Engineering Research Council and Ontario Power Generation Industrial Research Chair in Nuclear fuel Disposal Chemistry. He is an elected fellow of NACE International and the Canadian Society for Chemistry.

Moderator:

Prof. David J. Duquette

Dr. Duquette is the John Tod Horton Professor of Materials Science and Engineering at Rensselaer Polytechnic Institute in Troy, New York. His research interests include all aspects of corrosion with a special emphasis on localized corrosion and chemo-mechanical interactions such as stress corrosion cracking, corrosion fatigue, and hydrogen-induced cracking. Professor Duquette is an elected Fellow of NACE International, ASM International and the Electrochemical Society.

Executive Summary

The scientific controversy

In the Swedish high-level waste management programme, it has been assumed that copper metal cannot be corroded by pure oxygen-free water (i.e. water without any complexing ions such as sulphides and chlorides). This assumption has, however, been challenged by experimental results published by Hultqvist and Szakalos, researchers at KTH (the Royal Institute of Technology). They also challenge the assumption of thermodynamic immunity of copper in water at elevated temperatures.

Hultqvist and Szakalos refer to both experimental and theoretical observations and argue that these observations are consistent with their theory that pure oxygen-free water corrodes copper. In the process, hydrogen ions are reduced to hydrogen atoms and a corrosion product is formed whose identity and exact composition are not yet known. According to the research team, the hydrogen atoms will either form hydrogen gas molecules or be absorbed by and diffuse into the copper metal.

The researchers also concluded that when the partial pressure of hydrogen reaches a level of 1 mbar the copper corrosion ceased. The corrosion process continuous only if hydrogen is removed from the system so that the hydrogen pressure is reduced under this critical level.

SKB do not find the scientific evidence for the proposed reaction mechanism convincing concludes that no convincing evidence exists that water oxidizes copper. They will nevertheless include the effect of such a corrosion mechanism in the safety assessment, even though their opinion is that the actual corrosion mechanism will not limit the lifetime of the canisters in the final repository.

But what is the basis of this controversy? One important element is opposing views with respect to the interpretation of thermodynamic data. Hultqvist, Szakalos and others claim that thermodynamic data prove that copper is not immune in pure oxygen-free water. Hence, their result is actually thermodynamically expected, although at a slow reaction rate. One weakness in the work of Hultqvist and Szakalos is, however, that the corrosion product of their proposed reaction has not been identified. SKB argue that the results of Hultqvist and Szakalos challenge some basic principles of thermodynamics which constitute the scientific foundation of both physics and chemistry. They assert that one such principle is the change in Gibbs free energy (G), which predicts whether a reaction is probable or not.

As far as a specific chemical reaction is concerned (e.g. copper corrosion in water), its feasibility is determined by the change in Gibbs energy (ΔG). A spontaneous reaction is characterized by a decrease in Gibbs energy ($\Delta G<0$). In order to make a correct prediction, all the reactants and products in the chemical reaction in question must be determined with respect to their chemical identity. As mentioned earlier, the corrosion product in the reaction proposed by Hultqvist and Szakalos has not been identified, which makes it impossible to predict its spontaneity in terms of Gibbs free energy.

Can copper be corroded by pure, oxygen-free, water?

Corrosion reactions – consensus and dispute

In a KBS-3 type final repository, the copper canisters will be surrounded by a buffer of bentonite clay. The bentonite will gradually be saturated by groundwater. This gradual saturation process may extend over centuries and is a prerequisite for the assumed buffer safety function. A limited amount of oxygenated water is initially present in the bentonite, but the groundwater at that depth (about 500 m) is oxygen-free. There is also oxygen in the air that is present in the pore system of the bentonite before it is saturated.

In the KBS-3 repository, copper will react with the oxygen that is present in the bentonite and in the groundwater and form copper oxide. This is scientifically known. When the oxygen is consumed, copper will react with water containing sulphide ions that are naturally present in the bentonite and the groundwater. Copper species including sulphide are the products of these reactions. The corrosion reaction is slow, and SKB have carried out research aimed at minimizing the formation and transport of these ions in the repository, and studied how different concentrations of sulphide affect long-term safety.

When oxygen (O_2) is present in the repository system, copper will react with oxygen to form copper oxide. When the oxygen is consumed, copper reacts with sulphide ions present in the water to form copper sulphide. A third corrosion reaction involves chloride ions present in the water and forms copper hydroxyl chlorides. The latter reaction is however only expected to be significant in low-pH environments.

A consensus prevails regarding these reactions. However, Hultqvist and Szakalos suggest that another reaction can occur in an oxygen-free environment, namely that copper reacts with the water molecules to form copper hydroxide species and hydrogen gas. In this reaction, hydrogen may also be dissolved in the copper metal.

$$\text{Cu} + \text{water molecules} \rightarrow \text{Cu hydroxides} + H_2 + \text{H (in Cu)} \quad [1]$$

Reaction [1] is disputed among scientists. However, Hultqvist claims that they have evidence for a reaction product that is solid and porous and that molecular hydrogen can be measured in the gas phase. He also states that hydrogen is absorbed in the metal and that it can be measured. Hultqvist argues that since the pressure of hydrogen in his experiments (10^{-3} bar at a temperature of 20–80°C) is higher than the natural H_2 pressure in air ($5 \cdot 10^{-7}$ bar), it can be concluded that copper is corroded by water.

Is copper corrosion in oxygen-free water thermodynamically possible?

When a metal corrodes, it disintegrates into its constituent atoms, which are ionized due to chemical reactions (most commonly electrochemical oxidation) with its surroundings (in the presence of an oxidant such as oxygen). Typically oxide(s) and/or salt(s) of the original metal are produced as a result of such a reaction.

Thermodynamics deals with the concepts of energy and entropy and can tell us whether a reaction is possible or not. The first law of thermodynamics states that energy cannot be created or destroyed, it can only change forms (i.e. the energy of an isolated system is conserved or in other words constant in time). Hence, heat supplied to a system must equal the increase in internal energy of the system plus the work done by the system. Entropy is a measure of how organized or disorganized a system is. Thermodynamics states that the entropy of an isolated system which is not in equilibrium will tend to increase over time to a maximum value at equilibrium. This is the second law of thermodynamics. A special case of the second law is the concept of Gibbs free energy, which states that if the pressure is constant, a process will occur spontaneously if the change in Gibbs free energy is less than or equal to zero.

Szakálos claims that it is an undisputed fact among thermodynamics experts that copper is not thermodynamically immune in pure oxygen-free water. Among corrosion scientists, however, this is a controversy. Szakálos also states that their experimental results do not conflict with known thermodynamic principles with respect to the corrosion of copper in water. The results can be explained by the formation of an amorphous copper hydroxide. He asserts that several scientific publications suggest the existence of different amorphous hydroxides, including both monovalent and bivalent copper, which can easily be converted to oxides.

According to Szakálos, copper corrosion in oxygen-free water is a well known phenomenon in the industrial copper cooling systems and synchrotrons. All cooling systems for power generators and accelerators, such as at CERN in Switzerland, corrode in the region of a micrometer per year. This occurs in water that is deionized and degassed. The industry tries to reduce these corrosion rates and to achieve oxygen-tight metal fittings, such as UHV fittings. Nevertheless, the corrosion is still on the order of a micrometer per year. He illustrates the problem with the presence of partial plugging in the cooling systems by corrosion products such as oxides and hydroxides. The system clogs in a few years' time. The environment makes the copper hot, around 70 to 90 degrees, which is about the same temperature that the copper canister will attain. In the industrial systems there is, of course, no groundwater, but the water is pure.

SKB and several experts assert that the corrosion process suggested by Hultqvist and Szakalos, and specifically the claim that a new stable phase is formed, challenges some of the basic principles of thermodynamics which constitute the scientific foundation of both physics and chemistry. However, SKB contends that even if this reaction should occur, it would be of negligible importance and the extent of copper corrosion would still be determined by the amount of sulphide and chloride ions.

Different types of experiments

There are different types of studies that can be used to explore the different aspects of corrosion: laboratory studies, in-situ experiments and analogues (i.e., natural or man-made artefacts). The initial state of a *laboratory experiment* is well-known, and control of the environment in the experiments is very good. On the negative side, their representativeness is less, due to the simplified system and the short time scale. It is good to get quick results, but it is harder to evaluate the long-term effects. *In-situ experiments* are investigations in realistic environments, and therefore closer to reality than laboratory results (the real system is represented in the in-situ experiment). In this case the initial state is quite well-known and representativeness is rather good. It is possible to perform both short-term and medium-term experiments. In the case of the *analogues*, the initial state is unknown (e.g., the sample thickness is not known ????) and the environment cannot be controlled because the reaction has already happened when you look at it. However, the analogue entails a long reaction time, some parameters can be measured and representativeness can range from poor to good, depending on what aspect is being considered. All experiments have weaknesses. In weight loss experiments it is possible to determine how much has disappeared after a certain time, but it is not possible to distinguish between what happened in the initial phase, which might have occurred quickly, and what occurred over a longer period of time. Another weakness is associated with measuring corrosion depths and corrosion rates in specimens, since it is not possible to differentiate between different mechanisms that may have operated over different lengths of time. This makes it difficult to extrapolate experimental results for use in the safety assessment.

The experimental evidence of Hultqvist and Szakalos

In one of the experiments performed by Hultqvist, two glass vessels were used in which copper foils were kept in pure oxygen free water for 15 years. One glass vessel had a membrane of platinum so that H_2 was not evacuated. In the other glass vessel, H_2 was removed through a membrane of palladium. The latter vessel shows signs of corrosion: the foils turn black in colour. Hultquist argues that if H_2 is removed, which is always the case in an open system, this must be expected to happen. Hultqvist and Szakalos argue that the atomic hydrogen that is formed also can be absorbed into the copper metal. Hultqvist et al. have published proofs using two methods. Hydrogen was detected both by secondary ion mass spectrometry and by a quantitative study on out gassing in vacuum. Secondary ion mass spectrometry is sensitive to hydrogen.

It is concluded by Hultqvist and Szakalos that the process of copper corrosion in water has been verified by experimental results, such as the formation of hydrogen, increase of weight, hydrogen in the copper metal, chemical analysis of the corrosion product, as well as by visual inspection and metallographic examination.

SKB's corrosion studies

The purpose of SKB's studies of copper corrosion is to understand copper behaviour in water in greater detail. SKB's work on copper corrosion includes literature reviews and various kinds of experiments, both short-term and more long-term studies (gas measurements, some simpler glass container experiments as well as electrochemistry). Moreover, theoretical calculations are performed and they look into equilibrium reactions in water.

SKB have found that the corrosion rate decreases with time in the short-term electrochemical and laboratory experiments. Very few, if any, results indicate that the corrosion rate increases with time. In the in-situ experiments, copper(II) corrosion products are often found, indicating that the copper in the experiment has undergone periods of oxidizing conditions. The analogue experiments show that copper in its native form has remained stable for a very long time in both the natural state and engineered artefacts.

One of SKB's ongoing studies of copper corrosion includes first-principle computer calculations of the thermodynamic properties of Cu-O-H phases. The main objective of the calculations has been to look for a stable product (or phase) between copper, oxygen and hydrogen that could be the final product of the supposed reaction between copper and water that is suggested by Hultqvist and Szakalos. Other objectives are (i) to calculate, from first principles, the thermodynamic properties of known Cu(I)compounds with oxygen and hydrogen and (ii) to analyze the thermodynamic stability of copper and its compounds in oxygen-free water environment.

The compounds of copper(I) with oxygen and hydrogen are copper oxide (also known as cuprite Cu_2O) and copper hydride, respectively. Cuprite is a stable and well known substance with regard to both its chemical and electrical properties. Copper hydride, on the other hand, is a less studied phase. It does exist, but it is very unstable and loses hydrogen quickly with time. In the study, computer calculations were performed in an attempt to reproduce the experimental information on cuprite and copper hydride. They show that the reaction with copper and oxygen is energetically favourable and that the obtained thermodynamic properties of cuprite are in quite good agreement with existing experimental data. More or less good agreement with experiment was seen also for the hydride, although the reaction is shown to be unfavourable thermodynamically. Hence, it is known that the copper oxide is stable but the hydride is unstable.

The next part of the study was to search for other possible stable Cu-O-H phases. The study showed that copper oxyhydride is not a stable configuration. It also showed that copper hydroxide is a quite unstable species and its formation energy (ΔG) is experimentally known to be positive. If the copper hydroxide is condensed into a solid phase, it was found that the most stable structure was a combination of the structure of cuprite and the structure of ice, "cuprice". The hydroxide has a reasonable electronic spectrum compared with the spectra of cuprite and copper hydride. However, if the stability of copper hydroxide is compared with that of cuprite and water, it is found to be unstable. Thermodynamically it should decompose into cuprite and water. Hence, according to SKB's study cuprite is still the most stable of these compounds. Copper hydroxide may exist as a meta-stable phase, but its thermodynamic properties indicate that it is unstable compared with cuprite and water.

The use of archaeological analogues

One argument that is used by Hultqvist et al. to support their idea that water can corrode copper are the copper coins from the warship Wasa. The coins have been exposed to water for over 330 years and have been reduced in size. Hultqvist argues that this is due to the fact that copper is corroded by the water itself and not by sulphide, since copper sulphide has extremely low solubility. Hultqvist's interpretation has, however, been criticized by SKB and others, who claim it is the presence of sulphide that has caused the corrosion of the copper coins.

SKB also use archaeological analogues in their argumentation. They claim that the bronze cannons from the warship Kronan, which sank in 1678 and were raised in 1986, are good objects to study, because the environment – the sediment of the Baltic Sea, considered to be oxygen-free and with brackish water – is "similar to what the copper canisters will be exposed to" in Swedish repositories. This analogue is, however, criticized by Szakalos since the corrosion of bronze differs fundamentally from that of copper. Szakalos argues that because the formation of passivating tin on the bronze surface greatly reduces the corrosion rate in aqueous environments, the corrosion rate on these cannons is around 1,000 times slower than can be expected with pure copper.

What additional information is needed to confirm this specific corrosion process and to assess the importance of the process for the final repository?

Szakálos argues that the situation at the planned repository in Forsmark is complex and threatening from both corrosion and embrittlement points of view. The copper canisters will initially be exposed to atmospheric corrosion until the oxygen is consumed. Then there is corrosion by water, sulphide, salt, stress corrosion cracking, intergranular corrosion and evaporation-induced corrosion. Szakálos means that before the KBS-3 concept can be accepted, it needs to be tested in realistic conditions. He cites an SKI report from 1996: "Copper of identical composition as the future canisters should be placed in a future site environment, with artificial heating at about 80 degrees, with bentonite, etc. Such an experiment could be monitored for several decades. " He concludes by saying that the problem with copper is that it reacts slowly with everything.

The experts in the panel point to the necessity of further research on this topic to be able to assess whether the results of Hultqvist and Szakálos are realistic or not. Both Professor Latanision and Dr. Chuah argued that hydrogen may be produced by corrosion of copper in oxygen-free water, but that it is essential to know that the corrosion product is thermodynamically stable and that it can be identified and characterized. Latanision refers to the fact that there are a number of sophisticated surface analytical techniques that should be used to demonstrate that the proposed reaction products are indeed formed.

Professor Macdonald emphasizes that the kinetics must also be examined, i.e. both the corrosion mechanism and how fast the reaction occurs. He also stresses the importance of knowing that the water in the experiment is pure, since even very small amounts of monovalent copper ions and dissolved hydrogen gas in the water are of great importance. Considerable care must be exercised, when designing experiments aimed at demonstrating copper corrosion to ensure that corrosion is spontaneous upon initiation of the experiment.

Dr. Chuah suggests that more experiments should be carried out with the aim of (i) confirming or disproving the formation of hydrogen through direct detection by mass spectrometry; (ii) studying the experimental conditions of Hultquist and Szakálos under which hydrogen is formed; (iii) examining the reaction products formed on copper using *in-situ* methods to avoid any phase transformation on exposure to atmospheric conditions; (iv) measuring the strength of the exposed copper; (v) quantifying the thickness of the corrosion layers as a function of time; and other relevant tests.

Latanision suggests that well-controlled experiments (the reactants Cu and H_2O must be completely specified and controlled) that are definitive should be carried out at a third-party laboratory. He also suggests that the susceptibility of copper to embrittlement caused by absorbed hydrogen should be examined on copper tensile specimens that are electrolytically charged with hydrogen at cathodic current densities that correspond to the corrosion rates associated with the measurements reported by the KTH team. This research should also be performed by an objective third-party institution. Further, 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 research, the conditions which have led to corrosion need to be clarified and then either controlled or engineered out of the repository environment.

Macdonald argues for more research on the common contaminant bisulphide ions, HS^-, in groundwater and the corrosion that it causes. He says that a much more detailed analysis is warranted to fully define the conditions under which immunity of copper might be expected to exist. He also recommends what such an analysis should include.

Shoesmith points to the fact that some of the references cited by Szakálos do not stand up to scrutiny, and that Hultqvist and Szakálos have made an incomplete analysis of the available literature on corrosion of copper cooling systems. He states that a review of the literature provided for the workshop, the presentations made, and a personal search of additional literature indicate that there is no evidence that significant corrosion of Cu can be sustained by water reduction.

The workshop resulted in the following conclusions

It can be concluded that in theory copper may be corroded by pure oxygen-free water with respect to the following reaction:
$2\,Cu(s) + H_2O \leftrightarrow Cu_2O + H_2$.

Hydrogen atoms or molecules must be a reaction product, in addition to the possible formation of copper hydroxide or copper oxide species, because only protons can possibly accept electrons from copper atoms. Hence, the key issue is how far to the right the reaction above can proceed and the partial pressure of hydrogen that is obtained at equilibrium. According to Hultqvist et al. the hydrogen pressure is 1 mbar, which is much higher than the natural partial pressure in air. Then the corrosion reaction will proceed until the equilibrium pressure is attained, and if the hydrogen is continuously removed the corrosion may be extensive. However, thermodynamic calculations result in an extremely low hydrogen pressure at equilibrium, which is the theoretical justification for the general assumption that copper is resistant to corrosion in pure anoxic water.

If it is assumed that the system is open such that H_2 can be continuously removed from the reaction area, the reaction will be shifted to the right and corrosion will be favoured. There are however a number of questions that need to be answered regarding the experiment and results presented by Szakalos and Hultqvist. One such issue is that the proposed corrosion product needs to be identified and characterized. If the corrosion product is chemically characterized the formation energy can be computed and the overall spontaneity of the corrosion reaction calculated. Then a new substance has to be added to the thermodynamic data tables.

Moreover, based on available information presented by Szakalos and Hultqvist, it is not possible to state what the proposed reaction means for a copper canister in the repository environment. It is for instance unclear what the presence of the bentonite buffer will mean for the removal of H_2. It is also unclear how complexing ions such as sulphide and chloride that are present in the repository environment will influence the proposed reaction.

Hence, there are a number of issues that need to be addressed. The yet unknown corrosion product needs to be identified, the corrosion rate needs to be determined, and corrosion in a realistic repository environment needs to be studied.

The members of the panel also stated that further research is required to clarify the experimental results and the analytical methods used by Szakalos and Hultqvist.

Written statements by the panel members

Written statements by the panel members

Mechanisms of Copper Corrosion in Aqueous Environments

Summary Statement

G. K. Chuah
National University of Singapore

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 derived from 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 wide range of backgrounds.
2. In order to be in conformance with the known thermodynamics of 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 detected. The authors report that powder x-ray analyses on a number of different copper samples from the anoxic experiments showed spectra indicative of CuO and Cu_2O 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 H_2. 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 of what seems to be a violation of known thermodynamics, it is only prudent that more experiments be carried with the aim of (i) confirming or disproving the formation of hydrogen through direct detection by mass spectrometry; (ii) studying the experimental conditions of Hultquist and Szakálos under which hydrogen is formed; (iii) examining the reaction products formed on the copper by *in-situ* methods to avoid any phase transformation on exposure to atmospheric conditions; (iv) measuring the strength of the exposed copper; (v) quantifying 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 providing 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 of copper corrosion in aqueous environments. Without more studies of 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 techniques

including those of surface science are important. Surface science studies are relevant for a fundamental understanding of 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 disposal 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 offers 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 on 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.

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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 experiment, 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 materials balance 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 measure-

ments 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.

Is Copper Immune to Corrosion When in Contact With Water?

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Sweden's SKB-III plan for the disposal of high level nuclear waste (HLNW) is predicated upon the condition that copper, the material from which the canisters will be fabricated, is thermodynamically immune to corrosion when in contact with pure water. In the immune state, corrosion cannot occur because any oxidation process of the copper is characterized by a positive change in the Gibbs energy, rather than a negative change, as demanded by the Second Law of Thermodynamics for a spontaneous process. Accordingly, "immunity" is a thermodynamic state that must be characterized upon the basis of thermodynamic arguments.

Consider the lowest corrosion reaction in the copper/water system:

$$Cu + H^+ = Cu^+ + 1/2H_2 \qquad (1)$$

The change in Gibbs energy for this reaction can be written as

$$\Delta G = \Delta G^0 + 2.303RTlog\left(f_{H_2}^{1/2} a_{Cu^+}/a_{H^+}\right) \qquad (2)$$

which, upon rearrangement yields

$$log\left(f_{H_2}^{1/2} a_{Cu^+}\right) = \frac{\Delta G - \Delta G^0}{2.303RT} - pH \qquad (3)$$

where ΔG^0 is the change in standard Gibbs energy; i.e., the change in Gibbs energy when all components of the reaction are in their standard state with the fugacity of hydrogen, f_{H_2}, and the activity of cuprous ion, a_{Cu^+}, being equal to one. At equilibrium, $\Delta G = 0$, and designating the equilibrium values of f_{H_2} and a_{Cu^+} with superscripts "e" we may write

$$f_{H_2}^{e,1/2} a_{Cu^+}^{e} = 10^{-\left(\frac{\Delta G^0}{2.303RT} + pH\right)} \qquad (4)$$

We now define two quantities, *P* and P^e, as follows

$$P = f_{H_2}^{1/2} a_{Cu^+} \tag{5}$$

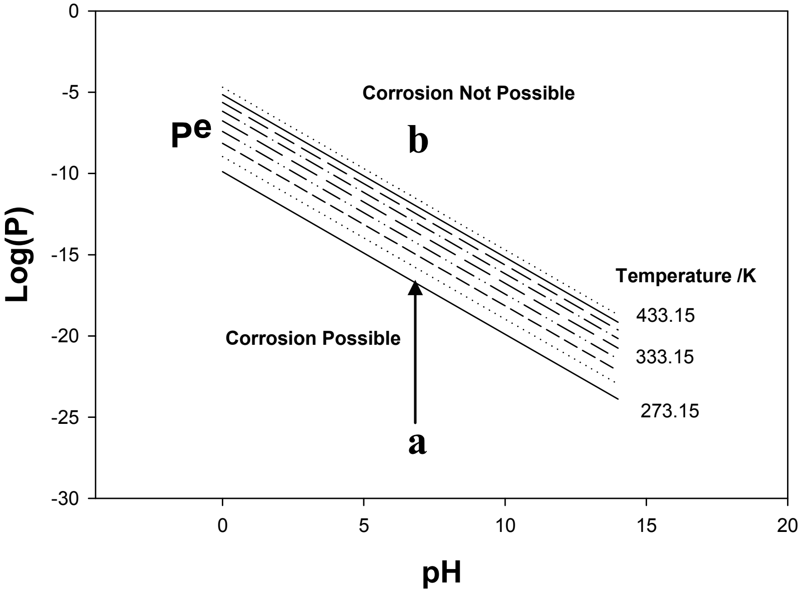
and

$$P^e = f_{H_2}^{e,1/2} a_{Cu^+}^e \tag{6}$$

The condition for spontaneity of Reaction (1) then becomes $P < P^e$ and immunity is indicated by $P > P^e$.

The quantity P^e has been calculated for Reaction (1) using Equation (4) and is plotted as a function of pH in Figure 1. These plots divide the P versus pH domain into regions of immunity (upper region) and corrosion (lower region). Accordingly, P^e versus pH divides the domain into regions of thermodynamic immunity (upper region) and corrosion (lower region). These plots clearly demonstrate that whether copper is immune (thermodynamically stable) depends sensitively upon the value of *P* and hence upon the initial conditions in the system. Thus, if *P* is small (e.g., at Point a, Figure 1), $P < P^e$ and the corrosion of copper is spontaneous as written in Equation (1). On the other hand, if the system is located at Point (b), Figure 1), $P > P^e$ and corrosion is not possible, thermodynamically, and hence the metal is "immune". Returning now to the case described by Point a, we note that as the corrosion reaction proceeds, the concentration of Cu^+ and the fugacity of hydrogen at the interface will increase, particularly in a medium of restricted mass transport, such that P will steadily increase with time until it meets the value of P^e at the corresponding temperature. At this point, the metal may be classified as being "quasi-immune"; "quasi" only because transport of Cu^+ and H_2 away from the canister surface, through the bentonite overpack must be matched by corrosion, in order to maintain $P = P^e$ at the metal surface. Accordingly, the corrosion rate ultimately becomes controlled by the diffusion of Cu^+ and H_2 through the adjacent bentonite overpack. Thus, we conclude that, for any system starting at a point below the Pe versus pH for the relevant temperature, copper metal is not thermodynamically immune and will corrode in the repository at a rate that is governed by the rate of transport of the corrosion products away from the metal surface. Of course, this rate is readily predicted by solving the diffusion equation, if the diffusivities of Cu^+ and H_2 in bentonite are known.

Figure 1 **Corrosion domain diagram for copper in water as a function of temperature**



As noted above, for any system whose initial conditions (value of *P*) lie above the relevant P^e versus pH line, copper is unequivocally immune and corrosion cannot occur as it would violate the Second Law of Thermodynamics. It is evident, that the conditions for immunity may be engineered in advance by doping the bentonite with a *Cu(I)* salt and a suitable reducing agent to simulate hydrogen, such that the initial conditions lie above P^e versus pH. It is suggested that cuprous sulfite, Cu_2SO_3, might be a suitable material. Of course, the dopant will slowly diffuse out of the bentonite and into the external environment, but it might be sufficiently slow that the conditions of immunity may be maintained for a considerable period. Thus, in a "back-of-the-envelope" calculation,

$$t = L^2/D \tag{7}$$

we choose $L = 10$ cm and $D = 10^{-9}$ cm/s to yield a diffusion time of 1011 seconds or 316,456 years. At a time of this order, the value of *P* at the canister surface will have been reduced to P^e and corrosion will have initiated at a rate that is determined by the transport of Cu^+ and H_2 through the bentonite overpack. It is important to note that the above calculation is only a rough estimate and that a more accurate value can be obtained by solving the diffusion equation with experimentally determined values for the diffusivities of Cu^+ and H_2. The important point is that immunity may be maintained for a sufficiently long period that the more active components of the HLNW will have decayed away.

Table 1 Prediction of copper corrosion in pure water as a function of solution composition at 273.15 K and at pH = 7. Activity coefficients assumed to be one. Log(P^e) = -16.895.

Case	a_{Cu+}	ppb_{Cu+}	f_{H2}	ppb_{H2}	Log(P)	Corrosion possible?
1	10^{-6}	63	10^{-6}	0.002	-9	No
2	10^{-6}	63	10^{-12}	2×10^{-9}	-12	No
3	10^{-6}	63	10^{-18}	2×10^{-15}	-15	No
4	10^{-6}	63	10^{-24}	2×10^{-21}	-18	Yes
5	10^{-6}	63	10^{-30}	2×10^{-27}	-21	Yes
6	10^{-6}	63	10^{-18}	2×10^{-15}	-15	No
7	10^{-12}	63×10^{-6}	10^{-18}	2×10^{-15}	-21	Yes
8	10^{-18}	63×10^{-12}	10^{-18}	2×10^{-15}	-27	Yes
9	10^{-24}	63×10^{-18}	10^{-18}	2×10^{-15}	-33	Yes
10	10^{-30}	63×10^{-24}	10^{-18}	2×10^{-15}	-39	Yes

To complete the discussion with regard to copper immunity, when in contact with pure water, we give in Table 1 various combinations of the fugacity of hydrogen, f_{H_2}, and the activity of cuprous ion, a_{Cu^+}, and the calculated values of P, together with a judgment on whether corrosion is possible or whether immunity should prevail. As can be seen from the values contained in Table 1, the values of $P^e = [Cu^+].p_{H_2}^{1/2}$, for equilibrium, assuming unit activity and fugacity coefficients, are very low and hence it should be relatively easy to ensure immunity by doping as indicated above. However, it is also noted that experiments that have been performed to detect the corrosion of copper in contact with pure water have yielded contradictory results, with some experiments indicating that corrosion occurs while others indicate that copper is immune. It is suggested by the present author that this unsatisfactory state of affairs stems from a poor definition of the initial conditions of the experiment, and in some cases the concentration of Cu^+ and H_2 may be such that P exceeds the equilibrium P^e versus pH correlation and hence the system pre-exists in the immune condition. In this case, no corrosion would be expected to occur as the metal is thermodynamically immune. On the other hand, in other experiments, the initial $[Cu^+]$ and p_{H_2} may be such that the system is characterized by a P value that lies below the P^e versus pH correlation shown in Figure 1, indicating that corrosion is spontaneous. In this instance, corrosion will occur until the concentrations of corrosion products build up in a closed system to render $P = P^e$. At that point, corrosion will cease. Clearly, considerable care must be exercised when designing experiments to demonstrate copper corrosion to ensure that corrosion is spontaneous upon initiation of the experiment.

The analysis presented above is restricted to the corrosion of copper in contact with pure water. However, groundwater is far from pure and a common contaminant is bisulfide ion, HS^-. This species arises from dissolution of sulfide minerals in the host rock of the repository, from dissolution of pyrite in the bentonite, and even from the decomposition of organic (plant) material. It is fair to conclude that bisulfide, and other sulfur-containing species are ubiquitous in groundwater environments at concentration ranging up to a few ppm, at least. It is also well-known that sulfide, including bisulfide, activates copper by giving rise to the formation of Cu_2S at potentials that are significantly more negative that the potential for the formation of Cu_2O. Thus, in the presence of bisulfide, the lowest corrosion reaction of copper may be written as

$$2Cu + HS^- + H^+ = Cu_2S + H_2 \qquad (8)$$

for which the change in Gibbs energy is written as

$$\Delta G = \Delta G^0 + 2.303RT\log\left(f_{H_2}^{1/2}/a_{HS^-}.a_{H^+}\right) \qquad (9)$$

As before, we define an equilibrium value of P as

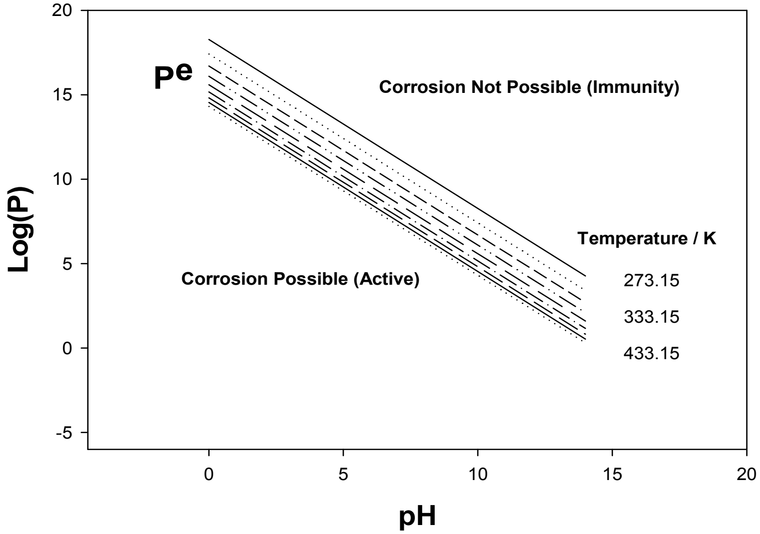
$$P^e = f_{H_2}^{e,1/2}/a_{HS^-}^e \qquad (10)$$

where

$$f_{H_2}^{e,1/2}/a_{HS^-}^e = 10^{-\left(\frac{\Delta G^0}{2.303RT}+pH\right)} \qquad (11)$$

Values of P^e versus pH are plotted in Figure 2 as a function of temperature for temperatures ranging from 0°C to 160°C in steps of 20°C. Again, P^e versus pH divides the diagram into two regions corresponding to spontaneous corrosion (lower region) and immunity (upper region). The reader will note that the P^e values for the lines are more positive than those for the Cu – pure water case by a factor of about 10^{27}, demonstrating that immunity is much more difficult to achieve in the presence of bisulfide.

Figure 2 **Corrosion domain diagram for copper in water + HS^- as a function of temperature.**

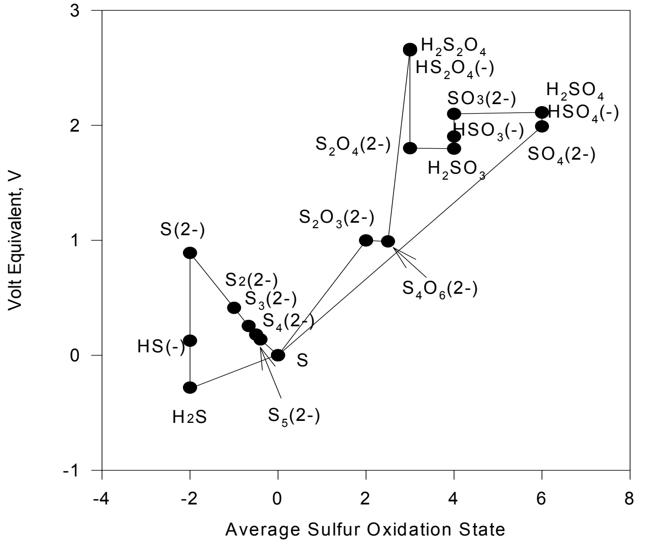


In order to illustrate the difficulties posed by small amounts of bisulfide in the environment, different combinations of the fugacity of hydrogen, f_{H_2}, and the activity of cuprous ion, a_{Cu^+}, together with the corresponding value of P^e for T = 273.15 K and pH = 7 ate given in Table 2. Noting again that immunity is achieved only if $P > P^e$, it is evident that the desired immune condition could only be achieved by having an extraordinarily low concentration of HS^- and/or an extraordinarily high partial pressure of hydrogen. For example, the two conditions that are listed in Table 2 that are predicted to yield immunity are Cases 4 and 9, which have [*HS*$^-$] and p_{H_2} combinations of 3.3 x10^{-10} ppm and 10^{-6} atm and 0.033 ppm and 10^{10} atm, respectively. In the first case, the concentration of *HS*$^-$ is orders of magnitude lower that the sulfide concentration in groundwater (a few ppb to a few ppm), particularly in the presence of bentonite, which commonly contains pyrite, FeS_2. In the second case, the required partial pressure of hydrogen (10^{10} atm) is impossibly high to be achieved and maintained practically in the repository. Accordingly, the prospects for achieving immunity of copper in a repository in which the groundwater contains a significant concentration of bisulfide must be judged to be remote. Of course, these predictions can easily be checked by experiments, and experiments to do so should be performed at the earliest opportunity.

Table 2 **Prediction of copper corrosion in pure water containing bisulfide ion as a function of solution composition at 273.15 K. Activity coefficients assumed to be one. Log(P^e) = 10.21.**

Case	a_{HS-} /m	ppm_{HS-}	f_{H2} /atm	ppb_{H2}	Log(P)	Corrosion possible?
1	10^{-4}	3.3	10^{-6}	0.002	1	Yes
2	10^{-6}	0.033	10^{-6}	0.002	3	Yes
3	10^{-8}	0.00033	10^{-6}	0.002	5	Yes
4	10^{-10}	0.0000033	10^{-6}	0.002	7	Yes
5	10^{-12}	3.3×10^{-8}	10^{-6}	0.02	9	Yes
6	10^{-14}	3.3×10^{-10}	10^{-6}	0.02	11	No
5	10^{-6}	0.033	10^{-4}	0.2	4	Yes
6	10^{-6}	0.033	10^{-2}	20	5	Yes
7	10^{-6}	0.033	1	2000	6	Yes
8	10^{-6}	0.033	10^{2}	2×10^{5}	7	Yes
9	10^{-6}	0.033	10^{4}	2×10^{7}	8	Yes
10	10^{-6}	0.033	10^{6}	2×10^{9}	9	Yes
11	10^{-6}	0.033	10^{8}	2×10^{11}	10	Yes
12	10^{-6}	0.033	10^{10}	2×10^{13}	11	No

Figure 3 Volt-Equivalent diagram for the *S/H_2O* system at 25°C, pH = 0.



Volt Equivalent Diagram for S/H2O System at pH=0 and at 25 C

As noted above, the calculations presented above are of a "back-of-the-envelope" nature and a much more detailed analysis is warranted to fully define the conditions under which immunity of copper might be expected. The analysis should involve the following activities:

1. The analysis should include the full range of sulfur species, as defined in the volt-Equivalent diagram (e.g. Figure 3). All of the species plotted in this diagram, except sulfite and sulfate, can donate atomic sulfur to the copper surface and hence, potentially, are strong activators of the metal, thereby making immunity harder to achieve. Other activating species should be included in the analysis, including chloride, bromide, and other anions. It is important to note that the sulfur species used to construct the Volt-Equivalent Diagrams are very labile and hence readily change from one to the other as conditions change in the system. Accordingly, a prime objective will be to ascertain which of the species are the most effective at destroying immu-

nity on copper. This can only be done by comparing the Corrosion Domain Diagrams (e.g., Figures 1 and 2) for the reaction of copper with each of the sulfur species.

2. The system should be modeled along the corrosion evolutionary path, which is defined by the variation of temperature, pH, [HS^-], and p_{H_2} as the repository ages; note that these four quantities are the primary independent variables for Reactions (1) and (8). The time dependences of pH, [HS^-], and p_{H_2} must be modeled by solving the transport equations for the transfer of H^+, HS^-, and H_2 across the bentonite layer, recognizing the existence of a source term for bisulfide in the bentonite (dissolution of FeS_2). Solution of the thermal diffusion equation will yield the temperature as a function of distance from the copper surface and time. Because the diffusivities of H^+, HS^-, and H_2 are temperature-dependent, as is the rate constant for FeS_2 dissolution, the system of equations that will describe the evolution of the repository and hence will indicate whether and under what conditions immunity may be achieved, will be highly non-linear and must be solved numerically.
3. The possibility of doping the bentonite with a $Cu(I)$ salt, such as Cu_2SO_3, should be explored to determine whether immunity might be maintained over extended periods. Thus, the "back-of-the-envelope" calculations reported above suggest that immunity might be sustained over periods of several hundreds of thousands of years. Given that the performance horizon of the repository is 10,000 years, it may well be possible to impose immunity on the system over the entire planned storage period. Practically, this issue could be explored by inserting source terms in the model outlined in 2 above for Cu^+ and SO_3^{2-} from the bentonite overpack.

MECHANISM OF COPPER CORROSION IN AQUEOUS ENVIRONMENTS

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INTRODUCTION

Szakalos and Hultquist have proposed that the corrosion of copper in water leads to the production of hydrogen and a previously unreported H_xCuO_y phase [1–8]. It is claimed that the mechanism of this reaction involves the dissociation of water to produce this phase and H atoms. Subsequently, this surface species may dehydrate to yield the known phase Cu_2O and the H atoms either combine to evolve H_2 or absorb into the copper. Even in the presence of dissolved O_2 it is claimed that corrosion occurs via this mechanism and that the O_2 present is consumed, not by a direct reaction to corrode copper, but by reaction with the H atoms produced by water decomposition, thereby leading to further corrosion of the copper by water decomposition and reaction with H atoms.

This mechanism represents a radical new view of the process of copper corrosion which contradicts our present understanding of the thermodynamics of copper corrosion as well as proposing a new reaction pathway at odds with a wealth of published information. These results are then used to estimate rates of corrosion of copper nuclear waste containers which are orders of magnitude greater than those calculated by SKB and other national nuclear waste disposal programs.

THE WORKSHOP PRESENTATIONS

At this meeting Hultquist, Szakalos, and SKB had the opportunity to present their research results and/or their approach to investigating the copper corrosion process as it pertained to buried nuclear waste containers. SKB (Lilja) chose to present its wide ranging and extensive program on copper corrosion and also the results of first principles calculations of the thermodynamic properties of Cu-O-H, the phase claimed as a corrosion product by

Hultquist et al. Hultquist presented the results of his research conducted over the last 23 years, which was already well documented in the available published papers provided before the workshop.

The presentation by Szakalos, however, merits more detailed comment, since it started with the claim that the instability of copper in pure O_2-free water was undisputed among thermodynamic experts, which rather pre-empted the purpose of the meeting. A case was made that many of the rates measured in the Swedish (SKB) and other national programs (Canada, Finland, Japan) were in the range measured by Hultquist et al., implying, without explicitly stating, that even the SKB measurements justified their claims.

In the subsequent discussion period a number, but not all, of these assertions were challenged. For instance, Fraser King (a consultant to SKB) pointed out the inconsistency in comparing predicted corrosion rates in the Swedish/Finnish programs (0.33 mm in 10^6 years) to the results of conservative estimates based on mass balance calculations in the Japanese program (18–26 mm in 10^3 years) (Quoted from SKB report TR-01-23). Other references quoted in this presentation also do not stand up to scrutiny. For example, it is implied that the observation of intergranular corrosion on copper in *aerated* sulphide-containing salt water by Al. Kharafi et al. [9] indicates this process will occur under anoxic repository conditions, but does not acknowledge the positive electrochemical potentials used in the experiments described in the paper. Such redox conditions are only achievable under fully aerated conditions in the presence of sulphide. The authors' [9] claim that "The present results are immediately relevant to the discussion of the proposed use of copper containers for the disposal of Swedish, Finnish and Canadian high-level waste deep in granite environments" is incorrect, but accepted by Szakalos.

The claim that the corrosion of copper cooling systems is an example of copper corrosion in O_2-free water is a further example of what can only be described as an incomplete analysis of the available literature. The corrosion processes occurring in these systems are well characterized and known to be due to the in-leakage of oxygen [10]. To quote from Park et al. [10], "These problems have been understood from the relationship between the corrosion rate of copper and a DO (dissolved oxygen) concentration. The experimental results showed a bell-shaped relationship (3 references given). The corrosion rate in LOWC (low-oxygen water chemistry) is satisfactorily low owing to its (Cu) thermodynamic stability, and is reduced significantly in HOWC (high-oxygen water chemistry) owing to passive oxide formation. However, intermediate oxygen water chemistry (IOWC) (50 ppb < DO < 2 ppm) results in much higher corrosion rates. The IOWC may occur when air leaks into the system."

In fact, contrary to supporting the claim that the extensive corrosion and finely divided corrosion product observed in the 15-year test [7] is due to Cu corrosion by H_2O to produce H_2, these observations suggest the copious corrosion observed was due to the maintenance of IOWC conditions or a cycling between LOWC and HOWC conditions. As in the Cu cooling systems, the maintenance of totally anoxic conditions would have been very unlikely. King [11] makes a similar point in his review of the experiments of Hultquist et al.

REVIEW OF THE CORROSION MECHANISM OF COPPER UNDER ANOXIC CONDITIONS

The two key processes involved if the corrosion mechanism proposed by Hultquist et al. is to occur are the production of H_2 and the formation of a stable corrosion product at potentials well below those presently accepted in thermodynamic calculations.

Hydrogen Production

The key feature of the corrosion process proposed by Hultquist et al. is the production of H_2. In their initial publication [1], H_2 was detected using a solid-electrolyte H_2 probe, pre-calibrated over a range of H_2/N_2 mixtures. In other experiments (with the much more readily corrodible Zn [2]) the response of this probe was validated against manometric measurements. They also used an ion pump to measure pressure build-up, assumed to be due to H_2 formation, and eventually thermal out-gassing coupled to mass spectrometry to determine hydrogen present in corrosion products and the Cu itself. Except in this last case, there are no grounds to unequivocally dispute that H_2 was formed, despite the number of experimental uncertainties noted by King [11].

Except for the initial study the authors claim that the development of a H_2 pressure within a sealed vessel will suppress corrosion as thermodynamic equilibration is approached. This argument is used to explain apparent decreases in H_2 generation rates with time, and to account for the major differences in the extents of corrosion observed on specimens corroded over a 15-year period in vessels sealed with Pd (through which, they claim, H_2 can escape and extensive corrosion is possible) and with Pt (through which, they claim, H_2 cannot escape and corrosion should be suppressed). It is also assumed, to account for apparent imbalances in the extent of corrosion and the amount of H_2 detected, that considerable amounts of H are absorbed into the Cu. This last conclusion must be treated with suspicion, since the solubility of H in Cu is known to be small (as pointed out by King [11]) and the only analytical evidence provided by Hultquist et al. comes from out-gassing experiments on specimens covered in corrosion products whose degree of hydration is unknown. A similar reservation applies to the SIMS analyses of Hultquist et al., and the claim that the heavily corroded specimen from the 15-year experiment is H embrittled since it cracked on bending is speculative at best. The reference offered in support [12] is not relevant since it involved hydrogen charging of Cu at currents greater than 10 $mA \cdot cm^{-2}$, which is many orders of magnitude greater than could possibly be sustained by corrosion.

The Corrosion Product

For a corrosion process to be sustained by H_2O reduction, the formation of an anodic corrosion product must occur. This introduces a dilemma since, with the exception of copper sulphides (Cu_xS with $x \sim 2$), there are no known stable corrosion products, according to accepted thermodynamic reasoning, if the corrosion potential is maintained in the range where water reduction is thermodynamically possible. The corrosion product formed in their experiments [5] was analyzed by X-Ray Diffraction (XRD) and Secondary Ion mass Spectrometry (SIMS). XRD indicated the presence of CuO and Cu_2O and the SIMS showed a range of products with varying O and H contents. Consistent with earlier observations [3], the H content of the products was higher in tests performed in the absence of O_2. Despite the XRD results, the authors claimed the formation of a new phase, H_xCuO_y. Unfortunately, both techniques are ex-situ and the phases observed may not be those formed by corrosion, but a combination of the oxides present at the start of the experiment, the corrosion products, and their conversion products when exposed to air prior to analysis. Consequently, these analyses neither confirm nor disprove the formation of H_xCuO_y. In response to comments that oxides (particularly Cu_2O) initially present on Cu specimens at the start of their experiments were ignored, Szakalos et al. [8] claimed that they would have been reduced by the H_2 formed in their experiment. This argument is unconvincing since there is considerable evidence to show that air-formed films on Cu are notoriously difficult to fully reduce, even electrochemically [13, 14].

To justify their claim that the phase, H_xCuO_y, was energetically possible, Hultquist et al. [8] used molecular dynamics simulations to obtain a free energy of formation for the reaction

$$Cu + H_2O \rightarrow CuOH + H_2$$

of -311 kJ/mol. Such a value indicates this reaction is energetically favourable. As noted by King [11], this not consistent with the value of + 9kJ/mol calculated by Protopopoff and Marcus [15]. Even if the formation of such a *surface adsorbed* species were energetically possible (Protopopoff and Marcus give a value of -228 kJ/mol for the free energy of formation of $Cu(OH)_{ads}$ based on a considerable experimental database), it does not demonstrate that the formation of a three dimensional H_xCuO_y is, therefore, energetically feasible.

In fact, the first principles calculations of Korzhavji (presented at the meeting) showed HCuO to be an unstable phase with respect to Cu_2O. His calculations also showed that the corrosion of Cu by H_2O, taking into account the three dimensional nature of the corrosion product (as opposed to the two dimensional nature of a surface reaction) via the reactions

$$H_2O + 2Cu \rightarrow Cu_2O + H_2$$

$$2H_2O + 2Cu \rightarrow 2CuOH + H_2$$

were both energetically unfavourable. The values of ΔH and ΔG for these reactions were calculated to be large and positive, leaving little leeway to dispute the validity of the calculations.

Potential-pH Diagrams

Szakalos et al. [5] then proposed a modified potential-pH diagram to include the H_xCuO_y phase, assumed to be stable over a potential range from the stability line for Cu_2O formation to below the stability line for H_2O. There is well documented literature based on electrochemical measurements coupled to sensitive in-situ surface analytical techniques such as surface-enhanced Raman spectroscopy (SERS) [16], atomic force microscopy (AFM) [17], glancing incidence X-ray diffractometry (XRD) [18] and ellipsometry [19] demonstrating the formation of monolayer to sub-monolayer levels of a $Cu(OH)_{ads}$ species within the thermodynamically forbidden region of the potential-pH diagram. Two sets of authors [15, 17] have proposed modification of the standard potential-pH diagram to include these *surface* states.

The calculations performed by Protopopoff and Marcus [15] are particularly thorough and based on an extensive experimental database. They note that Cu shows an intermediate behavior between the transition metals (e.g., Fe and Ni), which strongly adsorb OH and H, and the noble metals (e.g., Au and Ag) which do not. According to their calculations there is a narrow underpotential deposition region where adsorbed H and OH could coexist, making it feasible that, on the monolayer scale, the decomposition of H_2O to produce H_{ads} and OH_{ads}, leading to the production of H_2 and $Cu(OH)_{ads}$ could occur. This would be minor in extent, since it would be limited by the ability to form only a monolayer of what would be the corrosion product, $Cu(OH)_{ads}$. Since their thorough review of literature could find no experimental evidence for the formation of H_{ads}, they assumed it would have a bond energy comparable to that for H_{ads} at the metal/gas interface.

Only one study [20], performed in alkaline solutions using SERS, has shown evidence of the formation of $Cu(OH)_{ads}$ via H_2O reduction,

$$CuO_{ads} + H_2O + e^- \rightarrow Cu(OH)_{ads} + OH^- \quad (X)$$

the key reaction according to Hultquist et al. It is clear from their Raman results that a pre-oxidized surface state (CuO_{ads}) is required for this reaction to progress. Maurice et al. [21] could find no evidence for this reaction using electrochemical techniques coupled to in-situ AFM. The latter authors noted that the key difference between these two studies was the state of the surface; electropolished and smooth in their case, but slightly roughened by an electrochemical oxidation-reduction cycle (necessary to activate the SERS signal) in the experiments of Hartinger et al. [20]. Activation of a SERS signal requires the formation of nanosized surface Cu particles, and the Raman results of Hartinger et al. [21] could be explained by the presence of CuO_{ads} surface species present due to the incomplete reduction of the oxide formed during the oxidation-reduction cycle. It was speculated than they could be subsurface, i.e., on the underside of the Cu nanoparticles.

The essential feature of this discussion is the formation of nanoparticulate material during the oxidation (to bulk oxide) – reduction cycle on Cu, as well as the possibility that mixed Cu oxidation states ($Cu/Cu^{I}Cu^{II}$) coexist on the surface. Such states are known to be catalytic for H_2O, but especially O_2, reduction [22]. This raises the real possibility that, in an experiment started with an oxide-covered surface and a solution containing dissolved O_2, the consumption of O_2 could lead first to the exhaustion of O_2 and then the reduction of the oxide. If, as in the case of the Cu cooling systems discussed above [10], this led to the formation of partially reduced Cu surface species (i.e., CuO_{ads}) then reaction X could be activated leading to the production of H_2. Of course, such a reaction is only sustainable on nano-particulate material until available surface O states are consumed. An ongoing process is only sustainable with a continuing supply of O_2, as indicated in the heat exchanger studies. Such a mechanism could explain the apparent limited production of H2 in some of the experiments with H and S. *(I am indebted to Roger Newman, University of Toronto, for the suggestion than the "violation of thermodynamics" would require the surface energy generated by the involvement of nanoparticles in the 2 to 3 nm size range)*.

The Corrosion Mechanism

Despite the fact that dissolved O_2 will be unavoidably present, at least initially, in their experiments, the possibility that dissolved O_2 was involved in the corrosion of Cu was not considered by Hultquist et al. Instead, O_2 was assumed to be consumed by reaction with H atoms produced by the reduction of H_2O. While this mechanism could apply if the metal was exposed only to the aqueous vapour phase with no condensed liquid phase present, it is at odds with the very extensive literature on the reduction of O_2 dissolved in aqueous solutions. This literature encompasses not only studies in corrosion science and engineering but also energy systems such as batteries and, in particular, fuel cells. This apparent dismissal of a very large body of published experimental evidence suggests a fundamental misunderstanding of the aqueous corrosion process. As discussed above, and in detail for Cu by King [11], the O_2 reduction reaction is strongly catalyzed on oxide/metal interfaces with mixed oxidation states (in this case $Cu/Cu^I/Cu^{II}$) at potentials where surface $Cu(OH)_{ads}$ species exist, but at potentials too positive for H_2O reduction. The adoption of a reaction mechanism that applies in the vapour phase ignores this well proven electrochemical mechanism involving the utilization of solution-connected anodes and cathodes. It would appear that this conceptual misunderstanding is a key premise in their insistence that H_2O rather than O_2 reduction dominates the corrosion process.

Anoxic Corrosion in the Presence of Other Anions

There is a wealth of available literature to show that many other anions besides OH^-, chemisorb on Cu surfaces. Particularly strongly adsorbed are the halides (I^-, Br^-, Cl^-) [23–26] and especially SH^-. Of particular interest in the present context are Cl^- and SH^- both of which are anticipated in the Swedish groundwaters to which waste containers would eventually be exposed. These adsorption processes occur in the potential region close to the water reduction region. Commonly Cl^- is more strongly adsorbed than OH^- and has been observed electrochemically to catalyze H_2O reduction to H_2 [25]. However, there is no evidence to show that stable chloride-containing oxide/hydroxide phases can be formed by H_2O reduction. On the contrary, Cl^- has been shown, by in-situ STM investigations, to be absorbed and desorbed reversibly without interfering with the surface structure of Cu [24]. Phase formation only occurs at considerably more positive potentials where H_2O reduction to H_2 is thermodynamically impossible.

Despite these published studies, Szakalos (in correspondence after the workshop) has claimed that the Cu hydroxyl chloride, paratacamite ($Cu_2(OH)_3Cl$), containing Cu^{II}) can form by water reduction under anoxic conditions. Offered in support of this claim is a statement from the UK Environment Agency Report [27] claiming this is the case. This statement is not referenced in the report. Also offered in support of this claim is evidence from a study of historical artefacts from which it is concluded that paratacamite is more stable than Cu_2O [28]. This claim is unjustified (and not made by the authors of the paper). Secondly, the conclusions drawn by Szakalos (that the evidence in this paper justifies his claim that paratacamite, and hence all the corrosion products in the 5-year LOT exposure test [29], were formed under anoxic conditions) are the opposite of those drawn by the authors. It is worth quoting the conclusions from the paper of Domenech-Carbo et al. [28]: "Thus "green' samples of C1-13 and C1-14 in which a significant amount of CuCl accompanies copper trioxychloride can tentatively be attributed to a corrosion process under wet aerobic conditions, while samples C1-9 containing copper trioxyhydoxychloride *(a category which includes paratacamite)* plus malachite probably corresponds to a region of the buried helmet in contact with wet oxygenated soil, then exposed to relatively high carbonate concentrations. Finally "reddish" deposits in sample C1-11 are formed by cuprite. Copper trihydroxychlorides accompany cuprite in sample C1-12 while CuCl is absent. These features suggest that the corrosion process in this portion of the helmet occurred in a relatively dry and aerobic environment." One can only conclude that the observations and conclusions in this paper strongly support the claims made in the 5-year LOT report [28] that the oxide/hydroxide/hydroxychloride phases observed are the products of Cu corrosion involving O_2 reduction.

The only anion for which there is thermodynamic and experimental evidence to show it can lead to the formation of bulk corrosion products by H_2O reduction is SH^-/S^{2-}. The available information has been comprehensively calculated, reviewed and discussed in SKB reports [30-32]. More recent studies have shown that the corrosion product is exclusively Cu_xS (with x between 1.8 and 2), with no evidence for the simultaneous formation of oxide/hydroxide/hydroxychloride corrosion products under anoxic conditions [33–36]. Even in solutions containing 5 mol/L chloride there was no evidence for any product other than Cu_xS [37].

SUMMARY AND CONCLUSIONS

- A review of the literature provided for this workshop, the presentations made at the workshop, and a personal search of additional literature shows there is no evidence that significant corrosion of Cu can be sustained by water reduction.
- The claims that H_xCuO_y and/or $Cu_2(OH)_3Cl$ are formed as stable corrosion products by the anoxic corrosion of copper cannot be justified. In the case of H_xCuO_y no experimental characterization is available and theoretical calculations show the phase to be unstable. In the case of $Cu_2(OH)_3Cl$ the published literature shows it is a product of the aerobic, not the anoxic, corrosion of copper. Its observation in long-term tests in which the exclusion of oxygen cannot be guaranteed is to be expected.
- It may be possible that the reduction of oxides/hydroxides present at the start of experiments could lead to nanoparticulate copper able to temporarily support water reduction and the production of hydrogen. However, for such a process to lead to the accumulation of meaningful corrosion damage would require the presence of dissolved oxygen at least intermittently.
- There is evidence to show that the maintenance of low levels of dissolved oxygen (50 ppb to 2 ppm) could lead to much more extensive corrosion than lower or higher oxygen levels. This offers a potential explanation for the extensive corrosion observed by Hultquist et al. in one of their 15-year experiments.
- The only anionic species for which there is thermodynamic and experimental evidence to show it can sustain the anoxic corrosion of copper is sulphide. In this case the stability of the corrosion product (Cu_xS; $1.8 < x \leq 2$) is well characterized.
- It can be concluded that the anoxic corrosion of Cu can only be sustained in the presence of sulphide.

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Edited transcripts from the workshop

1. Questions, hypotheses and facts related to corrosion of copper in water, by Associate Professor Gunnar Hultquist, Royal Institute of Technology, KTH

The Swedish method of copper containment of spent nuclear fuel was launched in early 1980s during political turmoil in Sweden and the model was claimed to be based on proven science. The method was also intended to be used by other countries. At that time a plan for the final disposal of spent nuclear fuel had to be presented before any new power plant could be commissioned. One million years of safe containment was originally required, but today a life of "only" 100,000 years is claimed with a canister thickness of 50 mm of copper. Even with this thickness, a risk of local attack is considered to exist in the Swedish method, and general corrosion is assumed to be zero in the presence of pure water.

The KBS-3 method was developed 30 years ago and consists of a copper canister surrounded by clay deposited 500 m down in the Swedish bedrock. It differs from other countries' concepts in that it assumes thermodynamic immunity in water, i.e. copper is assumed to withstand water even at elevated temperatures. But, says Hultquist, this assumption of immunity is disputed.

Corrosion reactions

Hultquist presents the main corrosion reactions that take place in the repository environment:

Cu + O_2 (dissolved in ground water) ⇒ Cu oxide

When the oxygen is consumed:

2) Cu + sulphide ions in water ⇒ Cu sulphide

3) Cu + water molecules ⇒ Cu hydroxides +H_2 +hydrogen in Cu metal

He says that there is a consensus regarding reactions 1 and 2. Reaction 3, however, is disputed and is the topic of discussion of this seminar.

"What happens with copper in water?" he asks, and answers:

"We have proved that we have a reaction product, which is solid and porous. Molecular hydrogen can be measured in the gas phase. We also have hydrogen in the metal, which can be measured."

The question is how copper is corroded by pure water?
In Hultquist´s experiment, the pressure of hydrogen is 10^{-3} bar at a temperature of 20–80°C. Since the natural H_2 pressure in air is $5 \cdot 10^{-7}$ bar, and Hultquist measures a higher hydrogen pressure in the experiment, it follows that copper is corroded by water. He shows: ($H_2O \Rightarrow OH^- + H^+$) $\Rightarrow$ CuOH + H_2 + hydrogen in Cu where $H_2 \approx 10^{-3}$ bar at 20–80°C.

Hultquist and his colleagues have been criticized for the way they have dealt with the issue in a Pourbaix diagram. In response to this criticism, he says that the hydrogen content of the air must be considered. In the diagram, the hydrogen pressure is normally set to approximately zero and this, he argues, does not represent the complete truth. In the Pourbaix diagram presented by Hultquist, this "new" situation is shown by displacing the "hydrogen borderline" and thereby adjusting it to the actual hydrogen concentration in air.

If copper is immersed in water, a solid product can be observed to form. A by-product is also created by this: hydrogen in atomic form, not molecular, which can react in different ways. Either the hydrogen is absorbed into the copper metal or it is accumulated and exerts a pressure in the experimental glass jar.

To demonstrate the experiment theoretically, Hultquist calculates the bond between copper and, in this case, OH, which is always present in water. First principles simulation results in the strong bonding of an OH-group to a Cu-(100) surface, leading to the formation of a 3-dimensional copper hydroxide.

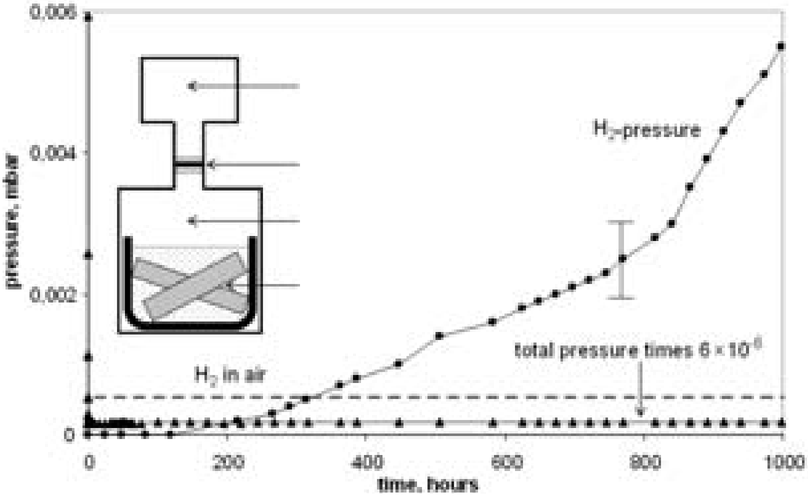
"Depending on the strength of the bond, we think this shows that a three-dimensional growth of monovalent copper hydroxide is possible."

Experiments in practice

The figure below shows that hydrogen produced by copper corrosion at room temperature exceeds the existing hydrogen pressure.

"Well, it is up to you if you believe that this difference in copper coin size is due to reaction with sulphide," says Hultqvist. "I don't believe it myself, because copper sulphide has extremely low solubility in air."

Figure x Hydrogen from copper corrosion at room temperature exceeds the existing hydrogen pressure.



Hultquist presents data from the experiment and says that it is a simple but carefully planned set-up, where materials and joints need to be corrected. The experiment is based on well-known ultra-high-vacuum components. Two stainless steel parts are used. In the upper one, which is initially evacuated, the hydrogen pressure is measured. It has a membrane of palladium that only permits the passage of hydrogen.

When the experiment is started, the air contained in the water is removed as quickly as possible by pumping. The available counteracting pressure of H_2 for copper corrosion by water, $5 \cdot 10^{-7}$ bar, is indicated on the slide. After some time, the hydrogen pressure in the experiment builds up and exceeds $5 \cdot 10^{-7}$ bar. The question is now how far the corrosion process continues.

To ensure that the hydrogen evolves from corrosion, Hultquist evacuates the hydrogen from the system, seals it and permits the process to start again. The pressure rises to 1 millibar, where it is shown that the corrosion process levels out and stops. No more hydrogen is evolved above this pressure. The higher pressure that has evolved equalizes in the whole system, in both the lower and upper parts of the experimental set-up.

An illustration of another experiment shows the two glass vessels where copper foils in pure oxygen-free water have been kept for 15 years. In one glass vessel, the H_2 was not evacuated due to its membrane of platinum. In the other one, with a membrane of palladium, H_2 was actually removed. The latter shows signs of corrosion: the foils have turned black. Actually, different kinds of corrosion can be seen.

Hultquist argues that if you remove H_2, which nature always does, we must expect this to happen. It is not enough to have copper isolated from molecular oxygen or air.

The researchers at KTH also analyzed hydrogen that has diffused into the metal. Hydrogen is transported everywhere, it is just a matter of time, Hultquist says. They have published proofs, using two methods: Hydrogen was detected both in secondary ion mass spectrometry and in a quantitative study on out-gassing in vacuum. Secondary ion mass spectrometry is sensitive to hydrogen. The result is sometimes difficult to interpret, but Hultquist states that this is not a reason not to use it.

Evidence of copper corrosion by water has been verified by various experiments with results such as: hydrogen formation, increase in weight, hydrogen in the copper metal, chemical analysis of the corrosion product, visual inspection and metallographic examination.

Hultquist shows a picture of two copper coins from the warship Wasa that were exposed to water for over 330 years. Dagens Industri published this picture in 1984. “Well, it is up to you if you believe that this difference in copper coin size is due to reaction with sulphide. I don’t believe it myself, because copper sulphide has extremely low solubility.”

Hultquist published evidence of copper corrosion back in 1986 in a peer-reviewed journal (Corrosion Science), but it was not until 2009, after new publications, that the scientific debate started in earnest. One hypothesis that is consistent with all experimental observations is that copper is corroded by water itself, which means that copper corrosion takes place even without molecular oxygen. We cannot blame molecular oxygen all the time.

Implications and suggestions

Hultquist illustrates what might happen to copper if it were exposed to water for a very long time, such as 100.000 years. After 1,000 years the general corrosion depth could be 10 mm.

"I don't say that this will be the case. But there is a substantial risk that this could happen. In my opinion we have to try to find some solution to this problem."

2. Thermodynamics and kinetics of copper corrosion in oxygen-free water, by Peter Szakálos, Royal Institute of Technology, KTH

Peter Szakálos concludes that it was already known 30 years ago that copper was not thermodynamically immune in pure O_2-free water, and that this fact is undisputed among thermodynamic experts. In fact, this contention is disputed within the scientific community. The research done by the KTH group does not change the known thermodynamics of water corrosion of copper. The results can be explained by the formation of an amorphous copper hydroxide. Several scientific publications suggest the existence of different amorphous hydroxides, both monovalent and bivalent, which can easily be converted to oxides. This makes them more difficult to study.

Szakálos has looked at papers that SKB usually refers to when company representatives argue that the KTH group's findings are wrong (see Christina Lilja, who spoke before Szakálos at the seminar). Two were published in *Corrosion Science*, in 1987 and 1989, and both of the experiments had O_2, oxygen gas, in the setup, and it was easily seen. One experiment was performed with nitrogen gas, which always contains a ppm level of oxygen. Szakálos states that no one today would use that kind of experiment for these exposures.

In the other paper, an oxygen peak was detected.

"This is important. Only one or attempt has been made during the last 23 years to repeat Gunnar Hultquist´s initial experiment. The experiment was carried out at the Swedish National Testing and Research Institute, SP, in Borås and the results were incorrectly described as showing that Hultquist´s observations could not be repeated. The truth is that the only experiment that was carried out according to his instructions did in fact indicate that copper corrodes in O_2-free water. However, no follow-up was ever done, Szakálos says.

It has been claimed that copper canisters should be corrosion-resistant since native copper is found at a few locations in the world. However, Szakálos argues, the situation is the same for native iron and nickel, zinc, etc, but no one uses this argument to claim that iron is corrosion-resistant in groundwater containing chlorides, sulphides, sulphates and methane/acetate, etc.

There has also been a lot of discussion about "archaeological analogues" recently. It has been stated in the news that bronze cannons from the warship Kronan, wrecked 1678 and retrieved in 1986, are good objects to study, because the environment is "astonishingly similar to what the copper canisters will be exposed to," in other words the environment in Swedish repositories. Szakálos questions the word "environment". What is it?

"It refers to the sediment of the Baltic Sea. It is assumed that the sediment will be O_2-free and contain brackish water. A lot of studies have been conducted on these bronze cannons. But the problem is, of course, that corrosion of bronzes differs fundamentally from that of copper. An accumulation of passivating tin forms on the bronze surface, which greatly reduces the corrosion rate in aqueous environments. It was documented 30 years ago that a layer of tin was found on the cannons. The corrosion rate on these cannons is around 1,000 times slower than you can expect from copper, which is confirmed by these reports. A possible explanation for why marine copper artefacts have not been used as "archaeological analogues" might be that they have corroded too much and obviously much more than bronze artefacts.

"Lots of copper artefacts have been found in the Baltic Sea sediment, but they are in quite bad conditions. If that is your analogue, you should be nervous."

He displays a copper compass from the same warship with severe corrosion.

"This represents a different corrosion process. Here it is obviously a sulphide situation. And the interesting part is that the copper coins on "Kronan" were more corroded than the "Wasa" coins, and several "Kronan" coins had no remaining metal core left."

A document published in 1965 shows a study by Olof Arrhenius, the son of the famous Nobel Prize winner Svante Arrhenius. He made a corrosion study of about 3,000 copper coins from the Wasa warship. He concluded that copper does corrode to the same extent as Hultquist reported in 1984 and 2009. These kinds of marine copper artefacts have never been studied as "analogues" for the KBS-3 model. Instead, SKB and others have studied bronze.

According to Szakálos, the KTH group has discovered hydrogen throughout the system in the course of their corrosion studies: in the metal, in the corrosion product, and possibly dissolved in water and hydrogen in the gas phase.

Copper corrosion in O_2-free water is a well known problem in industry. All cooling systems for power generators and accelerators, such as CERN in Switzerland, corrode several micrometers per year. This occurs in closed systems (no contact with air) containing water that is deionized and degassed. The industry tries to reduce these corrosion rates and to achieve oxygen-tight metal fittings, such as UHV fittings. Nevertheless, the corrosion rate still reaches micrometers per year.

He illustrates the problem with partial plugging of the cooling systems by corrosion products such as oxides and hydroxides. These systems clog within a few years' time. The environment makes the copper hot, around 70° to 90° degrees, the same temperature that the copper canister will attain. In the industrial systems there is, of course, no groundwater, the water being much less aggressive, i.e. pure water.

Another indicative example is an investigation covering five years of the copper corrosion rates in Swedish clay and soils, for example anoxic clay and sulphide clay. The redox potentials were recorded for some Swedish sites, at least some of which were regarded as O_2-free, basically due to biological activity; bacteria consume the available oxygen. The corrosion rates are still quite high, again in the micrometer per year range, often between 10 and 20 micrometers, despite the low average temperature of the Swedish soil.

Szakálos gives examples of measured corrosion rates in different studies by SKB as well as in studies in other countries. SKB and the Finnish nuclear power industry assume very low corrosion rates in their calculations, for example 0.33 mm in one million years.

"This is equivalent to a corrosion rate of 0.33 nanometer per year, or put another way, only two copper atom layers per year (!). This is an astonishingly low corrosion rate. Not even titanium or the best high-alloy materials could ever reach this range. The Japanese use rates that are closer to what we believe to be true."

He demonstrates that the KTH researchers, as well as other researchers, arrive at corrosion rates in the micrometer range.

"Some examples: Our results and a lot of other researchers' results are in the micrometer per year range. Whatever you do with the water environment, you cannot avoid those copper corrosion rates. Still we have SKB´s safety analysis indicating a corrosion rate of 3 ångströms per year. This value is totally new for me; they previously claimed around 3 nm. But even 3 nm per year is roughly 1,000 to 10,000 times lower than the corrosion rates measured by us and SKB and reported in other investigations. If you believe in an Ångström-level corrosion rate, then it could be up to 100,000 times lower than measured corrosion rates, see for instance the corrosion rates in Japanese groundwater/deep repository."

Szakálos refers to a study of copper corrosion in bentonite[1]. The two-year study indicates that the corrosion rate is quite high. The corrosion rate starts to level off after two years, but the rate is still about 10 to 20 µm per year. It involves a dissolution-precipitation process in contact with bentonite clay. The bentonite participates actively in the corrosion process.

"You have a solubility of copper in the bentonite pore water. It precipitates there as corrosion products, which is shown in the study. It is also stated that the oxygen transport was not rate-limiting. The corrosion did continue independently of the oxygen flux. This is not a surprise for us at KTH."

He reads from the report: "Precipitation of copper inevitably occurred in all of the tests, with usually more than half of the total copper corroded being in the form of precipitate, rather than being sorbed on the clay".

"I guess that it was initially thought that some copper could be sorbed on the clay particles. But we can see that it is really corrosion we're talking about here."

Significant corrosion is also confirmed by the LOT project in the Äspö laboratory, 500 meters down in the ground, under realistic conditions as can be seen in appendix 6 to the LOT report (official SKB report published in November 2009). The German

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[1] Corrosion Science, Vol 33, No 12, pp. 1979–1995, 1992 Printed in Great Britain A Mechanistic Study of the Uniform Corrosion of Copper in Compacted Na-Montmorillonite/Sand Mixtures, F. King, C.D. Litke and S.R. Ryan.

researchers[2] find an astonishingly high copper content in the bentonite immediately adjacent to the copper tube. A significant fraction of the copper in the bentonite is precipitated in the form of copper and copper-iron-sulphides, representing a corrosion rate of about 4 micrometers per year. Considering the total amount of copper in the corrosion product, bentonite and groundwater, it is most likely that the copper corrosion rate is at least 10 micrometers per year, not taking pitting corrosion into account. This is still very high.

Szakálos refers to work with the MICROBE laboratory in Äspö, because he believes it is interesting background information. The Swedish groundwater contains lots of sulphates, which in the repository will be converted to sulphides by bacterial activity. Acetate, produced by dissolved carbon dioxide and dissolved hydrogen gas, also occurs. The hydrogen gas could also be consumed by bacteria with formation of acetate. This activity affects the chemistry and redox potential of the groundwater as well as copper corrosion. Furthermore, acetate and sulphide are known to cause stress corrosion cracking in copper metal. There is a balance between sulphate and sulphide, mainly regulated by bacterial activity. The addition of copper to the system, which acts as a sulphide sink (CuS formation), causes more sulphate to be converted to sulphide by bacterial activity, accelerating the sulphide-induced copper corrosion. Copper corrosion is consequently accelerated by the precipitation of copper sulphides and copper-iron sulphides in the bentonite. The SKB LOT project confirms that the precipitation of those corrosion products continues on the bentonite clay particles.

Szakálos has constructed a corrosion model explaining the observations from the LOT project, see Figure 1.

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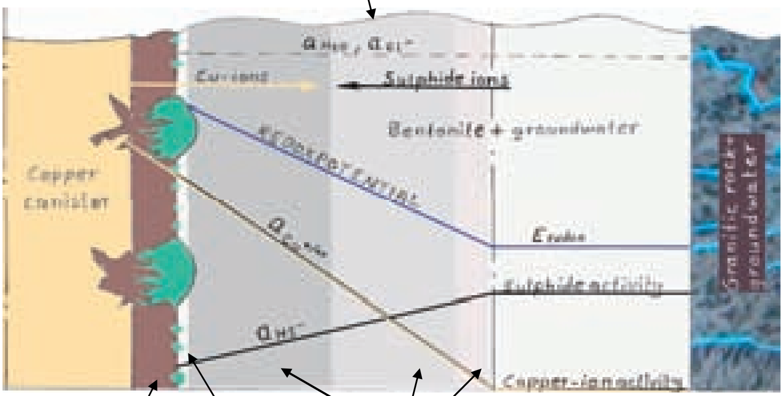
[2] Bundesanstalt für Geowissenschaften und Rohstoffe.

Figure 1 Corrosion model explaining the observations from the LOT project where copper was exposed in groundwater-saturated bentonite

Copper solubility in saline water at 80°C: 2300µg/L (POSIVA 2003:45)



Cu oxides, mostly Cu_2O
(LOT, Rosborg)

Cu hydroxides,
mostly Cu hydroxide chlorides
(LOT, Rosborg)

CuS and (Cu,Fe) sulphides
precipitated irreversibly on the bentonite particles
(LOT, BGR in Berlin)

He describes that the sulphides precipitate in a gradient, which means that the sulphide activity decreases to a very low level, possibly down to zero, but at least very low at the canister surface. The redox potential increases if the sulphide level is low. The result is formation of copper hydroxides and copper oxides, which is confirmed by, for instance, Rosborg (SKB LOT report Nov. 2009). This means that water molecules and chloride ions control copper corrosion at the canister surface. However, corrosion proceeds at several places simultaneously, as shown in the figure. Copper ion solubility is found to be several orders of magnitudes higher than thermodynamically expected, especially in salt water at elevated temperatures. So copper "dissolves" in the bentonite pore water and precipitates as different corrosion products on the bentonite particles. In presence of sulphide, the precipitation will be dominated by CuS, as shown in the figure. Bentonite represents a huge active surface for precipitation of copper corrosion products, thus driving the corrosion process forward.

"Here we have anoxic, or oxygen-free, corrosion, but we still get hydroxides and oxides. I think that it is our contribution to a better understanding of the corrosion processes that occur in such environments and of what happens with the copper canister. Our research shows that in pure anoxic water, you still have corrosion."

There are also other processes, such as intergranular corrosion, which is a more aggressive type of corrosion at the grain boundaries in the copper. This is documented by a study in Japan in a realistic environment (anoxic). The same phenomenon also occurs in an oxic environment. It was noted back in 2003 that copper materials containing phosphorus have been found to be highly susceptible to stress corrosion cracking. In 2008, quite new results were found: sulphide does indeed induce stress corrosion cracking in copper. The threshold sulphide concentration for the initiation of stress corrosion cracking is likely to be in the range of 0.005-0.01 M.

"This is somewhat higher than what you normally find in Swedish groundwater, but not very much. This is a warning that there is a clear risk in the "Forsmark situation," with hot copper and groundwater evaporation. Because the copper surface is hot, we have a kind of evaporation situation – salt/sulphide will be enriched. A concentration of those substances will result in stress corrosion cracking, especially if you have a phosphorus-alloyed copper. That is exactly what we have in the KBS-3 model."

There are many mechanisms of corrosion in a deep repository. Initially there is atmospheric corrosion, which can be very severe. Another mechanism can be referred to as O_2-depleted gaseous corrosion in combination with high concentrations of moisture and salts. A third mechanism is the evaporation-induced salt/sulphide corrosion that could contribute with a corrosion rate of several micrometer per year as general corrosion, but it could also be millimeters or centimeters per year if it induces intergranular corrosion or stress corrosion cracking. The situation where the groundwater takes up to 1,000 years to saturate the bentonite could involve another mechanism. As long as the copper is hot, the corrosion rate is high in a repository. There is also the problem of hydrogen embrittlement. Gunnar Hultquist showed 20 years ago that hydrogen is absorbed by copper during corrosion.

Corrosion of copper by oxygen-free water is a well-known mechanism in industrial copper cooling systems and in synchrotrons. Thermodynamically this is expected, says Szakálos. Although it says nothing about the corrosion kinetics.

It has been found experimentally that the corrosion rate of copper caused by water itself is in the order of one to ten micrometers per year. The same rates can be found in bentonite or soil, which means that the values are about 1,000 to 10,000 times higher than the theoretical assumptions in the safety analysis.

The canisters are exposed to elevated temperatures for at least 1,000 years. The situation at the planned repository in Forsmark is complex and very severe from both a corrosion and an embrittlement point of view. The copper canisters will initially be exposed to atmospheric corrosion until the oxygen is consumed, which could take some months or years. Then there is corrosion by water, sulphide, salt, stress corrosion cracking, intergranular corrosion, evaporation-induced corrosion and dissolution-precipitation in the bentonite, and naturally they should all be added together in order to get the total corrosion over time.

Szakálos says:

“Before we can accept the KBS-3 solution, we need to test it under realistic conditions.”

He cites an SKI report (96:38) from 1996: “Copper of identical composition as the future canisters should be placed in a future site environment, with artificial heating at about 80 degrees, with bentonite, etc. Such an experiment could be monitored for several decades. Even 10–30 years is a short period of time in the present context.”

“I think that must be done before we can accept this solution,” he says.

Finally, he uses an example of copper canisters stored 18 years in a moist cellar to point out that copper does not corrode fast, but copper reacts with every kind of pollutant. This is a known phenomenon.

“Everyone that works with atmospheric corrosion knows it. That is the problem with copper: it actually reacts with everything, but slowly.”

3. Copper corrosion processes in the Cu-O-H system, and their role in long-term safety assessments, by Christina Lilja, SKB

Christina Lilja opens by presenting the scientific body of knowledge that SKB uses as a basis for the performance assessment, and where thermodynamics is one of the cornerstones. She shows the Pourbaix-diagram, with its two types of copper oxides. There are other species as well, such as the intermediate phases of adsorbed copper hydroxide, that could form a sub monolayer.

"It's a precursor to the copper monoxide, and when you get a monolayer, it will convert to the stable oxide," she says.

The electrochemical approach is also very important to SKB. A voltammogram shows reactions including electron transfer. With these data it is possible to make Tafel diagrams, which can be used to identify the different reaction steps in a corrosion process. Impedance spectra where the frequency is varied provide information on, for example, rate-limiting steps as well as, if they are frequent. Electrochemistry can be used to make a probe and measure the corrosion directly by measuring the change in metal thickness. If it corrodes the metal thickness decreases, which changes the resistance, says Lilja.

According to Lilja, a large body of knowledge and a wide range of methods are available for studying corrosion. There are two well-known types of stable oxides, and SKB has performed several reviews and compilations to obtain state-of-the-art of the knowledge of copper.

Different types of experiments are used to study corrosion

SKB uses different types of experiments to study the different aspects of corrosion, all of which are valuable. Lilja points out that there is no single experiment that explains everything perfectly. All have their pros and cons. She takes the laboratory studies as an example, but SKB has also used in-situ experiments as well as analogues, which can be natural or man-made artefacts.

The initial state of a *laboratory experiment* is well-known, and control of the environment in experiments is very good. There are disadvantages, however. Representativeness is poorer due to the simplified system, and the time scale is short. Quick results are an advantage, but it is more difficult to evaluate long-term effects.

She continues with *in-situ experiments*, which are investigations in realistic environments and are therefore closer to reality than lab experiments.

"Here you have an initial state that is quite well-known. You can control it, since you can determine the environment for the experiment. Representativeness is rather good and you can represent the actual system in the in-situ experiment. Both short-term and medium-term experiments can be conducted.

In the case of *analogues*, i.e. studies of what happens in nature, the situation is the opposite of that in the initial state of the lab experiment.

"In the analogues, you have no knowledge of what the system looked like in the beginning, or how thick the sample was. You cannot control the environment, since the reaction has already occurred. You can measure some parameters. Representativeness could anywhere from poor to good, depending on what you're looking at. She says it takes a long time to get the results, but the analogue represents a long reaction time.

What kind of results does SKB have? A typical and expected type of result in short-term electrochemical and laboratory experiments is that the corrosion rate decreases with time. Very few, if any, results indicate that the corrosion rate increases.

In-situ experiments often result in copper(II) corrosion products. The copper in the experiment has undergone periods of oxidizing conditions.

"You can do in-situ studies too, but you have to bear the previous history of the artefacts in mind when evaluating the results," says Lilja.

The analogue experiments show that copper in the native form has been preserved stable for a very long time in both natural and man-made artefacts.

All experiments have weaknesses. In weight loss experiments – which are usually done in the laboratory, but may also be in-situ experiments – it is possible to determine how much metal has been lost after a given time.

"But you can't distinguish between what happened in the very first phase, which might have occurred rapidly, and what happened over a longer period. And if you measure corrosion depth and corrosion rates in specimens, for example in-situ experiments, there could have been different mechanisms operating during different periods. That's why it is so difficult to use extrapolate from experimental results for the safety assessment."

How SKB studies copper corrosion

The purpose of the SKB studies is to obtain a more detailed understanding of the behaviour of copper in water. According to Lilja, SKB carries literature reviews. The state-of-the-art report on copper corrosion from 2001 is being updated and will probably be completed by the end of this year.

A review of what has been published on the corrosion of copper in water is being prepared by Fraser King. A study by Pavel Korzhavyi on the properties of the copper(I)oxide will also be published. He has also reviewed the literature on the properties of the copper(I)oxide.

SKB is planning and carrying out certain experiments involving gas measurements as well as some simpler glass container experiments.

"We are also conducting electrochemical experiments. We have some short-term results ready for publication very soon. But we are also planning more long-term experiments that will take about a year. We are also performing theoretical calculations and examining equilibrium reactions in water," Lilja says.

SKB's conclusions from the copper corrosion studies

She goes on to present some of the conclusions from the review of the studies of copper corrosion in water and says that a lot of conclusions can be drawn from the different published papers and reports. But it is not easy to obtain a *single* consistent picture; the results are contradictory in certain respects.

"For example, the study from 1987 on electrochemistry published by Hultquist and co-workers gives a copper corrosion potential that is 155 mV more positive than the equilibrium potential at 1 atmosphere. If you compare some earlier papers with the later one, the reported hydrogen generation rate varies by a factor of 3,000 under apparently the same conditions. And temperature has no effect.

She says that these observations have not been reproduced by other researchers. There have been some studies, early in 1987 and 1989 on H2 evolution. One study was initiated by the authorities in 1995 with palladium and platinum-sealed vessels, and measurements were made of corrosion in oxychloride water in 2003.

"We also found conclusions regarding the adsorbed copper hydroxide species. It is known to form below the potential for copper(I)oxide in water. It's hard find an account of the evolved H2. In contrast with this proposed mechanism, there is no evidence in aqueous systems that oxygen gas is consumed by a reaction with hydrogen atoms produced by the reduction of water. This casts some doubts on whether evidence from gas phase studies can be used to infer mechanisms in aqueous phases."

She emphasises that whenever new results emerge they are taken seriously by SKB and are analyzed in the context of earlier results. SKB is conducting additional theoretical and experimental studies to learn more about these corrosion processes.

"Our conclusion is that there is no convincing evidence that water oxidizes copper."

Safety assessment and safety assessment methodology

Two things are needed for a safety assessment: scientific knowledge and methodology. The SKB methodology, which has 10 steps, was used in the SR-Can safety assessment and will be used in the upcoming SR-Site safety assessment. To compile all existing knowledge, a structured, hierarchical documentation is needed that includes all features, events and processes that exist in the repository system.

"Each process is then described and put into a process report, and then you describe how you're going to handle it in the safety assessment. We need to have a multidisciplinary description of the evolution of the repository system. We need to look at the geology, the hydrogeology, the chemistry, the climate, bentonite, the copper canister, radionuclides, all of this."

A *strategy* is needed to do calculations. An appropriate mix of pessimistic assumptions and more realistic descriptions is used, along with a mix of simplified and complicated models. When evaluating the results, Lilja points out the necessity of integrating different disciplines.

"Being pessimistic can mean that you only look at the amount of material that could react and disregard the fact that it needs to be transported to the reaction site, the copper canister, to be able to react. Or you only count the rate of one process and disregard the possibility that there could be other rate-limiting processes. Another way to be pessimistic is to assign very high values to the driving forces."

When this principle is applied to the calculation strategy for the corrosion calculations, SKB starts by performing a mass balance and then looks at how much material is available for a reaction, disregarding transport. For example, this method is used for the pyrite in the bentonite, and for oxygen which is initially entrapped in the bentonite.

The next step is to look at a mass transport-limited process, which is used for the sulphide in groundwater. Mass transport involves considering advective transport with groundwater to the buffer, which is how the sulphide is transported by the water. Mass transport also includes diffusion over the groundwater-buffer interface and then diffusion through the buffer. Diffusion refers to transport through the water.

SKB disregards kinetics, the rate of the reaction itself, for copper reactions and instead assumes that they occur instantly. Lilja says that this is one of the pessimistic assumptions that she talked about.

Tools are also needed to do the safety assessment. For mass balance, simple multiplication can be used. For diffusive transport, simple equations are often used. More complex mass transport in the repository requires the use of the concept of equivalent flow, which was primarily developed for radionuclide transport and sulphide corrosion, but tool is also applicable to other corrosives or corrosion products.

"You use the same models but adjust the concentration gradients and the diffusivity.

It is also necessary to look at the site and to know how the water is moving. Mass transport calculations have resulted in transport properties or flow conditions for 6,000 positions at Forsmark."

Lilja also includes data from modelling hydrogeology, climate evolutions and chemistry.

Copper corrosion in safety assessment

It is, of course, necessary to include copper corrosion by oxygen in the safety assessment, Lilja says. First there is the initial atmospheric corrosion, which is assumed to have a very limited duration, from fabrication until the canister is deposited. SKB uses experimental data on copper corrosion in the atmosphere. Pessimistic mass balance calculations are used for the initially entrapped oxygen in the bentonite.

"We have to look at the possible penetration of glacial meltwater after a glaciation. This meltwater could contain more oxygen than the groundwater. We also look at mass transport. All copper oxygen reactions and their effects should be added to the corrosion of copper by sulphide, which is the most dominant process in the safety assessment results. And the reaction is mass transport-limited.

She also points out that when she has performed the corrosion calculations, she feeds them into the radionuclide transport calculations, which provide a measure of the risk, which in turn is compared to the limit set by the authorities.

In the safety assessment, SKB also formulates a reference evolution and scenarios that are assumed to represent the most probable state of affairs. The company also uses "what-if" calculations, which are not included in the risk assessment, but can be used to analyze the effect of any process. To evaluate the corrosion process suggested by Hultqvist and Szakálos, SKB makes a what-if calculation using a one mbar equilibrium pressure and puts this into the mass transport calculations.

The results of the calculations are divided into two stages. In the initial stage, the bentonite has not yet been saturated by water.

"We make a pessimistic assumption that we fill all the unsaturated void volumes in the bentonite backfill, with hydrogen gas to 1 mbar and then let it diffuse outwards through the water. There is always water outside, as the repository is situated below the groundwater table. If we make the pessimistic assumption that it takes 1,000 years for the buffer to become saturated, we get a corrosion of less than 1 mm."

In the next stage, water saturates the repository. In a pessimistic assumption, SKB disregards the hydrogen gas in the groundwater. According to Lilja, it has been measured and most probably corresponds to a pressure of about 1 mbar in the groundwater. If there is hydrogen in the water, the reaction will stop. It is the transport rate of the hydrogen that determines the corrosion rate. Hydrogen gas has a higher diffusivity than sulphide and is therefore transported more easily. SKB examines hydrogen transport both in the buffer and in a partly eroded buffer. With the flow conditions at Forsmark it is assumed that all of the canisters are intact after 10 million years.

In other words, Lilja states that the copper corrosion caused by sulphide is small, and any corrosion due to the proposed mechanism would be even smaller.

Conclusions

SKB asserts that there is no convincing scientific evidence of a reaction mechanism driven by a proposed new phase that is more stable than the known copper oxides. Within the framework of the safety assessment methodology, SKB argues that the process could be handled as any other process. “What-if calculations” of the effect of such a corrosion mechanism will be included in the assessment. It is the view of SKB that the corrosion caused by these mechanisms will not limit the lifetime of the canisters in the final repository.

4. Thermodynamic properties of Cu–O–H phases from first-principle calculations, by Pavel Korzhavyi, Royal Institute of Technology (KTH) and consultant to SKB

The goal of Pavel Korzhavyi´s computer calculations, which he describes in his presentation, has been to look for a stable product, a stable phase between copper, oxygen and hydrogen that would be a good candidate for the final product of a supposed reaction between copper and water. He has tried to find the final product of the corrosion reaction that the KTH group has been presenting. If the reaction had occurred, there should be some ”rust”, i.e. the corrosion product, and it should be stable.

“This product is not very well-known to those who work with corrosion of copper, whether it is an oxyhydride, a hydroxide, or whatever else forms there. It is not very well studied, and it’s quite interesting to find some unexplored area there, because corrosion of copper is an old story," Korzhavyi says.

His goals are also to calculate, from first principles, the thermodynamic properties of known and unknown Cu(I)compounds with oxygen and hydrogen. He also intends to analyze the thermodynamic stability of copper and its compounds in the oxygen-free water environment.

He describes the approach using a simple example of a hydrogen molecule. In the computer exercise, his research group first positions two nuclei of this molecule at some distance from one another, and since the nuclei are heavy and the electrons are light, they find the equilibrium configurations of the electrons and compute the energy of the system.

"But this is not yet the energy of the whole system. Until now we have solved quantum-mechanical equations only for the electrons. We can compute this energy as a function of the distance between the protons and what we find is the energy of a stable arrangement of the electrons in the field of *static* nuclei. However, we still treat the nuclei as classical particles. We must solve another Schrödinger equation, now for the nuclei, in order to get the final energy of the system of electrons and nuclei altogether.

He presents some results of a real calculation for the H_2 dimer, O_2 dimer, copper(II), etc. He optimizes or calculates the energies as a function of inter-atomic distance in the molecules. He says that the minimum point here is not the energy of the molecule, or the equilibrium.

"We have to include the zero-point energy, because nuclei cannot be determined at a fixed position. The uncertainty principle makes them move, and the energy of their motion is the zero-point energy, which can be calculated in the following way: We treat this [dependence of energy on the internuclear distance] as an effective potential, and then we solve the Schrödinger equation for that effective potential. When the main quantum number is zero, we get zero-point energy, which is related to the vibration frequency of this molecule. We get the harmonic part, the anharmonic part, summing up all together, and then we get these energies in these very strange units, which are inverse centimetres.

These units are very familiar to spectroscopists, but for chemists and other specialists it is necessary to convert these energies, or frequencies, into something more familiar such as electronvolts: 1,000 inversed centimetres is equal to 0.12 electronvolts or 12 kilojoules per mole. These figures correspond to the accuracy we are aiming to achieve in the calculations. It is quantum mechanics, but it is not completely free from approximations. These approximations give rise to large errors for objects like hydrogen or oxygen molecules. The accuracy of existing approximations, as well as their strictness, increases continuously. But it is not yet possible to reproduce, for instance, the dimerization energy of an oxygen molecule. In order to eliminate that big error from the very beginning, we can use reliable experimental data, which fortunately exist, on dimerization energies of O_2 and H_2.

Korzhavyi says that he will show that for known phases of copper with oxygen and hydrogen, the methods can provide the accuracy that SKB is aiming for. The known compounds of copper(I) with oxygen and hydrogen are copper(I) oxide and copper(I) hydride. Copper(I) oxide (cuprite) is a well-known and well studied material. It's thermodynamic properties, electrical properties, etc. are well-established. It was the precursor of semiconductor technology. Copper hydride is a less known phase. It does exist, but it is very unstable. By performing a computer calculation, he had tried to reproduce the experimental information on the cuprite and on the hydride, a stable phase and an unstable phase, to see how it works.

He skips the electronic part, and goes directly to the atomic motion in the cuprite, or copper(I) oxide, structure. The phonon spectrum is plotted in Figure y. This is the spectrum of the energies of the atomic vibrations, dependent on the way the atoms move. Sound waves in the lower part are the acoustic part of the spectrum. The upper part reflects the vibration of an oxygen ion in the cage of the copper cations in the structure.

"It is a very high frequency, and in order to maintain the accuracy of the calculations all these phonon spectra and phonon energies have to be taken into account, in addition to the energies of the electrons."

He shows the dots, which are the experimental data. The lines are in agreement with experimental observations.

Korzhavyi performs these calculations as a function of volume as well.

"Under compression the lattice becomes stiffer. It is normally observed that the frequency of vibration increases upon compression. This is however not valid for all the vibrations in the cuprite.

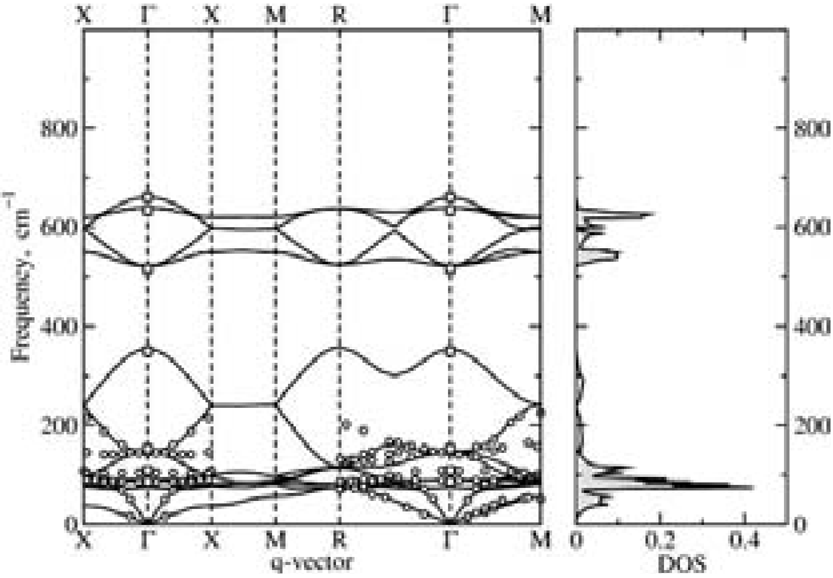
"It is valid for the oxygen in the cage. But some other peaks that can be seen in the density of states, for example these low-frequency acoustic modes, get softer when the lattice is compressed.

"You can see now, when I compress the lattice, this peak moves up in the frequency, and that one goes down."

He also shows the peak going down upon compression, and says that it is an anomalous peak. The peak whose frequency increases upon compression corresponds to the vibration of an oxide ion inside the tetrahedron of copper cations.

"We believe that the anomaly occurs when these tetrahedral units are rotating with respect to each other. They can rotate more easily if the lattice shrinks a little bit. And so it does, when these vibration modes are excited at low temperatures."

Figure 2 Phonon spectrum of cuprite Cu_2O. The dots correspond to experimental data and the lines to experimental observations.



Both in experiments and calculations, the result of a negative thermal expansion of cuprite can be seen at low temperatures. As higher and higher energy vibration modes are excited, they behave normally and restore normal (positive) thermal expansion.

If the phonon spectra are known, then many properties of the material can be calculated. In order to obtain the thermodynamic properties, the heat capacity can be accurately calculated from the phonon spectra. He shows a comparison with experimental data for the stable phase of cuprite.

"In the case of the hydride, you have a more extreme frequency of hydrogen vibrations. It's very high, about 1,000 inverse centimetres. Hydrogen also vibrates in a tetrahedral cage. Copper hydride has been synthesized in aqueous solution. Its optical spectra have been measured, and this hydrogen line has been detected. The hydride is a very unstable phase. It loses hydrogen very quickly with time, and the intensity of the hydrogen line quickly decreases."

He emphasizes that other thermodynamic properties of copper hydride also are in quite good agreement with existing experimental data: the crystal structure and the lattice parameters. Thermal expansion is normal in this case, and the correct structure is obtained. The hexagonal form of copper hydride is found to be more stable than the cubic form.

The heat capacity is in good agreement with experimental data for temperatures below 170 K. What happens above is that the hydrogen lattice most probably undergoes a superionic transition, it becomes liquid. This can be seen from the very high amplitude of hydrogen vibrations in the hydride structure, Korzhavyi argues.

Summary of thermodynamic properties

"For the Cu_2O, these are the calculated results at 0 K. We can calculate the properties at finite temperatures, using the phonon spectra and integrating them. This is how it compares with the thermodynamic tables, showing that this reaction between copper and oxygen [to form Cu_2O] is energetically favourable," Korzhavyi says.

His approach has been tested on the other oxide, copper(II) oxide. The research group can also see more or less good agreement with experimental data for the hydride.

"We get the reaction [between Cu and H_2 to form CuH] to be unfavourable thermodynamically, therefore copper hydride cannot be formed spontaneously from hydrogen and copper, which is also known experimentally. It has to be formed from a solution. The calculated energy is within the experimental accuracy."

He says that it is very difficult to perform experiments on this material, and starts describing the search for the other possible stable phase. Some suggestions come from the researchers; some hydrogen, some oxygen and some copper(I). Korzhavyi considers various possibilities. Hydrogen can be in the form of a hydride ion, H^-, as in the hydride, or in the form of a proton, H^+, as in the hydroxide. Oxygen is present as O^{2-} and copper as Cu^+.

"We require global charge neutrality. We distribute these atoms over various candidate structures, relax the structures, and then compute the energy. We also compute the phonon spectrum to get the zero-point energy and finite-temperature properties."

He describes the first expedition into the unknown, which he is investigating.

"We know that oxide is stable, hydride is unstable, but maybe there is something in between these two, which could be more stable than either one. We distribute all the ions in various configurations, and then relax the resulting structures. In Configuration 1, the anions, H^- and O^{2-}, are too close. The anions are negatively charged and they repel each other. We don't expect this structure to be stable. In Configuration 2, two hydride ions H^- are too close, first neighbours. We don't expect this configuration to be stable, either. But with Configuration 3, we have a chance. All the anions are second neighbours in that structure. Let's compute the energies.

"The phonon spectrum of Configuration 3 is almost okay. There are some instabilities in the structure, showing that it is not completely healthy. But this phonon spectrum can be used, after resetting the imaginary frequencies to zero, in order to compute the energies. The results are shown in Table 4: the first configuration was found to be very unstable, so we did not compute the phonon spectrum from it, but for the second and the third configurations we could compute the free and total energy. We find that the oxyhydride is not a stable configuration. It decomposes readily into the stable phase (oxide) and even forms the unstable phase (hydride).

The second proposal concerns the hydroxide, H^+, O^{2-}, Cu^+, which is a molecule known to exist and its geometry and dissociation energies are known experimentally.

"If you take that experimental information, then of course it is a quite unstable molecule, with respect to hydrogen, oxygen, and copper in their standard states. Its formation energy is experimentally known to be positive. But maybe if we condense it into some solid phase we can obtain energy benefits."

Korzhavyi continues:

"When we investigated that, we found a stable, solid phase, composed of these molecules. In order to describe the structure that we get in the result, the most stable structure, we explored many possibilities. The most stable was some combination of the structure of cuprite and the structure of ice."

In order to introduce these structures, he carries out an exercise, going from the cuprite structure to the structure of ice. The structure of cuprite, the Cu_2O is composed of two lattices. Within each lattice there are balls connected by sticks, and sticks are the chemical bonds. However, there are no bonds connecting the blue and the red lattices together. They are completely identical, and are held together by physical, not chemical interactions.

"In order to change to ice, we eliminate one of the identical sublattices, and now we are left with the anti-cristobalite structure. To change to ice, hydrogen is needed in place of copper, but hydrogen doesn't like to sit in between the oxygens like copper does. In water or in ice hydrogen moves closer to one of the oxygen atoms, forming a water molecule. We have the freedom to distribute the water molecules in various ways; it will all be the same structure."

Korzhavyi shows two variants of the copper hydroxide structure, drawn from the calculations. It is an intermediate structure between those of cuprite and ice which Korzhavyi calls "cuprice."

"We have linearly coordinated copper cations, and hydrogens sitting like they sit in the ice. The bonds and the atoms are in the same environment as in the stable phases in water [ice] and cuprite. Hydrogen bonds connecting the O^{2-} and H^+ species are shown by broken lines. We find actually not only one structure, but a whole family of structures with similar energies."

The hydroxide has a reasonable electronic spectrum compared to the spectra of Cu_2O and copper hydride. Both the stable (Cu_2O) and unstable (CuH) materials are semiconductors, which "cuprice" also is. It has a band gap separating the occupied and unoccupied electronic states. It has a normal, all positive vibration spectrum.

"If some experimentalists wish to use all this data in order to find these species as corrosion products, they are welcome. We have hydrogen lines, oxygen lines, OH stretching and bending lines and whatever in these infrared spectra and it all looks reasonable."

Korzhavyi points to the most important thing: Thermodynamic properties.

"The negative enthalpy of formation means that the formation of this substance from the elements in their standard states is energetically favourable. The free energy of formation of CuOH is a negative number. If we now compare the stability of this copper hydroxide relative to cuprite and water, it's unstable. Thermodynamically, it should decompose onto cuprite and water. If we evaluate the enthalpies or free energies of the reactions of copper with water (crystalline copper and liquid water) to form either cuprite or copper(I) hydroxide, we get positive numbers. These are energetically, or thermodynamically, unfavourable reactions. This is the conclusion.*"

From all these exercises, Korzhavyi concludes that cuprite is still the champion of stability among the considered compounds. Copper(I) hydroxide may exist as a metastable phase, but its thermodynamic properties are such that it is unstable with respect to the stable phases, which are cuprite and water.

Korzhavyi acknowledges his collaborators Professor Börje Johansson, Inna Soroka and Mats Boman at Uppsala University, and Evyas Isaev at the University of Linköping.

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5. Hearing and panel discussion

Topic 1: Fundamental understanding of the corrosion characteristics of copper in oxygen-free environments

Gaik Khuan Chuah: Do you plan to conduct more experiments on the evolution of hydrogen, especially with other than aqueous solutions, aqueous water or pure water?

Peter Szakálos, KTH: Not at the moment.

Gunnar Hultquist, KTH: An experiment like the one we have already performed is being conducted at this moment, and the results will be published in 2010. There will be another proof for hydrogen in copper metal, based on long-time exposure, where we continuously measure hydrogen in the gas phase. There will also be analysis of hydrogen in the metal. Detection of the gas phase continues. We can see that hydrogen must come into the metal. It is difficult to explain how it is possible, but you will be able to see it.

Gaik Khuan Chuah: When I read your published paper, I would like to have a more detailed description of the experiments, the valves, the gauges, the names, and even the gas analysis, so I can be sure, rather than be satisfied with an indirect explanation, by means of iron pump current or pressure gauge. I think that would really leave me with no room to wonder what else there is that can explain this, in terms of artefacts.

Peter Szakálos: It is true. We should continue to analyze the product, which is not characterized very well. If it is an amorphous product that easily converts to oxides, that is not easy. But we perform experiments with a critical eye, and really try to sort out errors. Something still happens. The evidence of hydrogen in the metal compared with the hydrogen content in the beginning is really striking. Something unknown is going on. But more detailed studies on this product and how this corrosion actually occurs are needed.

Digby Macdonald: I was part of the National Academy of Sciences' review of the SKB-2 plan. Implicit in that was the idea that you could control the electrochemical properties of the bentonite to ensure that copper would remain immune over a long period of time, forever. Is the same concept being carried through in the SKB-3 plan, and exactly what is being done to ensure that?

Christina Lilja, SKB: The concept is the same, but the description of the evolution of the repository is now more detailed regarding the mechanisms. In the beginning, it was a simplified description of the concept.

Digby Macdonald: Does pyrite exists within the bentonite? If the bentonite has got pyrite in it, the pyrite will react with oxygen and produce all those nasty sulphur compounds that I showed in the volt equivalent diagrams.

Christina Lilja: There will be pyrite in the bentonite. We have set limits on how much we could allow and it is included in the safety assessment, by mass balance calculations.

Digby Macdonald: One way of getting rid of the pyrite, is to give the clay a hydrogen peroxide wash, and you oxidize the pyrite up to sulphate.

Christina Lilja: That is maybe one possible way, but it must be a product which is possible to make blocks out of, and then to sell and manufacture. If there are very special treatments, it may not be the best way to go.

Digby Macdonald: As I showed, as time goes on and the copper one plus concentration builds up at the interface, and the hydrogen concentration as well, it will move the point P up until you meet the equilibrium line, at which point you have achieved immunity. One way of doing that is to put a copper(I) salt into the bentonite. Preferably a salt that has a reducing anion. You keep the redox potential low, which will simulate the addition of hydrogen. If you use cupruous nitrate, for example, you might be able to maintain copper in the immune state, right from the beginning.

Christina Lilja: Theoretically that may be possible, but that will make the system more complicated. We strive for as simple a system as possible, with the copper and the bentonite in the rock. I do not think that will be a solution for the repository.

Fraser King, consultant for SKB: I have two comments. Firstly, by adding copper(I) to the bentonite to achieve immunity. My comment there would be: It is not necessary, there is enough of a corrosion barrier there. Even with the oxygen present in the bentonite, we use so little of the corrosion barrier, that it's not necessary to add any copper(I).

Digby Macdonald: No, nitrite, a reducing anion.

Fraser King: I don't think we should add nitrite, because it causes stress corrosion. Pick another anion, if you want, but don't use that.

Digby Macdonald: Details.

Ron Latanision: In the case of the experiment with the palladium membrane, the argument is that hydrogen is being produced by the corrosion reaction with copper, and the hydrogen is penetrating through the membrane and being released. As the hydrogen is being produced by the reduction of protons, the pH of the solution should simultaneously increase. I wonder whether you have examined the pH change during the course of those experiments?

Peter Szakálos, KTH. In the closed vessels we haven't had the opportunity to measure the pH, but in the other experiment we have. Gunnar has also published a paper that shows the pH difference for different metals: copper, iron and zinc.

Gunnar Hultquist, KTH: In 1986, I measured and published the pH. It was 6.9. That means, that the pH doesn't change significantly. My interpretation is that both OH^- and H^+ were consumed. This means, indirectly, that water was consumed, because there's a consumption of water by a production of H^+. The ion product, you can't avoid that.

Ron Latanision: Your suggestion is that both hydrogen ions and hydroxide ions are consumed at the same rate?

Gunnar Hultquist: If it's exactly the same pH, or about the same, of course. But we have to calculate, we have to look into the system. In the experiment, there was a lot of water.

Ron Latanision: This is in the context of experiments that may be critical to understanding. I would be concerned that perhaps with the volume of water, whatever change in the hydrogen ion and hydroxyl ion concentrations may occur may be overwhelmed by the volume of water. I would suggest a very useful experiment: you can use a smaller volume of H_2O, measure the hydrogen which is released through the palladium membrane, and perform a mass balance, because that hydrogen that has been produced by the reduction of protons should allow you to determine how many hydroxyl ions were produced. That should equate to a change in pH. It's one of the pieces of a puzzle that would hopefully fit, or not fit.

Gunnar Hultquist: I fully agree. I think this is a critical experiment.

Dave Shoesmith: I didn't follow the details of the calculation that you presented, Gunnar. It looked like it was a calculation of an interfacial reaction and that it was a copper surface with single atoms adsorbed, or coordinated, to the surface.

Gunnar Hultquist: I didn't say anything about numbers. I only concluded that this calculation showed that the bond between copper, in that case (100)- surface was enough. It is possible, that a three-dimensional monovalent copper hydroxide is growing.

Dave Shoesmith: My questions are about the details of that calculation. That was an interface with a single atom? It didn't incorporate any questions of whether that species adsorbed on the surface would be interacting with the medium, which it would if it was water.

Gunnar Hultquist: We discussed this with Anders Rosengren and agreed that the best thing to mimic the situation about pure water is to do it that way. It's very difficult to have OH^- approaching. We always have this OH^- in pure water. In the simulation, OH^- was first at an infinite distance from the copper surface, and then it went down.

Dave Shoesmith: But was the counterbalancing influence of the interaction of the OH- with the water matrix included in that calculation?

Anatoly Belonoshko, KTH: Those calculations have been done without accounting for the water medium.

Pavel Korzhavyi, KTH, consultant for SKB: Yes, the water that we have dissociates into H^+ and OH^- fragments of the water molecule. Whereas in the calculation, an $OH^{\bullet}$molecule is considered, without any surrounding water. That molecule, if it is electrically neutral, is known to be radical, a very strongly reactive species, which is lacking one electron. There is one vacancy in the oxygen p-shell. The radical wants to stick to anything that has a more or less loosely bound electron. To me, there is no surprise that this molecule adsorbs to anything, including gold. I would accept this calculation as a valid calculation of an adsorption energy of the OH radical to a metallic surface. But, it can't serve as an estimate of the heat of formation or the free energy of formation of copper(I) hydroxide.

Ron Latanision: I'm interested in your "cuprice." We've heard a number of comments about adsorption. I'm just wondering whether you have chemical adsorption of either electropositive or electronegative species onto the surface of "cuprice." Could you determine from your calculations whether that would increase or decrease its stability, by injecting electron density into the density of states diagram? Is that possible?

Pavel Korzhavyi: You see the density of states in the bottom panel. This is the density of states of the "cuprice." There, for the hydroxide. The presence of the band gap, at the Fermi level, tells us that all the bonds in this compound are chemically saturated.

Ron Latanision: I accept that. Suppose you had an electronegative adsorbate, which in fact withdrew charge from the density of states. Would that destabilize "cuprice" from your point of view?

Pavel Korzhavyi: Normally, when the bonds are saturated, this is the most stable configuration you can have. If you add something or remove some charge, you also induce an imbalance, which makes the system metallic. That usually destabilizes the thing. I tried to create as stable configuration of the ions as possible. To me, the presence of the band gap, which is quite comparable to the band gaps of cuprite and copper hydride, is evidence that if something is going to be more stable than that with this composition (CuOH), it's not going to be much more stable. I am confident that all the atoms in this structure are feeling well.

Ron Latanision: I'm not so comfortable. I'll just repeat. You have a lot of density of states illustrated. If they're fully saturated, then I would agree with you. But if there is some opportunity to inject electron density into the p-level, for example, that would presumably increase its stability, unless it's fully saturated. You're confident that you've got fully saturated density of states. Is that correct?

Pavel Korzhavyi: You can go in several directions. For instance, the copper(II) hydroxide could be formed, by putting in more OH-groups. That would also be metastable. You can also desorb, you can remove hydrogen from here, or water molecules from this compound. It will become more stable, because then the cuprite will form. It is a stable situation, or at least the configuration is stable. But you can remove species from there, and you can add species there, to form more stable compounds.

Ron Latanision: One way of doing that would be through chemical adsorption of adsorbates, whether they are electropositive or electronegative. Isn't that correct?

Pavel Korzhavyi: Yes.

Ron Latanision: I think this is very interesting. My point is not to put you in a difficult position. I'm just interested in what you've said. I think there may be some implications that could be important, and we should not dismiss them.

Martin Bojinov, VTT Technical Research Centre One point that you wrongly pointed out is that you have to consider that it has been shown by Marcuse and co-workers, that copper OH, or OH adsorbed, is more stable as a surface adsorbate than copper two O, as a treaty(?) compound. They are actually different types of calculations. I wouldn't say that they can be compared directly.

Gunnar Hultquist, KTH: This is more or less a surface science approach at a very low temperature. It's only a question about how far, at a certain temperature, by diffusion these species move. This approximation is not relevant for a long-term discussion of what will happen. We saw water already, partial dissociation of water produce OH and H^+. In some way, we have to consider both; I think some people here realized that. So, we can't forget this H, we can't leave it out, it must be introduced into the discussion. Where does it go? My experiments show that it goes into the metal. Marcuse, he does the experiment at room temperature, and waits only hours. Over years it's another thing.

Martin Bojinov: You really can't extrapolate things from ten hours to 10,000 years. But this is a different situation to make surface calculations and also [???] calculations. The Marcuse approach is consistent with both the STM and thermodynamics, and I tend to believe more in that.

Gaik Khuan Chuah: You mentioned the fact that there was no convincing evidence for the corrosion of copper in water, and that this was proven. I also read in the draft report that was given to me on Friday, by Fraser King, that there was a mention by Möller in 1995 that he repeated the experiments with platinum and palladium foil, and found no corrosion. May I know whether such reports of the work that was carried out, are actually available in the public domain, or is this exclusive to SKB?

Christina Lilja, SKB: It has been available at the authority's website for at least ten years.

Gaik Khuan Chuah: Is there any reason why there is a discrepancy? Was there any dialogue between SKB and the researchers to find out why there was a difference?

Christina Lilja: Yes, as far as I know. Gunnar was involved in the experiment that was required by the authorities.

Gunnar Hultquist, KTH: Yes, I tried to. It was me against ten people. There are two things that are not examined in these experiments. One: Choice of glass. It's well-known that quartz glass transports molecules. Actually quartz is used for calibration of helium. The second was, that there was, also said by Möller, that if he changed these tubes to sodium glass, then he saw something that I could see. This is left out in your report.

Christina Lilja: It's not left out, but he didn't draw any conclusions about that. There were minor effects that he couldn't draw conclusions from.

Gunnar Hultquist: Partly left out.

Digby Macdonald: What is interesting is the accumulated corrosion damage. How much of the copper canister is going to be lost in a million years, or whatever the number might be, 100,000 years. In order to do such a calculation, you have to specify the corrosion evolutionary path, which is the path that the system takes in terms of those independent variables that have a significant impact on the corrosion rate: pH, hydrogen, etc. What work has been done on defining the corrosion evolutionary path? SKB probably have to take into account ice ages and other things as well.

Christina Lilja: The SR-Can safety assessment is an extensive description of the evolution of the repository, over the long-term. It is opposed[?] to the hydrology, the chemistry, and the climate influence.

Digby Macdonald: Did you try to predict how the chemistry is going to change over the storage period, and if so, has it been published?

Christina Lilja: Yes.

Allan Hedin, SKB, responsible for the long-term safety assessment: I'm not sure. Our corrosion calculations are based on mass transport. We identify the species that cause corrosion, and we limit and estimate the mass transport of those. We are not trying to establish a corrosion rate based on the chemical conditions. We just establish which species could cause corrosion and limit it by the mass transport of those species. I think you had the impression that we were doing something different.

Digby Macdonald: Any factor that affects the corrosion rate defines the corrosion evolutionary path. Then to calculate the accumulated damage is simply to integrate over that path.

Allan Hedin: Essentially, that is what we are doing.

Fraser King, consultant to SKB: What is described in SR-Can is a very detailed description of what I would describe as the far field and how that changes. We have this state-of-the-art report, which also includes a description of how the near field environment changes, which is more important for the corrosion behaviour. In particular, I think SKB, perhaps by adsorption, has used information that was developed in the Canadian programme, where we've developed a mixed potential model, which takes into account the various reactions in the bentonite buffer. Through that model, we predict the time-dependant evolution of the concentration profiles of the eleven species we include in that model, which includes chloride, oxygen, iron species, adsorbed copper(II), precipitated copper(II), and so on. We calculate a corrosion potential, which is of more interest. That's our detailed analysis of how the corrosion behaviour would change over time. What's in the SR-Can report is a detailed description of how the groundwater chemistry changes, and also the buffer chemistry, in terms of changes in the pore water chemistry and in the buffer. We have all that information, in reports.

Ron Latanision: Peter, there is clearly a corrosion product that you can see in the metallographic section. Have you identified it?

Peter Szakálos, KTH: Yes, we know that the most of it is the monovalent oxide, Cu_2O. There was also some hydroxide, on the top, identified by ESCA. In this case, with the palladium membrane, the hydrogen pressure will not be 1 mbar inside. It would be infinitely low. Theoretically, you could form any kind of oxide. It doesn't have to be a monovalent hydroxide.

Ron Latanision: Are your findings stable copper compounds?

Peter Szakálos: Yes.

Ron Latanision: It appears to me that there is some evidence of intergranular penetration. Am I seeing that correctly?

Peter Szakálos: Yes. As the general corrosion is visible, in the bottom line. There are some parts that go deeper.

Ron Latanision: Is this a precursor? You also mentioned in your presentation concern about hydrogen embrittlement and mechanical behaviour of copper, when hydrogen has been adsorbed. Is this a manifestation of some of the concern you have about mechanical behaviour? Are those cracks, or what are we looking at?

Peter Szakálos: They are not actually cracks. In detail we could see that the grain boundaries are kind of corroded. The basis for this hydrogen embrittlement thinking is that the bulk metal contains a lot of hydrogen after this exposure. I don't know exactly how much hydrogen you must have to get true embrittlement. But in the literature you can find that all of the mechanical properties do deteriorate because of hydrogen.

Ron Latanision: Do you mean hydrogen embrittlement, or do you mean that there is some perceptible effect on mechanical properties, broadly?

Peter Szakálos: We haven't measured any deterioration in mechanical properties in a scientific way, but we can see that it is done in the literature. There are studies that have shown, by increasing the hydrogen content in the copper metal, that it is susceptible to hydrogen embrittlement. That is not big news.

Ron Latanision: I have to admit I haven't seen that literature. What sources are you thinking of?

Peter Szakálos: I have referred to them in a draft report's comments regarding the BRITE-report. The last paper, number 44, S. Nakahara, "Scripta Metallurgica", which is submitted to you. There it is stated that hydrogen embrittlement is observed in copper, silver, and gold. These metals are quite insensitive, but it does happen.

Ron Latanision: Is the embrittlement intergranular? Have they looked at the fracture surfaces? What do we know about this embrittlement?

Peter Szakálos: The references can be read in "Scripta Metallurgica".

Ron Latanision: This is an important issue. I find it hard to accept the concept that copper is embrittled by hydrogen without seeing evidence of either fractured surface, or mechanical data, or whatever.

Peter Szakálos: If you do it by gas phase, you're totally correct. You need a huge pressure. But during electrochemical charging, it does happen to a degree, it's measurable. This is relative hydrogen content, and not the best paper. You can see that it starts to deteriorate directly when you charge it. In this case, it is a relative embrittlement ratio. It is a problem, but it's not ppm levels here. It's hard to tell when it starts, when it becomes dangerous. But it does have effects. This was also "Scripta Metallurgica", with two or more references.

Fraser King, consultant to SKB: The current density there, 25 milliamps per square centimetre: That's enormous.

Ron Latanision: Mr moderator: Do you remember whether the embrittlement occurs as intergranular or not? Do you remember off-hand?

David Duquette: In ultra pure copper it's transgranular, and in commercial copper it can be a combination of both. The hydrogen goes to the grain boundaries, because it acts like a sink, basically. In order to get it electrochemically, we have to charge at almost a 1,000 millivolts through a reversible potential. The amount of hydrogen we were charging into it was incredible. Anything below that didn't get much embrittlement. It's very difficult to embrittle copper with hydrogen.

Peter Szakálos, KTH: The other problem is a hydrogen sickness. That is not the same as the normal embrittlement effect. This is from a friction stir weld. It is coupled to oxide inclusions. It is also stated that the hydrogen could precipitate in these locations. It's a complex situation.

Dave Shoesmith: In the present discussion of how hydrogen gets into copper, we have a discussion about the formation of the corrosion product, and the discussion about how hydrogen gets in. But the diffusion rate of the proton, generally speaking, in an oxide-hydroxide film, is 10^{-17} centimetre^2 per second. It's not clear to me, that you don't have a barrier.

Peter Szakálos: We have looked at this in electron microscope, and under anoxic conditions, it is really a porous product.

Dave Shoesmith: That's a point I have. I have not seen a characterization, or a visualization of the corrosion product, that I could evaluate, in what you have published.

Peter Szakálos: If you look at the ECC paper, there are pictures taken with SEM. I can also show a paper from Kunze, "Corrosion Science," 2004. In this simple manner, it might be shown that it is porous. It is a layer of, in this case, bivalent hydroxide.

Dave Shoesmith: Isn't the diffusion barrier one nanometre Cu_2O?

Peter Szakálos: Yes, but I wouldn't call that a perfect diffusion barrier. These are a kind of porous products. It looks nice in this shape, but, as you see…

Dave Shoesmith: Are you telling me that the Cu_2O is porous? It generally isn't on copper.

David Duquette: I'm not sure why KTH, or the work that has been done by Gunnar and Peter, really requires that hydrogen embrittle copper, except to say that you got hydrogen in the copper and the fact that it might embrittle is evidence for hydrogen in it. It does not strengthen your argument, and those of us who've done a lot of cathodic charging of copper, and other metals over the years, would argue that it's a very difficult process to embrittle. The amount of hydrogen that you are producing is not large. I think it would be difficult to support.

Peter Szakálos: These kinds of crystals are Cu_2O. This is the oxide. These crystals are quite dense. Something else is growing here, probably hydroxides. Also, deeper down. This is not a crystalline product; it's a kind of porous sponge structure. It's not a protective product. It looks bad. If you do this in an anoxic environment that differs from an oxic, if you have dissolved O2, I think the product looks much better. It gets, as you said, more of a passive layer. In this situation it is porous. How much hydroxide, even though it would be a monolayer of hydroxide, I think it could be quite much, but I'm not sure of it.

Dave Shoesmith: I think the conventional wisdom of a passive layer would accept that 10 microns isn't enough to see what we perceive to be a 1 nanometre barrier layer. There is no evidence in that particular picture that that system is porous through to the metal surface.

Peter Szakálos: No, but the corrosion rate implies that. The corrosion rate is in the micrometer per year range, and it couldn't be protective.

Ron Latanision: Christina Lilja mentioned the use of electrochemical tools. You talked about voltammetry, and so on. Much of what we've talked about today, in assessing the hydrogen fugacity, for example, at various stages of proposed process, has been based on equilibrium thermodynamics. But corrosion is not an equilibrium process, and it would seem to me to make sense to apply potentials and drive the reactions that are concerned – whether you're looking at it from KTH's point of view or from your point of view – to assess whether or not, by driving the potential, you can increase the rate of hydrogen evolution, if that's occurring. Or did you, by suppressing the potentials even further – if you don't see hydrogen evolution, that would be equally interesting. Why has no one chosen, in this debate, to look at the application of a driving force, a polarization experiment?

Martin Bojonov, VTT Technical Research Centre: We have an ongoing study on that. We have been using polarization curves, or current versus potential curves, and even spectroscopy to follow processes in the vicinity. An example: If the corrosion potential is at minus 200 millivolts, in a system that has been anoxic, and closed for up to three weeks, then we haven't observed any evidence of hydrogen evolution.

Ron Latanision: You see no evidence?

Martin Bojinov: If you polarize the system to minus one volt, you will of course get a hydrogen evolution, but this was, so far, for the closed system. Now we have a system in which we have the palladium membrane installed. We have been following this for some time, but I won't say more for the moment, because these are ongoing experiments.

Ron Latanision: Let me understand the experiment, though. You began your experiment at an open circuit potential, which is above, or below, the reversible hydrogen equilibrium?

Martin Bojinov: We begin our experiment at the corrosion potential. We pump gas that contains 5 ppb of oxygen in the gas phase.

Ron Latanision: It's an oxidizing process?

Martin Bojinov: It's not oxidizing, it's an anoxic environment. It is 5 ppb in the gas phase, but then it is consumed for a couple of hours in the system. After that, it's an anoxic environment. We follow the potential, and then we reduce the system, but mildly, not to go into the "hydrogen evolution region". We follow the process by several electrochemical means, including impedance spectroscopy and measurements of the concentration of copper in the solution, with an ion-selective electrode. We will be presenting these results publicly rather soon, and then we'll see what the scientific community has to say about it.

Ron Latanision: Peter, have you looked at polarization phenomena in your experiments?

Peter Szakálos, KTH: That is not my way of doing research. I haven't done that. I don't work with electrochemical methods at all.

Gunnar Hultquist, KTH: There is a paper published by me and someone named Håkan Herö in "Corrosion Science" 1984. I know that the interpretations of these potentials are very difficult. You can get very low potential only due to adsorption on gold. For one and the same sulphur content, sulphur adsorption on gold is lower than on copper. How to study this? The interpretation is very difficult. It may be useful to conduct these kinds of experiments, but it will never stand on its own. It has to be verified, again, by other measures.

Digby McDonald: Do you know the nature of that localized attack? Is that classical pitting corrosion?

Peter Szakálos: It as a kind of pitting corrosion, but, if you look at the literature, some conditions need to be met in order to get pitting corrosion. It's strange that we can monitor, or see, this in a very clean environment.

Digby McDonald: I would find pitting corrosion to be a phenomenon where differential aeration has been established. Whereas you get the cathodic reaction occurring on the external surface, and the anodic reaction occurring inside the cavity. Putting it another way: Do you see pitting corrosion in any of your experiments?

Peter Szakálos: We have seen that in this 15-year exposure, so it is a slow process, if it's ongoing. This took 15 years to produce. But in a shorter exposure you just see even, smooth, general corrosion.

Digby McDonald: You don't see pitting at all?

Peter Szakálos: No, not at all.

Gunnar Hultquist, KTH: There's no pitting corrosion in the normal sense. I myself call it localized corrosion. There's no crevice, obviously, but it's local. For some reason, the corrosion preferred to take place locally on different spots. Sometimes along grain boundaries.

Dave Shoesmith: I wanted to question this mechanism for oxygen consumption. We assess that the primary consumption of oxygen is due to the decomposition products of water. What evidence do you have to support that? It's not the conventional wisdom.

Gunnar Hultquist: No, it's not and that's why we are here. If we rely on what we know already, we don't need to be here.

Dave Shoesmith: But when we can see oxygen reduction many hundreds of millivolts more positive than what we can see water reduction, how can you draw that conclusion?

Gunnar Hultquist: Because of the use of isotopes. When you use isotope 18 O you have molecular oxygen present, it comes from water, still. The pattern is better.

Dave Shoesmith: I don't think that proves that it's a hydrogen atom that's scavenging oxygen.

Peter Szakálos, KTH: It is shown by isotope studies. If you have an atmosphere with water and oxygen molecules, for example moist air, we find that the corrosion product is preferentially built up with oxygen from the water molecule – this is not unique for copper, it also happens to iron and zinc and other metals. By isotope sensitive analyses (i.e. SIMS) of the corrosion product you can see that most of the oxygen, including in the copper oxide, actually originates from the water molecule. The released hydrogen atoms will be consumed by the fast catalytic reaction with O_2 with the formation of "new" water molecules. Thus, you can't detect any hydrogen production caused by corrosion if O_2 is present. Oxygen is, actually, a kind of catalytic activator here. But the corrosion product is built up mainly from water.

Dave Shoesmith: What you're saying is that there's no role for oxygen in this corrosion process, exceptive of that route, or is this an alternative?

Peter Szakálos: I would say it's a catalytic.

Dave Shoesmith: Is this the only role?

Peter Szakálos: No, you also find O from oxygen molecules in the product, but the majority comes from the water. Both are ongoing. You can also find out that the new water molecules are formed with the isotope, let's say that is the isotope 18-18 O_2 in the experiment, then you find that in the newly formed water. However, oxygen from the O_2 molecule will also form corrosion products. As Gunnar showed in his paper, most of the oxygen in the product comes from water molecules. This was shown 15 years ago. There has been a lot of interest in this paper, and it's interesting that the community hasn't adopted this yet.

Dave Shoesmith: What is the condition of this experiment?

Gunnar Hultquist: The condition is published in "Corrosion Science." You asked about the role of oxygen. It's to keep the activity of hydrogen low. That's why it's necessary to avoid that. That is done by removing or only starting up experiments where we are certain we have no O_2.

Fraser King, consultant to SKB: This work was done in the gas phase. The partial pressure of water is very low, where you have sub-monolayer quantities adsorbing on the surface in the gas phase. There's no aqueous electrochemistry happening here at all.

Dave Shoesmith: There's no possibility in this experiment that you could couple separate anodes and cathodes through a water medium?

Fraser King: Correct.

Gaik Khuan Chuah: Basically, these kinds of studies with isotope labelling have also been done by others than Dr. Hultquist. Data have been published, and even in the presence of oxygen, the surface science studies show that water would preferentially adsorb onto the copper sites. There are references on this. Secondly, Dr. King mentioned that these are gas phase studies. I would just like to point out that in 2007 professor Gerhard Ertl got the Nobel Prize for studying reactions occurring on solid surfaces. He showed that the data from the gas phase or the surface science study are relevant to industrial processes, which involve very high pressures as well. You can see the equivalence in terms of gas phase to the aqueous phase. Basically, there is no pressure gap. For that, he got the Nobel Prize.

Topic 2: What additional information is needed to confirm this specific corrosion process and to assess the importance of the process for the final repository?

David Duquette: The main reason why we're here is to understand whether or not you can put copper into the earth for a million years and have it to last for some reasonable period of time. We will focus on: What additional information is needed to confirm the specific corrosion processes as it relates to the vault, and the copper in the vault.

Dave Shoesmith: This is not the time for specific comments, because there's a lot of discussion which is eye-opening, or different, to what we read in the papers. But, one thing that bothers me is the distance between some of the studies and some of the claims. Sometimes the answer to these solutions is detailed experiments at incredibly complicated levels. But the problems that we're dealing with are ones at specified, very general levels. Explaining those very general phenomena in complicated systems by detailed experiments is extremely difficult. It's not clear to me that the right techniques are necessarily always used in all experiments. That's not just a reference to one or other side of this discussion. That is not an easy problem. We've come down to arguing interpretations of individual pieces of data, and whether we believe this mechanism or that mechanism. If there is going to be a resolution (solution?), then some improved experiments are required, probably on both sides.

David Duquette: The real question is whether the results that have been generated both by the SKB and by the KTH team are relevant to the vault. In other words, if you're primarily looking at whether it's going to be a safe disposal of copper containers or not. Are these the experiments, that should be being performed? Are these the appropriate experiments to justify that? Are we getting the information that we need to convince ourselves as a community that you can put copper into bentonite, and bentonite into granite, for a hundred thousand or a million years?

Dave Shoesmith: It isn't simply a corrosion issue. The multi-barrier system alone is meant to make sure that we don't rely on one barrier. However, that doesn't mean to say that you shouldn't make a really good attempt to determine the specific mechanisms and appropriate experiments for individual barriers. When you make the extrapolation from whether we have the right issue on the table here to whether there is a solution to long-term containment of radioactive waste, you're asking a much bigger question. Such as: Do we accept the interpretations of these corrosion processes? I don't think the experiments are off-base, no. I think they are fine, but it will always be difficult to bridge that gap between something that you want to get, where you have a practical number from the large system, and then the experimental system which will generate the data. It will always end up in some computational model. It will always be obscure.

David Duquette: The last hour was supposed to focus on the science. We've discussed whether they made sense from a thermodynamically kinetic point of view. The question now, is: Do you need that level of science, is it relevant to safe disposal of copper? We have two different concepts of the mechanisms that exist. What has to be done to support one side or the other? Or, even if it's relevant, given the fact that it's not pure water and absolutely pure copper. What do you think these two proponents for their mechanisms have to do, to advance their case?

Dave Shoesmith: If I understand the SKB position correctly, sulphide dominates the system, which is what I agree with. I don't think the KTH team thought about sulphide, and therefore there's a bridge, or rather a gap, between those two approaches. The question is: Why haven't you considered sulphide? Or: Why do you think that sulphide is totally dominant? If sulphide is totally dominant, then there's no point in trying to resolve this argument.

Christina Lilja, SKB: Why we think sulphide is dominant? We think that these corrosion processes are mass transport-limited. If you look at the mass transport, then it's as simple as looking at the gradients and the diffusivities. Then you find that sulphide is dominant.

Peter Szakálos, KTH: There is a mass transport model, but it doesn't cover your long time exposure. The only long-term exposure experiment presented is the LOT project. It's a five year project. We understand that it doesn't fit with your model. The corrosion rate is very high. What you can observe is copper oxide. I think this was done at KTH. Actually, it's the LOT project, but it identifies oxides and copper hydroxides, or copper hydroxide chlorides. The German researchers at BGR have shown that in the bentonite there is a lot of formation of copper sulphides and copper iron sulphides. It means that the nature is more complex than the initial model. One way to see it is that if you take care of all the sulphides, the redox potential will be somewhat higher. If the redox potential is somewhat higher, still anoxic and still without oxygen gas, it will allow these products to form, in other words, corrosion by copper oxide and copper hydroxychloride formation. The situation is much more complex than previously thought. This is based on the results from the LOT research. I believe they are good results, because if you get a lot of sulphides here, it really means that you have reached an anoxic, or O_2 free, environment. I mean, if you have a model that is thirty years old, it is not strange that it has to be changed because of new results. That is normal. But from what I understand from the safety analysis, this is not discussed.

Fraser King, consultant to SKB: I am not exactly sure what the question is, but let me talk and then you can direct me if I'm going in the wrong direction. In the overall analysis, as Christina said, most damage occurs due to sulphide. Originally, there was an assumption that that was a transport-limited process. We now have experimental evidence to show that that's the case. Even under a relatively high rate of mass transport, with a relatively high sulphide concentration, the reaction is sulphide transport-limited. When you go to a bentonite system, you drop the diffusion coefficient by two orders of magnitude. Compared to these experiments you were increasing the diffusion layer thickness by two, or three, orders of magnitude. In the repository, the flux of sulphides is about five orders of magnitude lower than in the experiments. In the repository it's virtually certain that the reaction with sulphide is going to be transport-limited. This is sort of what you are showing here. In terms of modelling this whole scenario, we have a current program where we're looking at developing an extension to this model, that I was talking about previously, where we predict the evolution of the environment. Up to this point, we've just done it in the oxygen-containing system; also involves copper(II) being formed, and so on. We predicted in that case how the corrosion potential evolves over time, to the point that now we are dealing with the sulphide. We did some experiments many years ago in Canada where we simulated this on a very small scale. This potential – the corrosion potential, not the redox potential – as you add the sulphide, as the sulphide takes effect, the potential drops by 900 millivolts, because at that stage, water becomes an oxidant. We've always taken that into account, and that's why 95 percent of the damage that SKB takes into account is due to sulphide. We've had that analysis for a long time. We are at the stage of developing a reactive transport model to predict that the calculations we've done to date simulate almost exactly the experimental data that we developed in Canada ten or fifteen years ago, where the potential goes through this very dramatic drop, when sulphide reaches the copper surface. That's because we're changing the mechanism. The oxidant is changing from consumption of oxygen to the reduction of copper(II), to the reduction of water. You can just do a simple Evans diagram. When those rate-controlling steps change, and that potential comes down 900 millivolts, it's a process we've understood for a long time. It's a process we're now including in our detailed reactive transport model.

Peter Szakálos, KTH: I'm not satisfied with that discussion. If you figure out that you can produce oxides and hydroxides, and that is not included in the model? It was believed that sulphide ions produce a copper sulphide. Now we can see that, because we have some solubility of copper, you produce a lot of copper ions, and they go into the bentonite and will be consumed there when they encounter the sulphides. The diffusion distance will be changed, and you will have a continuous precipitation of sulphides in the bentonite. There is a reaction with water and chlorides, and that is not included.

Fraser King, consultant to SKB: You're correct up to a point, where I wouldn't agree with the last point. But, you're exactly right, the sulphide is precipitated in the bentonite, with the reaction with the iron(II) – there's always iron(II) in the bentonite – so you get a lot of that sulphide precipitating as amorphous FeS, which may to further to change into pyrite. But a lot of that sulphide won't reach the container surface, because it's precipitated.

Peter Szakálos: Yes, it takes care of it earlier.

Fraser King: But the potential, in that case, does not lower the water reduction potential. It stays poised at a potential, as we've seen in our experiments, of minus 400 millivolts, versus calomel. It's nowhere near the water reduction potential. Only when that sulphide reaches the surface does that potential drop. That's because in the presence of sulphide, water becomes an oxidant and then the potential drops. That's when water will be reduced, hydrogen is evolved, and that's the reaction we've taken into account through these mass transport sulphide calculations. Ever since KBS-3.

Peter Szakálos: We are just looking at the results here, and, we can see that it forms oxides and hydroxide chlorides.

Fraser King: In the LOT experiments, he's got oxygen in there, in those experiments. They are formed under aerated conditions, they're a remnant of the fact that he's had oxygen in there.

Peter Szakálos: In the LOT five-year exposure, oxides and copper hydroxide chlorides formed on the surface of your samples. I can't understand why you have oxygen there, and not here. Because if you form sulphides here, how could you have a high oxygen partial pressure here? Where is that coming from?

Bo Rosborg, Studsvik Water Chemistry, consultant to SKB: A great part of the exposure time is an oxic period.

Peter Szakálos: Is that true? Here you see that you form sulphides immediately. How oxic is it?

Bo Rosborg: I cannot tell how long the oxic period lasts. But of course, the ultimate experiment is to measure the corrosion potential here, to see if you have plus 200, or around zero, or minus 400, 500. Then you know where you are. It's easy to say, but difficult to do. We have made an effort, but we have too many stray currents around in the laboratory.

Peter Szakálos: It's kind of a good experiment. It's five years. We should approach a kind of thermodynamic situation here that is correct. If there was some oxygen from the beginning, I don't believe that it dominates this corrosion for five years. There are reports showing that bentonite itself consumes oxygen. A lot of reports indicate that's it anoxic within five days or so.

Dave Shoesmith: We're studying the transformation of oxides by sulphide, both in the copper system and in the iron oxide system. If it's Cu(I) oxide, then the sulphide would convert it chemically by an anion exchange process. You don't see the transition to the low potentials, until you break through. You see only the metal surface. If it's copper(II), or in the iron case, it's iron(III), then the sulphide is not nearly as reactive, because it needs a redox process. Therefore it leaves behind residues of the oxidized form. You would expect to see residues, irrespective of whether the sulphide broke through to the surface or not. You would expect to see residues of copper(II) oxide hydroxide, just as on gas pipelines and things we see residues of iron(III) oxide in the presence of sulphide. The fact that it is there could just be a residue of what has been suggested: a pre-period, and the conversion hasn't taken place.

Peter Szakálos: If you know the situation here, with heated copper. This is kind of a high value measured. What is the copper ion in salt water, chloride water? Then you have a process with copper ions leaving this copper surface and this process will continue. I can't see how it goes down to ångströms per year, or nanometres per year. That should be proven, before we can accept this model. Isn't that true?

Dave Shoesmith: My point is that sulphide reduces the potential, localized size, and leaves those residues behind. Then they become isolated insulators, not involved in the corrosion process. The corrosion process is taking place with the sulphide on the conductive regions of the surface. But just seeing an oxidized residue left behind doesn't mean that sulphide isn't doing anything.

Peter Szakálos: Do you feel comfortable with this situation, in that we have a theoretical model, and when we measure it, it's like ten to twenty micrometres per year in corrosion rate. It's not even close to the model. Or, do you believe that it, eventually, goes down to the ångström level, or the nanometre level?

Dave Shoesmith: Well, the rates are another issue. At 5×10^{-5} molar sulphide, under diffusion control, our rate is hundreds of nanometres per year, and we have no intermediate bentonites, no intermediate diffusion barriers. We're already down to hundreds of nanometres per year, with sulphide alone.

Peter Szakálos: Yes, with sulphide alone. But just considering this situation with the high solubility in saline water, you produce copper ions at kind of a high rate, and you get this form of precipitation here in the bentonite. You can't just look at it as a simple sulphide diffusion, producing a sulphide there. It is not happening. Wouldn't you agree that there is some question here?

Martin Bojinov, VTT Technical Research Centre: A comment on the value that you have shown, 2,300 micrograms per litre. It's our value, and I will tell you that we didn't believe in it much, because these are experiments that have been performed in stainless steel autoclaves with six-day exposure. We first performed the measurement without Oxisorb, which has been commented on by the professor from Singapore. We mentioned that we didn't achieve our mass balance, due to the fact that some of the copper was deposited on the autoclave walls. We didn't find a proper way to clean up this system, so the fact that these concentrations are higher in anoxic conditions is simply an artefact of the fact that we didn't achieve our mass balance. This data shouldn't be somehow used to produce theoretical calculations. This is mentioned in our report.

Peter Szakálos: The solubility is quite high anyway, if you look at the literature. It is extremely high. I was just stating that it is not a passivating metal, that gives you this problem. You produce ions, and the corrosion will continue. If I saw that the corrosion rate goes down to nanometres per year, I would be happy, but first this must be shown.

Digby Macdonald: You've drawn the redox potential as going up. Is that based on anything scientific, or is that just artistic licence?

Peter Szakálos: No, it's because we have some sulphide activity in the repository, and clearly no sulphides are formed on the copper surface, but instead a lot of copper sulphides precipitate on the bentonite particles at a distance from the copper canister. This means that the sulphide activity is lower and the redox potential is higher close to the copper surface. Thus we can understand the formation of copper oxides and hydroxychlorides close to the copper surface, caused by the anoxic and saline water, as observed in the LOT project.

Digby Macdonald: But the redox potential is going to be dominated by the hydrogen that's produced. In which case, it should go the other way.

Peter Szakálos: I just show that because of a lowering of the sulphide, you could have a situation here with saline water and not much else. This saline water could produce this kind of corrosion.

Digby Macdonald: Have you tried calculating the redox potentials?

Peter Szakálos: No, I'm just fitting the data to what has been published about this LOT project. It's just to show what they have reported about the LOT project, and what the model predicts. There is a big difference.

Bo Rosborg, Studsvik Water Chemistry, consultant to SKB: The model used in the LOT project is that you have divided time into an oxic period and an anoxic period. The model states that during the oxic period, you should have rates below seven microns a year. The last figures point to 4, or 2.4, or 3.5, which is well below the model values. Then the anoxic period starts, which we are discussing.

Ron Latanision: I like to turn the conversation a step back. As an educator, I taught my corrosion engineering students at MIT that one of the roles that they play, is to choose construction material for engineering systems, whatever those systems may be, based on the service environment in which those systems are intended to perform. I think that if we look at this better, in terms of the actual emplacement of a package, a waste container, in the repository, we're dealing with a circumstance in which we do believe the environment to be reducing. We do believe that sulphur, and sulphides in particular, would be present in a reducing environment. There is some evidence, that chloride would play a role. Now there's a question, obviously water plays a role from the very beginning. It is there to solvate species which carry charge, without which there would be no corrosion reaction. If this were absolutely dry, no one would be concerned. We know it's not absolutely dry, and therefore there is a question of what role hydrogen may play. We have a roughly thirty year old investigation which shows that water plays a role. That's a bit unusual, in terms of our historical understanding of the influence of sulphides and of chlorides, etc. That's important. But I think the ultimate question is whether or not the kind of role, that is being proposed, in the case of influence of water, overwhelms the effect that we know historically to be the case for chlorides and sulphides, and so on. At this early stage, in terms of my involvement in this conversation, I haven't been convinced that it plays an overwhelming role. It may play a role, but I do believe that the historical data base would suggest that sulphide concerns and chloride concerns are first-order. I'm not yet convinced that the questions of copper corrosion in a reducing environment to produce hydrogen is on the same first-order. I just don't know. Maybe. That's the first point I want to make. The second point is that corrosion engineers always ask: "What is the mode of corrosion? Is it uniform, is it localized, an embrittlement phenomenon?" Based on all the things I've read in preparation for this meeting, and all of the things that I've heard today, what would concern me most were if someone were to be convinced that hydrogen is being produced and embrittling the copper. As a personal judgement, that would concern me more than the rate of uniform corrosion or the rate of localized corrosion, because of the loss of off-loading capacity and the loss of the integrity of the package. There are some critical issues that we still need to resolve. What role is the licensing authority playing in this conversation? In the United States, the Nuclear Regulatory Commission, the equivalent of your licensing SSM, plays a pretty significant role in terms of license application, once it's submitted. Maybe even prior to its submission, in terms of conversations. Have SKB or the people from the universities had conversations with the licensing authority? What kind of response are you getting?

Bo Strömberg, SSM: We have been following these discussions and have had meetings with both Dr. Hultquist, his group of researchers, and SKB. And we've made also a sort of review of the experiment, which was actually done by Timo Sario. That document was included in the material that you have been looking at. We're also doing literature reviews, and are contemplating doing some kind of experiments of our own in this area. But our real sort of judgement will not count until we get the license application.

Ron Latanision: That's what I would expect.

Peter Szakálos, KTH: What do you think about these new results from Japanese researchers that sulphide does by itself induce stress corrosion cracking?

Ron Latanision: Copper is an unusual metal, and there is a lot of evidence, that, unlike most metallic alloy systems, relatively pure copper can experience stress corrosion cracking in sulphides, in chlorides, in other media, typically under oxidizing conditions. That's well-known.

Peter Szakálos: But this was reducing.

Ron Latanision: I haven't had an opportunity to examine this. When I look at fracture surfaces, I would like to know what's on the fracture surface. The fact that sulphide is in the environment, maybe it plays a role, maybe it does not. Maybe this problem is associated with segregated species along a grain boundary, which are interacting in some other way. I can't make a comment on that without knowing much more about it. It's intriguing, it would be unusual. But I think it does need to be explored.

Fraser King, consultant to SKB: The species that cause stress corrosion of copper are nitrite, ammonia, and acetate. Not chloride, not sulphide. Chloride is good and promotes active dissolution. I like chloride.

There's a huge long list for brass, but for pure copper, it's just the nitrite, acetate and ammonia. This issue with the sulphide. I have seen this paper, and it involved slow strain rate experiments in a range of sulphide concentrations in deaerated sea water, under anaerobic conditions. They were single, slow strain rate experiments. There's no obvious trend. There's some variability in the results. They're looking at strain to failure in these slow strain rate experiments. There isn't a consistent trend with concentration. But they did conclude that, based on this fractographic evidence and the elongation to failure, there was this threshold concentration of five to ten millimolar of sulphide where they didn't see any stress corrosion. Even if you assume that they're right, and this is stress corrosion, these concentrations – the groundwater concentration away from the canister is 10^{-5} molar sulphide. As we've heard it's transport-limited through the bentonite, and the interfacial concentration of sulphide is two or three orders of magnitude below that. Let's say we're down to 10^{-6} molar sulphide at the canister surface. We're four orders of magnitude below this value. If we believe this special value for the canister, and that's what we're sort of focussing on in this session. In terms of the canister, it's good news.

Peter Szakálos: I just saw that the sulphide concentration could be close to the range in the Finnish repository. It was published.

Fraser King: Somewhat higher sulphide concentration than in some of the Finish groundwater, but again, it’s in the groundwater. We’re concerned about what it is at the canister surface. A lot of that sulphide is precipitated in the bentonite before it gets to the canister. The interfacial concentration of sulphide at the canister’s surface, once it tries to diffuse, is very low. These experiments were done in bulk solutions. They put in 10 millimolar sulphide. It’s an incredible concentration, compared to what we have in the groundwater.

Peter Szakálos: Yes, but we have a problem here, with the “Forsmark situation.” There we have water entering the system, and continuously you will have a production of high ion rates of all the salts that we have there.

Fraser King: But this hot period here corresponds to the aerobic period. By the time you establish anaerobic conditions, the canister’s cooled.

David Duquette: Part of what we’re supposed to be doing in this section is identifying things that have to be followed up on. “Where are some unanswered questions that are showstoppers?” This is among them. I’m quite familiar with this work. These results were from relatively very low strain rate experiments. There weren’t large differences in the ductility, there was active corrosion going on the copper. They reported some evidence of stress corrosion cracking, but it wasn’t strong evidence. This is the kind of thing you have to be careful of. I would admonish you, Peter, about making presentations where you have single quotes from a paper. If you look at the whole paper, it wasn’t very much stress corrosion cracking. It wasn’t like you went from 30 percent ductility to 10 percent; it was 30 percent to 24 percent, or 26 percent. It is work that I think has to be followed up on, and I think what this session is supposed to be doing is identifying that kind of thing.

Fraser King: SKB is sponsoring a study at the University of Toronto on this very subject.

Digby Macdonald: In the case of the iron system, the reactivity of these sulphur species depends upon the ease with which they can donate atomic sulphur to the iron surface. For example, thiosulphate will induce stress corrosion cracking and sensitize 304 stainless steel. It’s directly related to the ability to donate atomic sulphur. Many of those species that I showed you in that list do have the ability of donating atomic sulphur. If there were a rational programme to look into this, there would be a systematic test done on each of these sulphur species to determine which ones are the most deleterious to copper. I'll have to echo Ron's comments. What I think is lacking is that I haven't heard a delineation of the critical issues in this whole technology. You know, what is it that's really important, that needs to be done? Maybe that's our task this afternoon, to delineate this. I'm a bit surprised that somebody hasn't put up a list of critical issues that need to be addressed in developing the technology.

Saida Laârouchi Engström, SKB: This is something we do for all the engineered barriers in our system. Every third year, we produce a research development report that we submit to the government. All the issues that need more research are mentioned in this report. It's divided into different barriers. There's the copper canister, there's the bentonite issues, and so forth. Each year these issues are discussed with the scientific community. A programme that is prepared after the regulatory review and the decision of the government determines the research to be conducted for the coming three years. We've produced nine of these reports over the years. The scientific community at large and SKB's research team have been intimately involved in identifying critical issues. These include corrosion, bentonite erosion and many other areas. The work proceeds continuously.

Digby Macdonald: I'm surprised we haven't seen a list of issues, though.

Saida Laârouchi Engström, SKB: They are in my reports. You are very welcome to them.

Digby Macdonald: I'm surprised we haven't seen a list here, during this debate that is going on.

Peter Szakálos, KTH: Maybe the panel also knows something about a Japanese concept. This is described in the SKB report. There is an astonishingly big difference between these situations, in the Japanese groundwater, compared to Sweden/Finland.

Digby Macdonald: A huge difference.

Peter Szakálos: We're talking about a corrosion rate of two copper atom layers per year here. In the Japanese case, they assume a 30,000 to 60,000 times higher corrosion rate.

Fraser King: That's taken out of context. The Japanese have taken all sulphates in the clay – and for those people who know bentonite, there's a huge amount of gypsum and anhydrite in this bentonite. They've done a mass balance calculation, and they've taken all of the sulphate and assumed that it, by some process, presumably microbial activity, has turned into sulphide. Then they apply all that sulphide to the canister. That Japanese number of 9 to 13 millimetres is a measure of how much sulphate, how much gypsum is in the bentonite. I don't want to be critical of the Japanese, but, in my opinion, that's an extremely conservative thing to have done. I wouldn't have done it.

Peter Szakálos: Do you mean that the Japanese people are quite conservative, and they go for safety first?

Allan Hedin, responsible for the safety assessments at SKB: I don't think we have to say so much more about this. You can be conservative and you can be super-conservative, and I think Fraser expressed it quite well, that the Japanese approach in this particular calculation could be regarded as super-conservative, in the sense that it doesn't really mean anything. This is nothing that one would, for any reason, expect would happen in the system. Whereas the way we handle it, the numbers we are comparing for the Swedish and Finnish systems, are aiming at something that is somewhat more reasonable, but still pessimistic.

Peter Szakálos: If your model was right, I would agree with that. But, then you must demonstrate that with full-scale experiments. That should be done.

Ron Latanision: I noticed in that the Japanese data there's discussion of a pitting factor. Are we distinguishing pitting from uniform corrosion in terms of the SKB approach and the Japanese approach? What is the importance of that pitting factor, from your perspective?

Christina Lilja, SKB: We haven't been using the concept of the traditional pitting factor, as the late analysis show that it's more of an uneven corrosion than real pits.

Fraser King, consultant to SKB: Going back to 1978, when SKB-TR 78-90, came out. In that analysis, SKB assumed uniform corrosion, and at that stage there were some question about whether there'd be localized corrosion. No experimental evidence under laboratory conditions was available at that time.

Ron Latanision: No evidence, then, of localized corrosion?

Fraser King: Correct. In order to maintain conservatism – because of the well-known pitting of copper hot water pipes – it was decided to take into account some possibility of localized corrosion. The treatment that was used was this pitting factor. To get a value for that pitting factor, they did an analysis of the NBS's, the National Bureau of Standards, corrosion data, the underground disposal data. From that, they came out with various measures of the pitting factor, based on that old data. At one stage it was 25, and that was the extreme value. That was in some kind of strange US ash type soil. A more realistic value is 5. Recently we've used the value of 3. Now, that still assumes that there's some classical pitting mechanism that separates anodic and cathodic sites. Now we understand from the experiments we've done under simulated repository conditions that that's not what we see. What we see is corrosion of the whole surface. If you look at the surface, it's roughened. It's not perfectly atomically uniform, there's a roughening. In SR-Can, the most recent analysis, SKB no longer uses a pitting factor. We use a surface roughening, and that's plus or minus 40 or 50 microns, and that's based on experimental data. In a chloride-dominated system, copper dissolves actively in the presence of oxygen. We have no evidence that we have permanent separation of anodic and cathodic sites. The Japanese are still using a pitting factor. SKB have now gone away from that, to this surface roughening technique.

Ron Latanision: I think that's a useful perspective, in terms of what's on this slide.

David Duquette: Do you agree that the pitting factor is unimportant?

Peter Szakálos: I think we have some kind of pitting corrosion, since there are bivalent corrosion products. It should be included.

Gaik Khuan Chuah: When you do the experiments at SKB, after that you write a report. Who reads the report and, after that, looks at it critically and suggests further things to do? When this report finally reaches the government, who in the government reads the report?

Saida Laârouchi Engström, SKB: By law, SKB is completely in charge of putting forward a proven and safe solution for a final repository. We have to provide the Government with evidence and submit an application, which will happen in one year. The research report I talked about is also required by law. It's getting disseminated to 30 or 40 organisations like universities, people at KTH and others. Everybody will review and give their point of views on what SKB should be putting their effort into solving. That goes for engineered barriers, safety analyses, and so on. Once we've done that, the authorities will compile the viewpoints of all the different organisations and submit them, along with their evaluation, to the Government. The Government issues directives regarding to what extent the research we are conducting is okay, and what other things we should be doing more of. This has been done every third year, and we have submitted nine of these reports. The research reports that we publish are publicly available. We are 100 percent open with our research. You can download most of our reports – which are published and quality assured – on our website. And we have been doing this for the last twenty years. SKB is required by law to come up with a solution. The authorities will review it and then make their recommendation to the Government. This will be submitted along with a ruling by an environmental court that will do the same thing, subject to the provisions of the Environmental Code. The Government will thus receive two proposals. One from SSM, with their opinion of the application that SKB will be submitting in one year, and one under the provisions of the Environmental Code. Then the Government will make their own ruling. But nobody expects politicians to be corrosion chemists, or radiophysicists. They will have to rely on the environmental court and their competent authorities in the field.

David Duquette: Do you get a technical response about the details of your research, with comments about what you should do, to improve the quality of the research, and/or its reproducibility?

Saida Laârouchi Engström, SKB: Yes, from the competent authority, SSM. They have their own experts in the field that critique us and indicate the areas where they think SKB is not doing enough.

But this is actually secondary to the judgements of our own in-house experts. We are actually our own best critics, in our own organization. Our experts will also suggest what should be done in different areas in order to be able compile sufficient evidence when the application is submitted to the Government.

David Duquette: But proposal and prescription are two different things.

Bo Strömberg, SSM: Maybe I can clarify. The difference between the Swedish system and the US system is that we take a less prescriptive role. We make recommendations to SKB, but these are rather general and cover the overall direction of the programme, progressing in sort of the right direction. We don't always comment on the technical details. But we have our own experts, with whom we discuss these matters, and we write review statements. The intention of being less prescriptive is that we should not go so far that we start to design the repository from the regulatory side. Then we would have difficulty in reviewing it objectively when we get the license application.

Gaik Khuan Chuah: I didn't quite understand. Didn't SKB itself have technical experts, who would look through the results, to answer questions that have been raised? Are these consultants?

Saida Laârouchi Engström, SKB: Yes, we have our own in-house experts, but we have also an external expert group that reviews our work and gives us suggestions, or recommendations, on how to carry out our research. That group includes experts not only from Sweden, but also from outside Sweden.

Gaik Khuan Chuah: Could you give us an idea of how, over the nine reports, the questions have changed? What is the trend?

Saida Laârouchi Engström: These reports deal with the whole issue of a final repository. What we are discussing here is the process in one of the engineered barriers, which is a very important one for our system. The research that we carry out is actually intended to prove the safety of our final repository, which you cannot extrapolate directly from one process. Those reports cover all kinds of issues, such as fuel dissolution, bentonite behaviour, copper and mechanical issues, from the viewpoint of corrosion. The reports are not only about canisters, they deal with what research, in general, and in detail, should be done to prove the safety of the final repository. When we get the Government's ruling on the report and our research, they either confirm what we are doing – "Go ahead, this is okay for this area" – or generally, as has been the case, they will say, "Well, this looks good, but do more of that work on this area or that area." These reports have been very important to us, just to confirm that the work we are doing, with our own experts, and the experts outside the organization, is on the right track. This is not research that has been done in a laboratory in splendid isolation; the scientific community, at a very high level, has been very much involved.

Ron Latanision: It's not unusual in our interactions in the United States, as the Yucca Mountain project evolved, that there were lots of questions. There was a lot of research that was identified that led to some concerns about the viability of the waste package in oxidizing environments. They were always presented in a relatively timely way. Why has it taken so long for the question of hydrogen to surface here? It has been going on for thirty years, has it not? Am I missing a point?

Christina Lilja, SKB: It's not new; it's been in the safety assessment for a long time. I mentioned the process reports that include a structured list of every process. It's been dwelt on earlier. But it has been discussed more now that we've taken a deeper look into the area.

Allan Hedin, SKB: This issue was raised for the first time in 1986. Some attempts to reproduce the results were made, and as those failed, the question faded away. In recent years, there have been new publications. We have, for the last couple of years, been working actively in this area. It has been a two-stage thing. Right or wrong, but this is how it has evolved.

David Duquette: What if Peter and Gunnar are correct, and the corrosion rate is 10 microns per year? Where do you go?

Christina Lilja, SKB: We're going to the mass transport calculations, because we think the process is mass transport. It is already included in the safety assessment.

Gaik Khuan Chuah: Did SKB contact Gunnar when you couldn't reproduce the results? You did your experiments. You couldn't prove it, but since you have the advantage that you are both in the same country, wouldn't it be easy to get Gunnar over and plan and do the experiments together? Just to prove, once and for all, this way or that way.

Allan Hedin, SKB: I think it is too early to say today. We have been in contact with Gunnar and his colleagues during this phase that we have seen now. But there has been no attempt to do a joint experiment. I'm not sure we will do that in the future either. It needs to be further looked into, experimentally. Even if the results that we have seen are right, even if hydrogen is produced to an equilibrium pressure of 1 mbar, it is fully possible to make the safety case, based on mass transport considerations, that this will not limit the lifetime of the canisters.

Peter Szakálos: Only theoretically.

Allan Hedin: The calculation is theoretical. Any prediction about the future is theoretical. So are yours.

Peter Szakálos: You must fit the data to what everyone can measure. We're talking about corrosion rates of micrometers per year that are the weak point. You must do some full-scale tests and show how it works.

Allan Hedin: We are proceeding with this issue. We have to. Whatever we measure in the laboratory, to make any sense of that, in the repository environment, it has to be adapted to the conditions that prevail in the repository environment. That's exactly what we do in the safety assessment. You cannot just measure a corrosion rate in the laboratory and then take that and multiply it by the number of years and get the actual amount of corrosion. I think that is also very well accepted by everyone that reviews us.

Peter Szakálos: We haven't seen those results, from a full-scale test. That is what we are looking for.

Allan Hedin: We have discussed the LOT results, for example, today.

Peter Szakálos: They don't fit your model.

In 2010 the Swedish Nuclear Fuel and Waste Management Company, SKB, plans to submit its license application for the final repository of spent nuclear fuel. The proposed method is the so-called KBS-3 method and implies placing the spent nuclear fuel in copper canisters, surrounded by a buffer of bentonite clay, at 500 m depth in the bedrock. The site selected by SKB to host the repository is located in the municipality of Östhammar on the Swedish east coast.

The copper canister plays a key role in the design of the repository for spent nuclear fuel in Sweden. The long-term physical and chemical stability of copper in aqueous environments is fundamental for the safety evolution of the proposed disposal concept. However, the corrosion resistance of copper has been questioned by results obtained under anoxic conditions in aqueous solution. These observations caused some head-lines in the Swedish newspapers as well as public and political concerns. Consequently, the Swedish National Council for Nuclear Waste organized a scientific workshop on the issue "Mechanisms of Copper Corrosion in Aqueous Environments".

The purpose of the workshop was to address the fundamental understanding of the corrosion characteristics of copper regarding oxygen-free environments, and to identify what additional information is needed to assess the validity of the proposed corrosion mechanism and its implication on the containment of spent nuclear fuel in a copper canister.

This seminar report is based on the presentations and discussions at the workshop. It also includes written statements by the members of the expert panel.

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