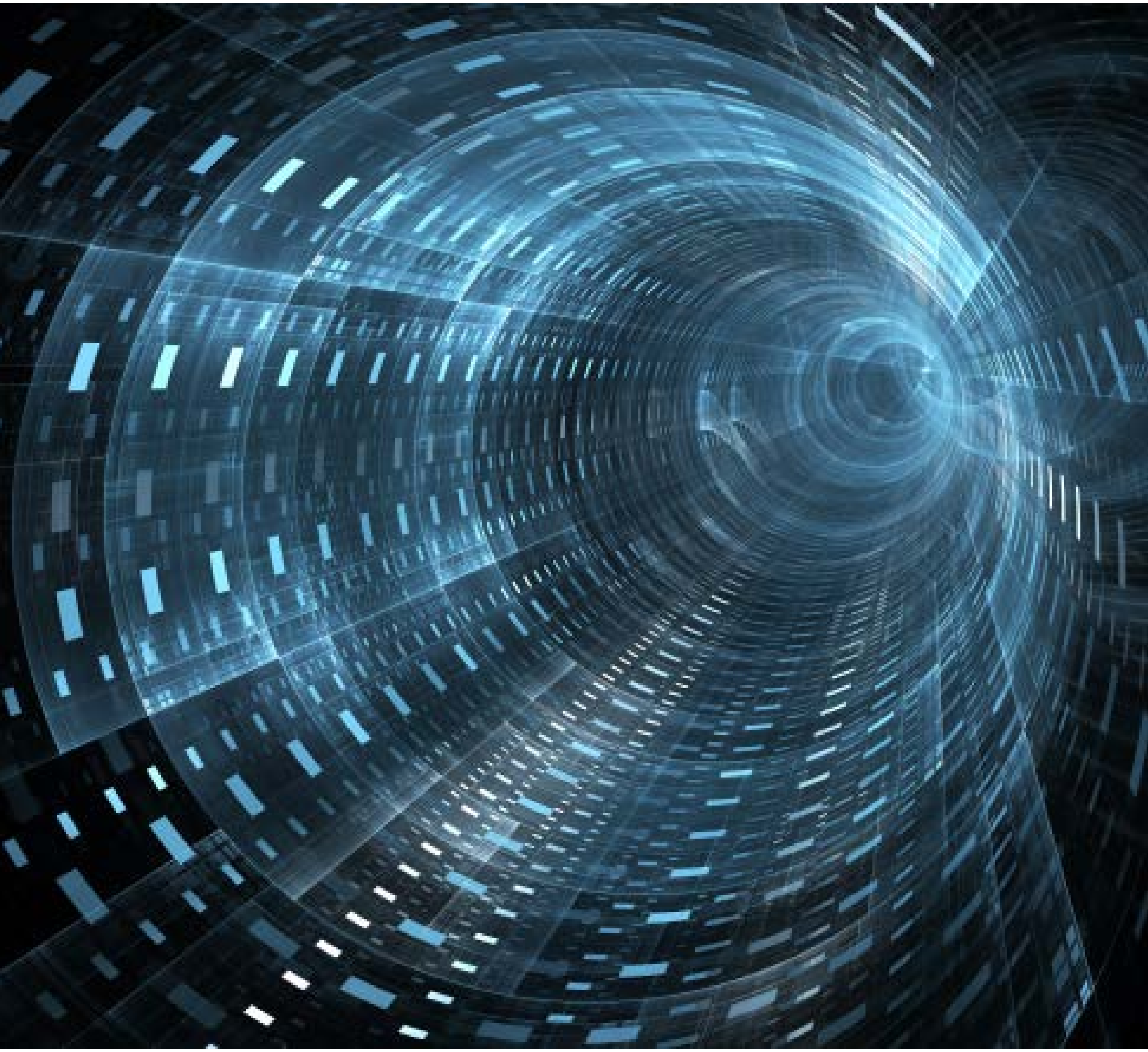
Report 2014:1e from the Swedish National Council for Nuclear Waste

KÄRNAVFALLSRÅDET
Swedish National Council for Nuclear Waste

SWEDISH GOVERNMENT INQUIRIES



New insights into the repository's engineered barriers

A report from the Swedish National Council for Nuclear Waste's scientific symposium on November 20–21, 2013

New insights into the repository's engineered barriers

A report from the Swedish National Council for Nuclear Waste's scientific symposium on November 20-21, 2013

Report 2014:1e

Stockholm 2014

SWEDISH GOVERNMENT
INQUIRIES

**The Swedish National Council
for Nuclear Waste**
(M 1992:A)

Swedish National Council for Nuclear Waste
SE-103 33 Stockholm, Sweden

Text processing and layout: Government Offices of Sweden, Office for Administrative Affairs/Committee Service Unit

Author: Marie Beckman.
Cover: Jonas Nilsson, Miljöinformation AB.
Cover photo: Fotolia.com.

Stockholm 2014

ISSN 1653-820X

Preface

In November 2009, The Swedish Council for Nuclear Waste arranged a scientific workshop on copper corrosion in anoxic water. On that occasion, new experimental results were presented and discussed by invited international experts. A special report - Report 2009:4 *Mechanisms of Copper Corrosion in Aqueous Environments* has been published and is available on the Council's website (www.karnavfallsradet.se/en).

The discussion on copper corrosion has continued and other issues relating to the engineered barriers in the repository for spent nuclear fuel proposed by SKB have surfaced. The Swedish National Council for Nuclear Waste therefore arranged another international symposium on the function of the engineered barriers for the final disposal of spent nuclear fuel focusing on the environmental conditions in the repository. The symposium took place in Stockholm on November 20-21, 2013.

At the symposium, recent results of the current research on the copper canister and the bentonite buffer as well as their interplay with the surrounding rock were presented. The engineered barriers are crucial factors for guaranteeing the long-term safety of the KBS-3 method. The interaction between the barriers and the surrounding rock is of vital importance for the evolution of the repository and its capability to meet the requirements of the safety assessment. The evolution of the repository will include periods of drying and water saturation of the buffer and backfill as well as extremely cold and warm periods. The copper canister will suffer from relatively slow alterations such as corrosion, hydrogen absorption and creep. The long-term integrity of the canister in the anoxic environment of the repository has been questioned by some scientists. They claim that the alterations undergone by the canister may be devastating for its capacity to isolate the fuel from the surrounding subsoil water. The bentonite buffer will surround the canister in the deposition hole, acting as a barrier to prevent corrosive ions from reaching the canister and prevent radioactive nuclides from a damaged canister from reaching the environment. The function of the buffer is influenced by various processes such as erosion, drying and water saturation, cementation by mineral transformation, and diffusion of ions, colloids and gases. Recent results indicate that if the function of the copper canister as an impervious barrier is to be sustained in the repository, it has to be protected by a well performing bentonite buffer.

On behalf of the Swedish National Council for Nuclear Waste, I would like to express our gratitude to the experts who prepared and presented lectures at the symposium. I would also like to express special thanks to Willis Forsling (Professor Emeritus of Inorganic Chemistry, Luleå University of technology, and longstanding member of the Council). Over the years he has played a key role in the discussion and has also been responsible for the preparations for the symposium.

Furthermore, the Council is grateful to Science Communicator Marie Beckman for preparing the report (reviewed by Willis Forsling).

Last – but not least – the Council's secretariat with Holmfridur Bjarnadottir, Peter Andersson and Johanna Swedin deserves the gratitude of the Council for contributing to the practical arrangements for the symposium.

Stockholm in June 2014

Carl Reinhold Bråkenhielm
Chairperson of the Swedish National Council for Nuclear Waste

Contents

1 New insights into the repository's engineered barriers – symposium on November 20–21 2013

1.1 SKB's method for disposal of nuclear waste

The method proposed by the Swedish Nuclear Fuel and Waste Management Company (SKB, Svensk Kärnbränslehantering AB) for the final disposal of spent nuclear fuel in the municipality of Östhammar in Sweden is called the KBS-3 method. It consists of a multi-barrier system that is expected to provide the long-term safety required by the legislation. Currently, SKB's application for the use of the KBS-3 metod is under review by the Swedish Safety Radiation Authority (SSM, Strålsäkerhetsmyndigheten) and the Land and Environment Court (mark- och miljödomstolen). The Swedish National Council for Nuclear Waste (Kärnavfallsrådet) has also been asked to evaluate the application.

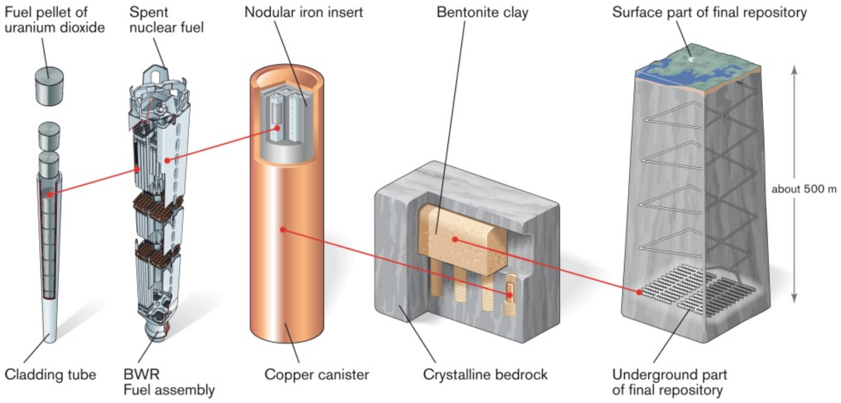
The KBS-3 method involves enclosing the spent fuel in a cast iron insert and encapsulating this insert in a copper canister overpack (Figure 1). The copper canister is embedded in bentonite clay at a depth of about 500 meters in the bedrock. Each of the three barriers – the copper canister, the bentonite clay and the bedrock – performs a special function, and taken together they are intended to ensure a durable and safe repository.

The copper canister is the primary barrier for preventing radionuclides from escaping into the environment, and SKB describes it as the most important isolating component in the repository. Thus, the integrity of the copper canister is crucial.

The bentonite clay is intended to serve three functions: (1) prevent corrosive substances in the groundwater from reaching the canister, (2) protect the canister from minor movements in the rock, and (3) retard any radionuclides that may escape from a leaky canister.

The bedrock isolates the waste and gives the canister and the clay a stable chemical environment.

Figure 1. The KBS-3 concept (SKB)



Source: SKB Art817, Environmental Impact Statement. Interim storage, encapsulation and final disposal of spent nuclear fuel, page 12.

The interaction between the barriers and the surrounding rock is of vital importance for the evolution of the repository and its ability to meet the safety requirements. Among the major challenges are an extremely long operating time (one million years), temperature variation due to climate change, swelling of the bentonite clay and corrosion of the copper canister in contact with sub-soil water. Clearly, intensive research and development are needed to demonstrate the long-term protective capacity of the copper canister and the bentonite clay.

1.2 Purpose of the symposium

The purpose of the symposium *New insights into the repository's engineered barriers* was to provide a forum for the presentation and discussion of recent research on the copper canister and the bentonite clay, including their interaction with the surrounding rock. The symposium was hosted by the Swedish National Council for Nuclear Waste on November 20–21, 2013. A number of invited experts from the fields of chemistry, materials science and engineering presented their findings. This report summarizes the results presented and the discussions held at the symposium. The report is aimed at scientists doing research in the field, experts and stakeholders in the field of nuclear waste management, and interested members of the public. The main focus of the symposium was on a follow-up of the controversy surrounding the integrity of the copper canister in pure oxygen-free water that surfaced at the workshop *Mechanisms of copper corrosion in aqueous environments*, which was arranged by the Swedish National Council for Nuclear Waste in 2009. The workshop examined the corrosion characteristics of copper in oxygen-free environments and the considered what additional information was needed to clarify these characteristics as well as their importance for the long-term safety of the final repository.[1] The presentations from the workshop 2009 and the symposium 2013 are available at www.karnavfallsradet.se/en.

1.3 Can copper corrode in pure water?

In the final repository, the copper canisters (initially at 90 to 100°C) will be surrounded by bentonite clay. The bentonite is expected to be gradually saturated by groundwater in a process that may extend over centuries and is a prerequisite for the assumed buffer safety function. Before the bentonite clay is saturated, oxygen will be present in the air inside the pores in the clay. Initially, a limited amount of oxygenated water is also present in

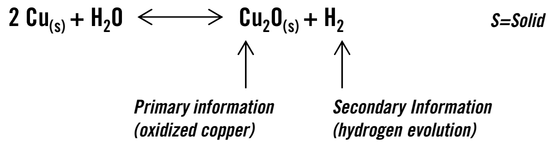
---

[1] Report 2009:4 *Mechanisms of Copper Corrosion in Aqueous Environments. A report from the Swedish National Council for Nuclear Waste's scientific workshop, on November 16,* 2009. http://www.karnavfallsradet.se/en/

the bentonite. However, groundwater at the depth of 500 meters is oxygen-free (anoxic).

There is a scientific consensus concerning the following copper corrosion reactions in the repository. First, copper reacts with the oxygen present to form copper oxide (cuprite, Cu_2O). When the oxygen is consumed, copper reacts with sulphide and chloride ions present in the groundwater to form copper sulphide and copper hydroxyl chlorides, respectively. However, the question of whether pure water (i.e. water lacking oxygen and complexing ions such as sulfides and chlorides) can corrode copper metal is controversial. In addition, the question of what impact such a process would have in a real repository environment is debated.

SKB's proposals for the deep geological repository have been based upon the assumption that copper cannot corrode in pure water. According to traditional thermodynamics, copper is immune in oxygen-free water. This means that the reaction described below is shifted to the left.



$$2\,Cu_{(s)} + H_2O \longleftrightarrow Cu_2O_{(s)} + H_2$$

However, this assumption was challenged by the experimental results of two researchers at the Swedish Royal Institute of Technology (KTH), Gunnar Hultquist and Peter Szakálos. Hultquist and Szakálos reported that pure water corrodes copper and that the corrosion process was consistent with both experimental and theoretical observations. They claimed that in the process, hydrogen ions are reduced to hydrogen atoms and a corrosion product, of hitherto unknown identity, is formed. In addition, it was suggested that the hydrogen atoms either form hydrogen gas molecules or are absorbed by and diffuse into the copper metal. See below for an illustration of the proposed reaction.

$$Cu(s) + H_2O \rightarrow \text{Cu hydroxides} + H_2 + \text{H in } Cu(s)$$

The hydrogen pressure observed (secondary information) during the process was one mbar, which is higher than the natural partial pressure in air. If the reaction can proceed to the right in pure water, a key question is at what hydrogen pressure equilibrium is reached. In other words, at what hydrogen pressure will the corrosion process stop proceeding to the right?

Due to a lack of consensus on this corrosion reaction, it was concluded at the workshop in 2009 that a deeper knowledge of the mechanisms of copper corrosion in oxygen-free water was necessary and a number of research projects were initiated, predominantly funded by SSM and SKB. The research funded by SSM includes additional studies on copper corrosion in oxygen-free water performed at Studsvik AB and at KTH. SKB funded different studies on the same topic at Uppsala University and at Microbial Analytics Sweden AB in Gothenburg. SKB has also funded research at KTH on the effect of radiation on copper corrosion. The results of these projects, together with recent research on the copper canister regarding creep and hydrogen absorption as well as crucial properties of the bentonite buffer, were presented at the current symposium.

1.4 The structure of the report

The structure of this report is in accordance with the agenda of the symposium. Chapter 2 renders the presentations and discussions on the long-term safety of the copper canister. In chapter 3, the presentations and discussions of the long-term performance of the bentonite buffer are rendered.

The report is based on audio recordings of the discussions and presentations given at the symposium. All quotations in the report are retrieved from the oral presentations by the lecturers.

2 THE COPPER CANISTER

Session chaired by Ron Latanision, Corporate Vice President and Director of Exponent's Mechanics and Materials Practice, USA

2.1 On the long-term durability of the engineered barriers in the final repository for nuclear waste, *Willis Forsling*

Willis Forsling, Professor Emeritus of Inorganic Chemistry at the Luleå University of Technology, member of the Swedish National Council for Nuclear Waste

Public opinion regarding the management of nuclear waste from nuclear reactors is often based on individual concerns regarding nuclear power as a source of energy. Nuclear energy appears to be more frightening and less controllable than other energy sources. Furthermore, it generates waste that has to be isolated for more than 100,000 years. The objective of this symposium was not to challenge anyone's opinions of nuclear energy but to present the most recent results of current research on the KBS-3 method's engineered barrier system.

Sweden's nuclear reactors will eventually produce about 12,000 tonnes of high level nuclear waste, and SKB has applied for a licence to build a geological repository for disposal of the spent nuclear fuel in very old granite rock at a depth of about 500 metres in Forsmark. Many countries besides Sweden are considering geological disposal of their waste at various depths. Usually, the surrounding rock is regarded as the main long-term barrier against the transport of radionuclides from the repository. The KBS-3 method is unique in claiming that the engineered barriers in the repository will ensure the isolation of the waste for more than 100,000 years.

The copper canister is the only barrier that is expected to remain completely tight during the whole period. Consequently, the copper canister may eventually be the industrially produced product with the longest operating life in history. Using the intricate game of chess as a metaphor for the evolution of the repository, the copper canister can be compared to the King. The King is protected by a number of pieces, the Queen being the most powerful one. The Queen can represent the bentonite clay, which has a number of crucial functions in the repository. The Queen has to defend the King from moves by the opponent, is in this case mainly the sub-soil water. Copper corrosion induced by chemical compounds is one possible future threat to the canister King. Corrosion in anoxic water would lead to the evolution of hydrogen gas. In this case, the partial pressure of hydrogen in the surrounding environment will determine how far this corrosion will proceed. However, hydrogen gas also functions as a potential barrier to further corrosion if it can be prevented from escaping. This is one of the Queen's (the bentonite clay's) duties, which has been assigned several strategic tasks over the 30 years of development of the KBS-3 method. It is expected to absorb water and swell, to adsorb corrosive substances from the sub-soil water, to act as a shock absorber against rock movements, to be hostile to microbes, to exert a constant pressure against the canister and the surrounding rock, to exhibit a self-healing capacity and to prevent radionuclides from the fuel from reaching the environment. In fact, the bentonite clay is destined to undergo several transformations during its evolution. The destiny of the chess pawns (the bentonite pellets) is also important, since some of them may ultimately be transformed into Queens on reaching the last row (as dictated by the rules of chess), in other words they will perform a necessary barrier function.

The evolution of the repository over time includes a number of obvious stages. The copper canisters will undergo processes including encapsulation, transport by ship, deposition in vertical deposition holes containing bentonite blocks (initial state), interactions with bentonite and sub-soil water (target state), and further processes before reaching an eventual steady state ($\Delta G \approx 0$).

The transitions are supposed to be driven by changes in free energy ($\Delta G < 0$), but there are some obstacles along the way.

The progression from initial state to target state may last for hundreds of years, and during this period the temperature of the canister will be higher than that of the surrounding rock. Water absorption and swelling of the buffer will therefore proceed under a temperature gradient, as warm water moves outward from the canister and cold sub-soil water moves inward. This leads to mineral transport and transformation of the bentonite clay, which will influence its long-term properties.

A long drying-up period may also affect the mechanical properties of the copper canister. Slow and uneven swelling of the bentonite clay may induce stress corrosion and facilitate creep in some parts of the canister.

Erosion of the bentonite blocks and pellets in the deposition holes and tunnels is another complication that depends not only on the ionic strength of the water but also on the sudden presence of fast-flowing water.

The processes between the initial state and the target state are extremely important for the long-term safety of the repository, but the actual time intervals will vary greatly between different deposition holes. Consequently, the evolution of the repository will vary considerably due to a varying rate of inflow of sub-soil water.

One way to minimize some of the above obstacles is to supply the bentonite clay in the deposition holes with purified water containing an optimal mixture of ions, in combination with a monitoring system to follow the evolution of the clay. A new wireless monitoring system to follow the evolution in the deposition holes during the operation period until the deposition tunnels are backfilled would increase reliability of the safety predictions.

2.2 Some pressing challenges in assuring the integrity of high-level nuclear waste isolation systems, *Digby Macdonald*

Digby Macdonald, Professor of Materials Science and Engineering in Residence, University of California at Berkeley, Berkeley, CA, USA

The safe disposal of High Level Nuclear Waste (HLNW) for periods ranging up to one million years rates as one of the greatest, if not the greatest challenge ever to be placed before the technical community and is unparalleled in the annals of human history. The storage horizon is so distant that the time that the waste must be isolated from the biosphere amounts to 125 times recorded human history (about 8,000 years) and encompasses ten ice ages (100,000 years between ice ages). Never in history has such an onus been placed upon one section of the technical community (corrosion science) to ensure that HLNW can be contained within canisters and isolated from the biosphere for one million years with a canister failure rate of less than 1 in 100,000.

The principal threat to canister integrity is corrosion. Metals have been used by humans for about 8,000 years, starting with the "native" or easily smelted metals, including: gold (c. 6,000 BC), copper (c. 4,200 BC), silver (c. 4,000 BC), lead (c. 3,500 BC), tin (c. 1,750 BC), iron (smelted c. 1,500 BC), and mercury (c. 750 BC), these being the metals of antiquity. These metals were known to the Mesopotamians, Egyptians, Greeks and Romans. Of the seven metals, five can be found in their native states [Au, Ag, Cu, Fe (from meteors) and Hg]. However, the occurrence of these metals was not abundant, and the first two metals to be used widely were gold and copper. Of these metals only iron (in the form of steel) and copper have been proposed as materials for the fabrication of HLNW canisters (Fe in France, Belgium, Japan, and the UK, and Cu in Sweden, Finland, and Canada). Others (e.g. the USA) have turned to "corrosion-resistant" alloys, such as the nickel-based Alloy 22. To put things in perspective, however, if the canister wall were 5 cm thick, the average corrosion rate must be less than 0.025 μm/year, allowing for 50% corrosion. In the case of corrosion of iron in the passive state at high pH (e.g. in contact with concrete pore water of pH = 13.5), this corrosion rate corresponds to a passive current density of about 2.1 nA/cm^2. This is about an order of magnitude lower than the passive current density measured on carbon steel in simulated concrete pore water in the laboratory under the most ideal conditions. The use of archeological artefacts (e.g. iron nails from Roman times, 2,000 years ago, 0 BC) or bronze swords from Crete (4,000 years ago, 2000 BC) to indicate corrosion rates that might be expected in a repository has been championed, particularly in France. While these times do not even remotely approach the HLNW storage horizon of 1,000,000 years, they are, nevertheless, the longest exposed corrosion objects in our arsenal and they serve as a valid check against laboratory data. This has been put to great effect by scientists at CEA, using Roman nails that were embedded in concrete two millennia ago – an environment that is surprisingly similar to modern concretes. The principal objection to this approach is that modern materials are vastly different than those that were available to the Romans and that the exposure conditions do not reasonably correspond to the corrosion evolutionary path (CEP) of a repository (particularly with respect to temperature). Thus, the iron archeological artefacts examined by Commissariat à l'énergie atomique et aux énergies alternatives (CEA) suggest an average corrosion rate of about 1 μm/year, which is a factor of 40 higher than that which is required. From this, we may conclude that the likelihood of identifying a material that is sufficiently corrosion-resistant to rely upon the canister alone to isolate the waste is remote.

It is apparent that the successful isolation of HLNW from the biosphere cannot rely upon the corrosion resistance of the canister alone, except under exceptional circumstances when it is demonstrated that the material is corrosion-resistant enough to meet the required performance criteria. In the author's experience, only one material meets these requirements: Alloy 22, which has been demonstrated to have a corrosion rate of less than 0.01μm/year in contact with geological groundwater. In the absence of such a low corrosion rate, the problem of HLNW isolation must be addressed by the "engineered barrier" approach to repository design. In this concept, one or more impervious barriers are inserted between the canister and the biosphere to impede the transport of corrodents to, or corrosion products from, the canister surface. The most commonly proposed near-field barrier is the clay mineral bentonite, which swells upon hydration and reduces the diffusivities of many species by a factor of 104 or more. Modelling has shown that this approach should reduce the corrosion rates of many metals and alloys (e.g., Cu, carbon steel) to acceptable levels. Two such models, one describing the corrosion of copper canisters in Sweden's proposed repository and the other describing the corrosion of carbon steel canisters in Belgium's "supercontainer"-in-a-clay-repository concept were reviewed in the presentation at the meeting. These models are deterministic in nature, in that they are based upon validated corrosion mechanisms and concepts and rely upon natural laws (conservation of charge and mass and Faraday's law) that will remain valid during the disposal period, with the model predictions being constrained to those that are "physically real" (i.e. those that conform to scientific experience). This is an important point, because the storage horizon is so far in the future that empirical methods of prediction cannot possibly succeed. However, empiricism still has a place in predicting the evolution of corrosion damage by defining corrosion mechanisms. A case in point is the corrosion of carbon steel in contact with concrete pore water. Experiment shows that the corrosion mechanism is accurately described by the Point Defect Model for the growth of the passive film, with most of the passive current density (and hence the corrosion rate) being due to the flow of iron interstitials through the barrier layer followed by ejection at the barrier layer-solution interface, where they hydrolyze to form a precipitated hydroxide/oxyhydroxide outer layer. The formation of this outer layer has minimal impact on the impedance of the iron-solution interface over periods of up to one year, although its presence can be detected using electrochemical impedance spectroscopy. However, modelling shows that over extended periods of time the outer layer will become compressed against the concrete and some of the material will penetrate unto the pores of the concrete, as is found upon examination of archeological artefacts. Compression of the outer layer reduces its porosity, and the outer layer is expected to become an effective barrier to the flow of water to the iron surface and thereby to effectively inhibit corrosion. The formation and compression of the outer layer is predicted to cause cessation of corrosion of carbon steel well before the storage horizon is reached, with the result that the outer layer of the passive film on carbon steel is an important contributor to the impedance of the interface and may, in itself, be regarded as an engineered barrier.

Possibly the most difficult aspect of the isolation of HLNW and the prediction of accumulated corrosion damage is developing a realistic CEP, which is the path taken by the system in terms of the independent variables as the system evolves from the initial state to the final (target) state. Only those independent variables that have a perceptible impact on the corrosion rate need be specified, but, again, the challenge lies in describing the evolution of the system to a horizon that is a million years ahead. This means that the horizon is ten ice ages away, and given the geological upheaval that accompanies each ice age, it is evident that the repository or at least its environment will change substantially. The importance of defining a viable CEP is simply that the accumulated corrosion damage is determined by integrating the corrosion rate along this path. The challenges that face the development of the "engineered barrier" concept for isolating HLNW are many and may be summarized as follows:

- Accurately defining the life of the canister relative to the storage horizon by accurately determining the corrosion rate of the canister material under the relevant conditions. These measurements must be interpreted in terms of a credible corrosion mechanism, because as the experience with Alloy 22 has demonstrated the corrosion rate may decrease over long exposure times. The cause of this phenomenon must be understood mechanistically and exploited to define the true performance of the material over the extended exposure times that characterize HLNW isolation systems.

- Any deficiency in the performance of the canister must be compensated for by the presence of engineered barriers to prevent the dispersal of HLNW into the near-field and far-field environments should the canister fail. The mechanisms for retardation of the radionuclides must be clearly defined and manipulated in order to enhance their performance. In other words, to as great an extent as possible, the engineered barriers should be "engineered" to achieve specific performance goals. For example, it is possible to engineer the near-field environment by defining the properties of the environment in contact with the canister in order to inhibit the corrosion of the canister, as exemplified by the supercontainer concept for the isolation of HLNW in Belgium. As another example, the original SKB concept for the isolation of HLNW in Sweden proposed engineering the redox properties of the bentonite clay to inhibit the corrosion of copper, but this innovation appears to have been dropped.

- It must be demonstrated by reasonable argument that the sequential failure of multiple barriers will be such that the longest-lived radiotoxic nuclides will not reach the biosphere until their activity has decayed to an acceptable level, commonly defined as ten times the half-life of the longest-lived radionuclide in the waste. The mechanisms by which these barriers will sequentially inhibit the dispersal of the waste must be clearly defined and articulated, so that the performance of the multi-barrier system can be assessed without actual experience.
- Perhaps the greatest challenge is to convince a skeptical public that HLNW can be effectively isolated. The actual isolation cannot be demonstrated empirically, due to the long time horizon (one million years in the future). Accordingly, successful arguments must be deterministic in nature, based on the argument that the natural laws are (presumed to be) space- and time-invariant. This is, perhaps, the greatest challenge of all.

2.3 Copper corrosion and its implications for the KBS-3 concept, *Peter Szakálos*

Peter Szakálos, Researcher in Chemical Science and Engineering, KTH, Sweden

Because the bedrock and the bentonite clay cannot block but only delay the transport of fluids and radioactive substances to the environment, Peter Szakálos stresses the importance of the integrity of the copper canister for the safety of the repository. He further points out that when the copper canister was chosen as a primary barrier some 30 years ago, it was based on the assumption that copper is thermodynamically immune in pure (oxygen-free) water. However Szakálos and Hultquist challenge this assumption, arguing that pure water can corrode copper. Szakálos also states that it is important to understand the corrosion of copper in pure water in order to understand other, more complex and aggressive, corrosion processes that are expected to occur in the repository.

2.3.1 Evidence of copper corrosion in pure water

A corrosion product containing hydrogen

Peter Szakálos presents Gunnar Hultquist's research, which questions SKB's assumption that copper oxide (Cu_2O) is the most stable oxide at both low and high temperature. He argues that the corrosion products formed on copper differ in terms of their properties depending on the conditions under which they are produced. Below approximately 250 °C, he claims that a hydrogen-containing oxide, including hydroxide, is formed from water in the absence of oxygen. Only above this temperature is copper oxide formed. In support of this conclusion, Hultquist presents experimental data on the hydrogen content of corrosion products formed on a very thin copper foil (0.1 mm) in the presence or absence of oxygen at different temperatures. Exposure of the copper foil to air results in a corrosion product containing very small amounts of hydrogen, as measured by thermal desorption spectroscopy. In contrast, Szakálos states that exposure of the foil to oxygen-free water for about two years results in significantly higher amounts of hydrogen in the product.

Szakálos also presents Hultquist's evidence for the ability of copper metal to absorb hydrogen during long term exposure to oxygen-free water. Thus, at a temperature below 250 °C, the researchers at KTH have detected hydrogen-containing corrosion products and absorption of hydrogen in the copper metal.

Because the copper canister will be kept below 250 °C, Szakálos and Hultquist argue that extensive knowledge of the hydrogen-containing oxides and their effect on copper is needed before the KBS-3 method can be applied. For example, it is important to establish what hydrogen concentration is required in the copper metal and in the gas phase to avoid the formation of a hydrogen-containing oxide by water.

Hydrogen gas evolution

Since 2009, several laboratories have shown that hydrogen gas evolves when copper metal is exposed to pure water (KTH, Studsvik AB, Aalto University, Microbial Analytics Sweden AB). Contradictory results have been obtained by Mats Boman and colleagues at Uppsala University. Their results are presented later in this report by Mats Boman. Szakálos presents the study performed by the company Microbial Analytics. Canister copper was immersed in oxygen-free water in special gas-tight glass vials that had previously been developed to study anaerobic (oxygen-free) microbiology. In a series of reproducible experiments, hydrogen gas was shown to evolve.

> "There are consequently no doubts that hydrogen can be emitted from copper immersed in anoxic water" says Szakálos.

Szakálos regards the result as important for several reasons. For example, it confirms that the hydrogen originates from a copper-water reaction and not from stainless steel or any other metal, which has been suggested for other experimental set-ups. It also confirms that the equilibrium hydrogen pressure at 70 °C is in the mbar range, which is one billion times higher than the thermodynamically expected value for the formation of a pure copper oxide (Cu_2O).

In addition, it shows that the oxygen in the water is consumed before hydrogen production begins. Previously, a reaction on the copper metal surface has been offered as an explanation for the hydrogen evolution. Based on the results from the laboratory of Microbial Analytics and their laboratory at KTH, Szakálos argues that a surface reaction cannot fully explain the hydrogen evolution because after the hydrogen was removed, hydrogen production continued at a rate of the same order of magnitude as prior to its removal. Finally, he stresses the need for other laboratories to repeat and confirm the findings of Microbial Analytics.

A solid corrosion product in the form of white crystals

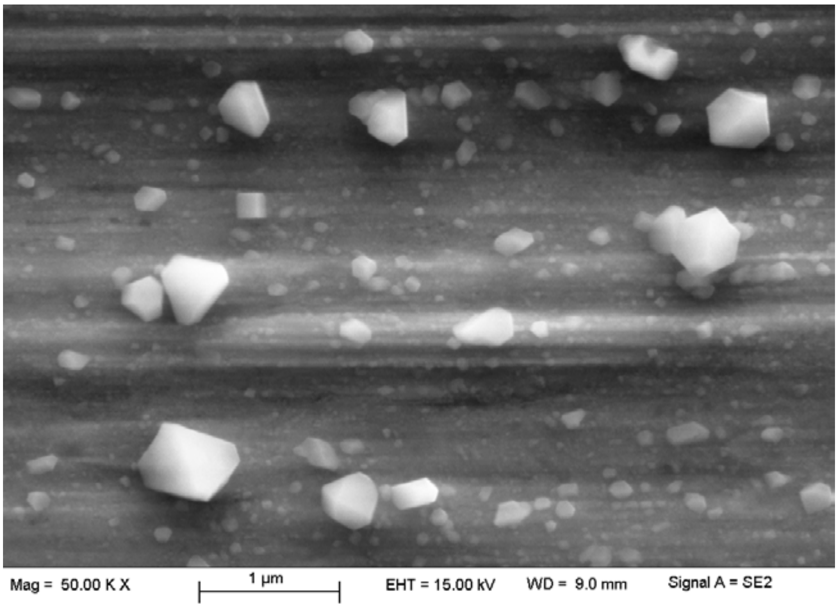
Although other laboratories confirm that hydrogen evolves when copper metal is exposed to pure water, the evidence of other corrosion product(s) is scarce. In other words, as long as the existence of primary corrosion products cannot be confirmed, the reaction is not fully understood. In his presentation, Szakálos proceeds to show an image obtained by electron microscopy of a copper surface with a solid corrosion product in the form of crystalline matter, light in contrast (Figure 2). The product is some hundred nanometers in diameter.

> "I would say that this really proves that we get a solid corrosion product under these circumstances because this copper surface was exposed to this pure anoxic water for one year and I took the sample directly from the water and inserted it in the electron microscope" says Szakálos.

Therefore, Szakálos excludes the possibility that the product was formed during transport of the sample in the laboratory. Furthermore, crystals are also observed by electron backscatter diffraction.

> "The computer software identifies it as a cubic crystal with the same structure as cuprite, Cu_2O. It is most likely not a conventional cuprite but a cuprite-like phase that contains hydrogen in some form and thus has different thermodynamic properties compared to pure Cu_2O"

Figure 2. Copper reacts with water molecules under formation of a solid corrosion product.



Anoxic copper corrosion in pure water at 50 °C, 1 year. Sample taken directly from water and incerted in the SEM-chamber. Unpublished results, but similar findings (SEM-micrographs) are published in SSM-report 2013-07. Peter Szakálos, November 20, 2013.

Belonoshko and Rosengren have published a theoretical model for copper corrosion in oxygen-free water, which predicts an equilibrium hydrogen pressure in the same order of magnitude as the experimental results, i.e. in the mbar range. Based on this model, Szakálos discusses the possibility of the copper hydroxide being the driving force for the corrosion in pure water. However, it would not be expected to be the end product. Copper hydroxide converts easily to copper oxide in air, which may provide an explanation for the corrosion product they detect. Szakálos continues to speculate that the product could be some kind of copper oxide containing hydrogen/hydroxide or crystal water or with other properties than the pure oxide. Furthermore, the monovalent copper oxide cannot be reduced by hydrogen unless the temperature is as high as 300 °C. Therefore, once formed, it can survive high hydrogen activities.

2.3.2 Copper corrosion rates in the repository

Finally, Szakálos discusses the expected copper corrosion rate under oxygen-free conditions in the repository. The theoretical KBS-3 study suggests the corrosion rate would amount to about one nanometer per year. In contrast, Szakálos refers to experimental studies that indicate substantially higher rates in the range of micrometers per year. Szakálos concludes that the theoretical KBS-3 sulfide diffusion model, in which the only expected corrosion product under normal repository conditions is copper sulphide, lacks support by experimental data.

> "The true story is that you have a lot of corrosion processes that take place without any long-distance diffusion needed [i.e. through 35 cm of bentonite]. It is shown in the Äspö Hard Rock Laboratory that many different copper corrosion products are found in the bentonite. So there is a problem here; the bentonite and copper actually work together and break each other down and the corrosion continues with short diffusion distances. Even today, the theoretical KBS-3 model with sulphide diffusion still finds no support at all in experimental data" says Szakálos.

In Forsmark, where the salt content in the groundwater is about one percent, Szakálos points out that another important corrosion process, "the sauna effect", may further increase the corrosion rate. Moisture from the saline groundwater could reach a canister through a fracture in the bedrock. Because of the temperature difference between the canister (50 to 100 °C) and the tunnel above the deposition hole (12 to 15 °C), moisture will be driven from the deposition hole to the colder tunnel and different salts will accumulate in the bentonite, affecting its properties, and induce salt corrosion on the canister. Only a few metals can resist the deposition of chlorine and sulphur salts during heating and evaporation. In industry, for example, either palladium-alloyed titanium or tantalum is used under such conditions. Szakálos suggests that estimates of the copper corrosion rates in a repository in Forsmark are in the range of one to three hundred micrometers per year, depending on the temperature, the local environment in the deposition hole and the amount of radiation.

2.4 Corrosion of copper in oxygen-free water, *Mats Boman*

Mats Boman, Professor of Inorganic Chemistry, Uppsala University, Sweden

Aiming at the cleanest possible experimental conditions

Similarities with the Studsvik study

The study of copper corrosion in oxygen-free water at Uppsala University differs somewhat in design from the studies done at KTH, Studsvik and Microbial Analytics. However, the equipment used is essentially modelled after Studsvik's set-up (Studsvik report 2011). Similar equipment is also used at KTH. In this set-up, evolving hydrogen selectively escapes through a palladium filter and the pressure above the membrane is measured.

> "This is a very sensitive method. You can detect very small amounts of hydrogen, and if hydrogen is then associated with corrosion, you can detect very small corrosion rates" says Boman.

Next, Boman presents results of the Studsvik study, in which hydrogen evolution and very small corrosion rates (a few nanometers per year) were detected over time. However, the experiment was stopped after 500 h (21 days) long before reaching a pressure in the mbar range as found by Szakálos and Hultquist. The concentration of copper in the water was also measured by very sensitive equipment (ICP-MS, Inductively Coupled Plasma Mass Spectrometry).

> "They get something like 50-100 ppm copper during those 500 hours."

Whether the copper is in the ionic or metallic state cannot be determined by ICP-MS.

Differences in the Uppsala study in relation to other laboratories

Boman states that the aim of the researchers at Uppsala University was to perform the experiments under the cleanest possible conditions and to perform a well-controlled surface analysis of the copper without exposing it to air. Differences in the experimental set-up include using a copper foil with a higher purity than the other laboratories (99.9999% versus 99.95%) and pre-treating the copper foil to generate a smoother surface. In the pre-treatment, the surface is electrolytically polished and oxides on the surface are reduced by hydrogen at 300 °C and heat-treated at 400 °C until no hydrogen is released to remove excess hydrogen and relieve strain. In the experiment, high quality water is used and oxygen is removed down to one ppb as measured by an oxygen probe. To further minimize exposure to oxygen, the experiment is performed in a glovebox with less than 0.1 ppm oxygen. Boman says that the background pressure of hydrogen is very low during the experiment, less than 0.01 torr (~ 0.013 mbar). In addition, the hydrogen produced is immediately removed in order to increase the rate of corrosion.

Results of the Uppsala study

After either 6 or 15 months of the foil in water, only a very small amount of copper (a few ppb) is detected in the water. X-ray photoelectron spectroscopy and Auger electron spectroscopy show that the copper surface is very clean after 6 months of exposure, almost identical to the surface at the beginning of the experiment.

> "We cannot see any oxide. If we had a few monolayers of an oxide, we would have seen that. Even after 15 months, we have a very clean copper surface" says Boman.

Next, they investigated whether any copper is deposited on the experimental glass beaker wall using X-ray fluorescence spectroscopy. For copper, the sensitivity of this method is about 0.1 to 0.2 nanometers, less than a monolayer.

> "After 6 months, we have less than a monolayer of copper, perhaps, on the surface."

Hydrogen is produced during the experiment, but in a much lower amount than that detected by other laboratories. The amount of hydrogen was estimated to be a few 10-6 moles per year. The reference experiments produced similar amounts of hydrogen, likely due to outgassing from the equipment of stainless steel.

Boman states that this observation is consistent with the lack of other corrosion products in the experiment.

> "If you include [the hydrogen in] the palladium membrane, if it is 40 ppm [hydrogen in the membrane], if we can trust the results, it is much more, four times more, than we see in the gas phase. So, the palladium membrane can contain a lot of hydrogen and can act as a buffer. Anyhow, we see much more gas than we see corrosion products" says Boman.

In summary, the laboratory in Uppsala reports that hydrogen gas evolves but that the molar amount of copper corrosion products found on the copper surface, in the surrounding water and on the adjacent glass walls is only a small fraction of the detected molar amount of hydrogen gas. No corrosion product could be established with certainty despite a very sensitive method with a detection limit in excess of one nanometer of surface deposit. In addition, the amount of copper in the water was very low and no copper was found on the experimental glass beaker wall.

Because of this lack of agreement between hydrogen gas evolution and the detection of other corrosion products, Boman concludes that the reaction between copper and water does not seem to be the main source of hydrogen in their experiment. He also stresses that the background pressure of hydrogen was very low in their study compared to that of the other studies. However, in order to determine whether any hydrogen evolves due to a corrosion process, a new experimental set-up with a lower outgassing rate has been devised.

Why is the copper corrosion rate extremely low in the Uppsala study?

The findings of the Uppsala laboratory differ from the results at KTH and Microbial Analytics. Boman points out that a major difference resides in the quality of the copper substrate. The copper substrates in the Uppsala study are stress-free, oxide-free and flat.

> "They are very smooth since we have electropolished them"

He stresses that it is well known that copper surfaces with a rough topography have a higher corrosion rate than flat ones. In addition, the corrosion potential will be more negative, which also happens in strained copper with many defects. Boman ends his presentation with the open question of whether the high quality of the copper substrate could account for the lack of corrosion in the Uppsala study.

2.5 Discussion 1 – the long-term safety of the copper canister

Digby Macdonald, Peter Szakálos, Mats Boman and Ron Latanision (chair)

On copper corrosion

Latanision begins by reviewing the outcome of the 2009 workshop Mechanisms of copper corrosion in aqueous environments. In 2009, it was proposed that a hydrogenated copper oxide is the product of copper corrosion in oxygen-free water. However, it was concluded that this compound has not been identified in nature, nor does there appear to be any thermodynamic data in support of such a species.

Next, Latanision introduces another corrosion reaction that was presented in 2009 and discussed by Digby Macdonald, which describes the corrosion of copper in the presence of acid leading to the production of monovalent copper ions and molecular hydrogen.

$$\mathrm{Cu(s)} + \mathrm{H}^+ \leftrightarrow \mathrm{Cu}^+ + \tfrac{1}{2}\,\mathrm{H}_2$$

This reaction can proceed if the activities of the copper ions and the hydrogen are extraordinarily low or if the activity of the hydrogen ions is very high, i.e. the pH is very low. Latanision points out that little attention has so far been paid to the latter possibility. This is a thermodynamic reaction equation showing that there are circumstances under which copper can corrode and hydrogen evolve. Furthermore, it is possible thermodynamically to predict the conditions under which corrosion will occur.

> "Any metal will corrode if the circumstances are right. It does not establish in my mind that copper corrosion is a given, it simply says it takes extraordinary conditions" says Latanision.

Latanision is further intrigued by the evidence from the Studsvik and Uppsala studies of impurity elements found in the water in which copper had been immersed. He reasons that if there are metallic species of whatever origin such as aluminum, zinc or iron, oxidation of these metallic species will produce hydrogen. Therefore, Latanision regards the question of the presence of solutes and impurity elements as important and not yet fully addressed.

> "If, in fact, those impurity elements happen to be present as cations, then it is possible that metal cations may hydrolyze and that will produce acid. If that happens to occur during the process of the experimentation that had been under way, then you may have a sufficiently high population of hydrogen ions (sufficiently low pH) that in fact this reaction [copper corrosion in the presence of H^+] may proceed to the right" says Latanision.

Macdonald comments on the reaction equation for copper corrosion in the presence of H^+. He stresses the importance of being aware that the dissolution reaction is anion-assisted. This means that the initial step is copper plus hydroxide ($Cu + OH^-$), which produces a surface species of copper hydroxide (CuOH) that in turn will react with hydrogen ions.

> "So the postulate that CuOH is an important species is not unreasonable. It is almost certainly involved in the dissolution of copper, just as the chloride ion is involved in the dissolution of copper in a chloride-containing solution and [as shown] OH^- is involved in the dissolution of iron as a surface-absorbed species" says Macdonald.

Next, Peter Szakálos answers a question from Latanision concerning the possibility that copper hydroxide, subsequently oxidized at grain boundaries, could serve as a precursor to the crystal product detected at KTH. Szakálos refers to the theoretical model by Belonoshko and Rosengren, which shows that this route is "perfectly sound" from a thermodynamic perspective.

> "If you get a [copper] hydroxide into the grain boundary, it is expected that it can dissociate there. The hydrogen could go into the metal or produce gas and the oxygen [which moves slower than

> hydrogen] could create an environment that could possibly also produce copper oxide" says Szakálos.

After prolonged exposure, they also detect a higher content of hydrogen and oxygen in the copper, but Szakálos regards it as more likely to find the crystalline corrosion product on the copper surface.

> "I would say that it probably takes much longer before you see it inside the copper, but of course, if we look at the long time exposure of copper, say 15 years, there is actually precipitation in the copper" says Szakálos.

In response to Ron Latanision's question whether anyone from SSM would like to comment on the current findings, Bo Strömberg explains that the authority is following the issue with interest and has requested complementary information from SKB. In addition, SSM has funded several studies.

> "But because we are in the middle of the review process, we don't want to express any firm conclusions about it" says Strömberg.

On copper strain and corrosion

Roland Pusch from Luleå University asks Mats Boman for further information on the link between copper strain and corrosion. He explains that his question is related to the fact that the canisters of KBS-3 type will be exposed to tension, which means that shear stresses and tension in the copper are a practical issue. In his answer, Boman refers to an article in Surface Science, which presents the corrosion rate as a function of the strain. However, Boman points out that strain is not that well defined.

On the sensitivity of surface chemistry techniques

Christofer Leygraf from KTH is asked by Ron Latanision to comment on the surface chemistry of the presentations so far. Leygraf states that a broad arsenal of surface-sensitive techniques has been used. He believes that the differences in findings are more related to differences in the experimental conditions. Therefore, he reasons that it is more important to consider these conditions than the precision in the surface-sensitive techniques, which he contends are good enough. Leygraf also raises the issue of radiation, which he will address further in his presentation after lunch.

> "I think [the issue of radiation] really can have a lot of influence on several of the points that have been raised here today" says Leygraf.

On the reproducibility of experiments

Emil Schön, editor of the Swedish environmental magazine Miljötidningen, asks Boman why they didn't aim to duplicate the method used by Szakálos and Hultquist.

> "The main reason was to perform an experiment, to eliminate as many factors as possible. Then you can add factors and see what happens, what causes hydrogen evolution" says Boman.

Latanision returns to the recommendation from the workshop in 2009 that an independent laboratory should try to reproduce the study performed at KTH and asks for comments on this issue.

> "Obviously, the results are different. So, as long as we don't understand what these differences come from, then at least I have no trust in that we have really learned something. We need to understand why there are differences really, what conditions have produced these differences in results. Otherwise, it will just be a discussion with words and nothing more" says Leygraf.

Leygraf also brings up the role of hydrogen in the observed differences between laboratories. He refers to Macdonald's introductory slides regarding the influence of different partial pressures of hydrogen, which he believes could be a good starting point for gaining a better understanding of the differences between laboratories.

> "I think it is fair to say that this [problem concerning reproducibility] is a characteristic of science. The harder you look, the more differences you find. That is just the nature of the problem. We all regard copper as being one of the most well understood metals in terms of its electrochemistry and here we are now deciding it is not. It is a complicated process and one that will continue the deeper we delve into what actually happens at the interface," says Macdonald.

> "I agree completely, each new question you answer, you raise immediately two new questions in different ways. The more you learn, the less you know" says Leygraf.

On the use of pure water instead of saline water

Juhani Rantala from VTT in Finland asks why corrosion is tested in ultrapure water instead of in chlorine-containing water, as ultrapure water will not exist in the environment of the repository.

> "Many people have looked at corrosion of copper in saline water. What we know is that HS- and other salt species activate copper towards corrosion. Chloride has a similar effect but not as strong as sulphur. The point is well taken, the repository is not situated in pure water, I agree" says Macdonald.

Comments on copper corrosion in pure water

Allan Hedin, Safety Analyst, SKB, Sweden

To support SSM's review of SKB's license applications, Allan Hedin states that the Swedish Government requested an independent review by OECD/NEA in which a team of ten international experts, including an expert on corrosion, was involved (The post-closure radiological safety case for a spent fuel repository in Sweden. An international peer review of the SKB license-application study of March 2011, final report available at www.ssm.se and www.oecd-nea.org). One conclusion in the report is that the discussion of copper corrosion by hydrogen evolution is important and must be resolved. SSM is currently requesting additional information in a number of areas, including copper corrosion in oxygen-free water.

Differences in experimental set-ups between laboratories

Hedin briefly reviews the results of the study performed by Microbial Analytics, which was also discussed by Szakálos. The use of canister quality copper at 70 °C in this set-up, with special gas-tight glass vials, leads to the production of hydrogen at a similar rate per unit area as in the study at KTH. The hydrogen pressure produced is higher than in the KTH study.

Next, Hedin summarizes the different experimental conditions in the studies that were performed at KTH, Studsvik, Microbial Analytics and Uppsala. He refers to established thermodynamics in which copper in equilibrium with oxygen-free water is expected to corrode under hydrogen evolution to a calculated equilibrium pressure of ~10-6 mbar at 25 °C. Thus, if there are neither copper ions nor hydrogen in the system to begin with, the expected equilibrium pressure of hydrogen is very low. Nevertheless, several groups observe much higher hydrogen pressures, up to a few mbars. In an attempt to provide an answer to this discrepancy, Hedin reviews the different experimental set-ups and shows that there are differences in several factors: copper purity, copper surface treatment, water purity (including initial oxygen levels) and background generation of hydrogen. The researchers in Uppsala used the purest copper with the "cleanest" surface, the researchers in Uppsala and at Microbial Analytics had the lowest initial oxygen content in water and the researchers at KTH, Microbial Analytics and Studsvik appeared to have the lowest background hydrogen. Therefore, to obtain the "cleanest" possible conditions, SKB decided to use the "Uppsala" copper (purity of 99.9999 % and surface-treated) in Microbial Analytics experimental set-up.

Test of purest copper in gas-tight glass vials

Testing two samples of "Uppsala" copper in Microbial Analytics set-up resulted in no hydrogen evolution above background.

> "The copper samples are indistinguishable from the background. It has been run for 120 days now at the last measuring occasion" says Hedin.

The experiment was repeated with two samples of the purest copper (99.9999 %) and two samples of less pure copper (99.9 %), which is even less pure than the copper used in any of the other laboratories. Importantly, all copper samples were surface-treated according to the Uppsala procedure.

> "Again, the same result. This has been running for a month and we got these results last week" says Hedin.

Hedin is careful not to draw a final conclusion based on these results. However, he discusses the following observations. First, the "Uppsala" procedure for surface treatment seems to remove the source of hydrogen evolution, implying that pure water does not corrode pure copper (within the detection limit of the experiment). Therefore, the bulk of the canister material does not seem to corrode in pure water, in agreement with thermodynamics. Second, some contaminant/surface condition is probably causing the hydrogen evolution in the other experiments. The observation that there was no hydrogen evolution in the samples of surface-treated but less pure copper supports this contention. Hedin points out that this surface condition should be further investigated, but believes it is probably of secondary importance for safety, being a transient phenomenon that will disappear over time. Third, it is important to determine that the surface treatment in itself does not alter the surface/sub-surface conditions, for example by introducing hydrogen into the copper metal, leading to a quenching of a potential hydrogen evolution. Fourth, the possibly unexpectedly high hydrogen content in the "Uppsala" copper has been an issue.

> "Mats Boman presented new results that even we were not aware of that maybe resolve that issue" says Hedin.

Currently, the source of the hydrogen in "less clean" experiments is not known.

> "But now we have access to a powerful set of investigation methods. A number of additional tests will now be made to shed light on what this process is" says Hedin.

2.6 Radiation-induced corrosion of copper for spent nuclear fuel, *Christofer Leygraf*

Christofer Leygraf, Professor of Corrosion Science, KTH, Sweden

Despite the potential importance of gamma radiation in copper corrosion, relatively few studies on this process have been reported. In addition, Christofer Leygraf states that the differences in the experimental conditions of these studies make it impossible to draw meaningful conclusions. Therefore, the present study at

KTH aimed to explore the effect of total gamma dose on copper corrosion under well controlled conditions.

> "[The spent fuel] emits gamma radiation, and that will of course penetrate into the outer layer of copper, and the question is what it can do there.// The dominant nuclide in the fuel responsible for the gamma radiation is cesium-137 (Cs-137), which has a half-life of about 30 years. Because of that, radiation-induced corrosion of copper is mainly expected to occur during the initial operating phase of the deep repository, and the outer copper canister surface will then receive an estimated maximum [total] radiation dose of approximately 100 kGy (1 Gy= 1 J/kg), mainly during the first hundred years of operation of the deep repository" says Leygraf.

The gamma radiation will lead to the radiolysis of water, producing short- and long-lived radiolytic products, two of which, hydrogen peroxide (H_2O_2) and hydroxyl radical ($OH^\cdot$), are thermodynamically capable of initiating corrosion of copper.

Circular corrosion features appear after irradiation of canister copper

Leygraf and colleagues performed a series of experiments in which samples of canister copper are irradiated with a Cs-137 gamma source at three different dose rates: 0.022, 0.103 and 0.213 Gy per second.

> "If we say that 0.1 Gy per second is around 700 times more intensive than during the initial phase of the repository, we have an acceleration of the gamma radiation but that is necessary from an experimental perspective, and I will get back to the possible influence of these higher dose rates. We can also say that this represents, since the copper is exposed to anoxic [oxygen-free] water, a sort of a worst-case scenario that we posit in order to understand what possible effects can occur on copper in anoxic water" says Leygraf.

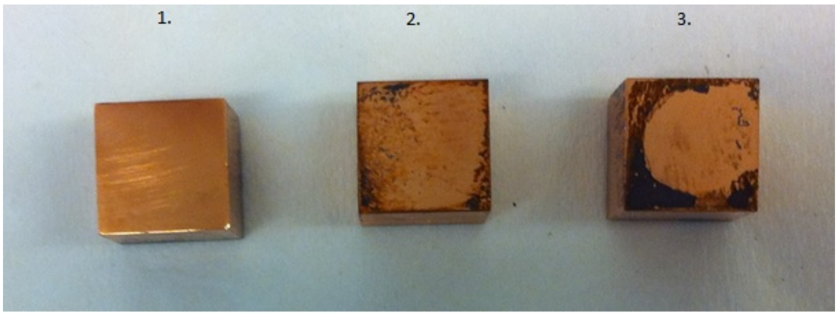
When copper corrodes, copper ions go into solution or redeposit as an oxide. The researchers at KTH characterize the corrosion products found in the water and on the copper surface both qualitatively and quantitatively via a range of sensitive techniques. Leygraf shows an image of the visual appearance of copper samples that have received a total dose of 62 kGy or 129 kGy (Figure 3).

> "You can clearly see, even with the naked eye, that we have visible corrosion effects on the irradiated samples that you do not see on the non-irradiated sample" says Leygraf.

Corrosion features induced by irradiation are further studied by scanning electron microscopy. The features induced by a total dose of 62.3 kGy at a dose rate 0.103 Gy per second differ in size, form and depth and are present all over the copper surface.

> "Several of these features are of circular shape and that is quite interesting" says Leygraf.

Figure 3. Corrosion effects observed on irradiated samples.



1: Non-irradiated

2: Irradiated, total dose 62 kGy

3: Irradiated, total dose 129kGy

Å. Björkbacka, S. Hosseinpour, C. Leygraf and M. Jonsson, Electrochemical Solid-State Letters, 15 (2012) C5

A closer inspection of the circular features reveals a rough area in the middle surrounded by a ring of copper that appears almost intact. Outside of this ring, the surface is rough again. Other, less circular, corrosion features often share the characteristics of a central rough area surrounded by a domain of intact copper surface and a rough, corroded, surface outside of this domain. Using confocal Raman spectroscopy to identify the corrosion products on the surface, Leygraf and colleagues found that the three different domains of the circular features all contain the copper oxide Cu_2O albeit to a varying degree. The rough central part displays the highest amount, followed by the rough outer area. The lowest amount of Cu_2O is found in the ring with apparently intact copper. Occasionally, copper oxide, CuO, is also detected.

The pit in the central part of the circular corrosion features has a depth around 0.5 micrometers as determined by atomic force microscopy. The average thickness of the oxide layer found on copper after exposure to a total dose of 73.9 kGy at a dose rate of 0.213 Gy per second is around 100 nanometers as measured by cathodic reduction. On non-irradiated copper, the layer is typically less than 5 nanometers.

> "So there is also a significant increase in average oxide thickness upon radiation" says Leygraf.

How does the dose rate influence the results?

Leygraf shows a plot of the concentration of dissolved copper (ppm) in the anoxic water as a function of total dose (Gy) received at different dose rates (Gy per second). The graph shows that at a given total dose, the rate of dissolution of copper is higher at a lower dose rate. In other words, a lower intensity of the gamma irradiation in combination with a longer duration of exposure results in a slightly but significantly higher concentration of dissolved copper. Next, Leygraf concludes from their experiments that the concentration of dissolved copper increases continuously with radiation dose up to 100 kGy, which corresponds to the estimated dose after a hundred years in deep repository.

What possible mechanisms underlie radiation-induced corrosion?

Previous studies discuss three mechanisms involved in radiation-induced corrosion: radiolysis in the aqueous phase, radiation-induced photo effects and destructive radiation effects in the solid state. Leygraf and colleagues conclude from experimental data and theoretical calculations that radiolysis of water alone can only account for a very small fraction of the experimentally observed copper corrosion induced by gamma irradiation. Consequently, Leygraf points out, other mechanisms, possibly of an electrochemical nature, must be involved.

> "The main mechanism governing this gamma radiation-induced corrosion of copper is the subject of further investigations"

2.7 Hydrogen absorption in copper and its implications for long-term safety, *Hannu Hänninen*

Hannu Hänninen, Professor of Mechanical Engineering, Helsinki University of Technology, Finland

Hannu Hänninen states that hydrogen absorption on copper can occur as a result of corrosion, during which hydrogen evolves. Because some water remains trapped inside the fuel assemblies after the copper canister is closed, hydrogen may be absorbed in copper not only on outside surfaces, as a consequence of corrosion caused by for example sulphide-containing water, but also on inside surfaces. Most of the hydrogen atoms formed during corrosion combine to form hydrogen gas, but a small fraction enter the copper metal.

The rate at which gaseous hydrogen is transported away from the canister also controls the amount of corrosion. The diffusion in compacted, water-saturated bentonite is estimated to be very low. In addition, ionizing radiation may enhance hydrogen absorption in copper in a number of ways.

The diffusivity and solubility of hydrogen in copper are low. Because permeability is the product of solubility and diffusivity, the permeability of hydrogen in copper is low. Thus, reaching equilibrium hydrogen saturation in copper takes a long time, except in the surface layers where nanovoids/bubbles filled with hydrogen gas may form. At ambient temperatures, the low solubility of hydrogen will nucleate these bubbles in copper or, if oxygen is present, produce water/steam.

> "Typically, hydrogen bubbles are initiated at grain boundaries and then hydrogen bubbles are filled with hydrogen molecules" says Hänninen.

Most of the absorbed hydrogen is found inside the bubbles. Only a small fraction enters the solid solution of copper. Hänninen stresses that it is necessary to understand how the high hydrogen concentration in the bubbles affects the diffusion of hydrogen and what effects hydrogen has on the bulk of the copper. Questions that need an answer are for example how many bubbles form and at what depth.

> "When hydrogen gas forms inside the bubbles, its dissociation is slow and therefore hydrogen remains in the copper. It does not readily diffuse out of the copper" says Hänninen.

Does hydrogen affect the mechanical properties of copper canisters?

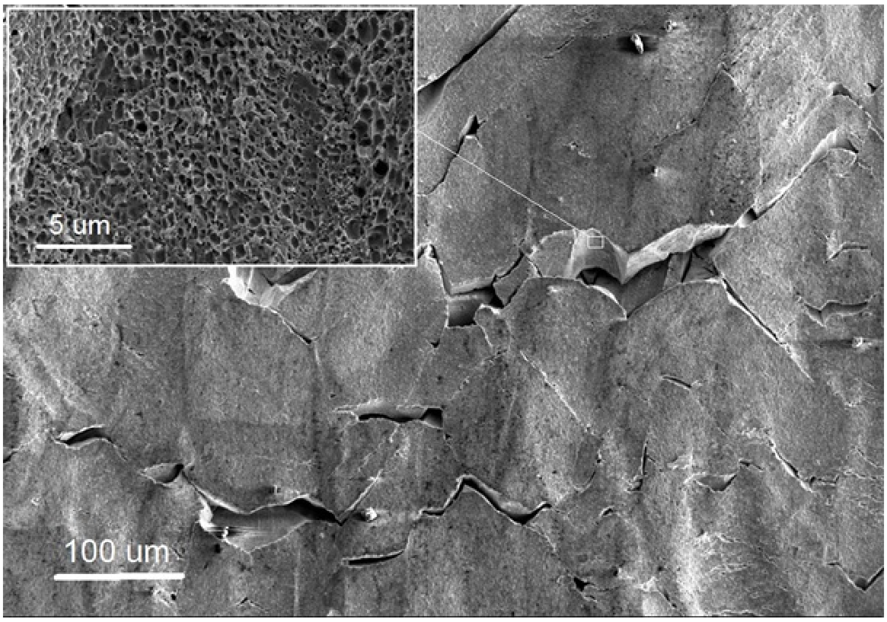
Hänninen performed tensile and creep testing of oxygen-free phosphorous-doped copper (OFP copper). The copper is initially pre-charged with hydrogen using an electrochemical method and subsequently continuously charged for the duration of the experiment.

> "We see some effect but quite small in tensile testing. We have been using different strain rates and typically we see a minor reduction in elongation to fracture and then a small reduction in ultimate tensile strength. But the interesting thing is that when we do hydrogen charging, we see a reduction in yield stress. The flow stress is also lower because yielding started earlier. These effects are, as I show later, clearly related to hydrogen bubble formation in the surface layers of the copper" says Hänninen.

After tensile testing, small cracks on the copper surface are also observed. These surface cracks are dimpled, and the shape and spacing of the dimples suggests that the cracks occur mainly by the growth and coalescence of hydrogen bubbles at the grain boundary.

In the creep tests, an enhanced creep rate is observed in the hydrogen-charged copper sample. This acceleration in creep rate is more pronounced at lower applied stresses. After creep testing, the surface contains cracks that appear similar to those obtained after tensile testing (Figure 4). The increase in creep rate at higher stress levels is probably related to the growth of the existing cracks that are induced by hydrogen charging. Studies by other laboratories also show that increased hydrogen concentration in copper shortens creep life and markedly reduces creep strain.

Figure 4. Cracks forming on side surface of Cu-OFP after CLT



Source: Presentation by H. Hänninen, November 20, 2013

What is the state of hydrogen in oxygen-free phosphorus-doped (OFP) copper?

To clarify the state and location of hydrogen in copper, an experimental system using thermal desorption spectroscopy was developed.

> "By means of thermal desorption spectroscopy we are able to analyze how hydrogen is trapped in the lattice and at what temperatures hydrogen is released from copper if it is there, and to calculate the binding energy of hydrogen to the trapping site" says Hänninen.

In as-received OFP copper, the results show hydrogen release at high temperatures (350-450 °C) from deep traps, presumably from hydrogen-filled bubbles and/or vacancy clusters. After electrochemical hydrogen charging, a new hydrogen peak appears at 200 °C, probably corresponding to hydrogen desorption from the copper crystal lattice or vacancies.

In corroded copper samples, hydrogen accumulates mainly in the sub-surface layer below the copper oxide film. Polishing of the sample does not affect the hydrogen content.

How are the hydrogen bubbles formed?

From theoretical modelling, Hänninen concludes that hydrogen absorption generates vacancies in copper, which enhances the formation of hydrogen bubbles at grain boundaries. The trapping of dissolved hydrogen at vacancies is enhanced by various impurities (O, P, S, Ag, Ni), which seems to be the mechanism for bubble nucleation in copper. Thus, impurity atoms, especially oxygen, act as hydrogen trapping sites that increase the hydrogen content in copper.

Future perspectives

Hänninen points out the importance of studying hydrogen absorption in copper from corrosion tests performed under ionizing radiation that simulates the final disposal conditions. In addition, the effects of hydrogen on the mechanical properties of copper, especially creep behavior, need clarification. Currently, the effects are not entirely consistent. Finally, it is well known that copper with oxide inclusions is embrittled by hydrogen, which reduces copper oxides, producing water/steam. The presence of oxide inclusions in friction stir welds may thus reduce the mechanical properties and creep life of copper canisters. Therefore, Hänninen strongly recommends starting mechanical tests of hydrogen-containing copper weld metals.

> "It will be very important in the future to perform creep testing and mechanical testing, combining the hydrogen effects in oxygen-containing and oxide particle-containing friction stir welds" says Hänninen.

2.8 The problem of creep ductility in copper, *Kjell Pettersson*

Kjell Pettersson, Matsafe AB, Sweden

Kjell Pettersson introduces the concepts of ductility and brittleness, which describe the manner in which a material may break. A material that has to be deformed so that it changes its shape before it fractures is referred to as ductile. Most metals are ductile at room temperature. In contrast, if a material breaks before it acquires a permanent shape change it has zero ductility and is called brittle. For example, glass at room temperature is brittle.

Petterson goes on to define creep as the slow deformation that takes place in a material under more or less constant load. In most metals, this process becomes important at high temperatures of several hundreds of degrees Celsius.

> "The interesting thing is that under the conditions of creep many metals have a very low ductility, or creep ductility as it is called. Alternatively, one can use the concept of creep brittleness" says Pettersson.

Pettersson describes the process of a metal losing its creep ductility as small cavities form in the grain boundaries of the material. The cavities grow with time and eventually the boundary fractures.

> "Early creep tests on high purity copper showed alarmingly low creep ductility. Specimens failed after less than one percent deformation, almost as brittle as glass" says Pettersson.

However, creep brittleness could be removed by adding about 50 ppm of phosphorus to the copper. This copper is termed OFP, whereas pure copper is called OF. SKB has chosen the OFP quality as the material for the waste canister.

> "We can identify three SKB positions with regard to the copper canister. First, that creep ductility is one of the most important properties of the canister in order to perform its barrier function. [Second] the required creep ductility should be higher than 15 percent. Why they have chosen the number 15 percent I have no idea. It cannot be found in their reports. [Third] the most important thing, OFP copper with 30 to 100 ppm phosphorus fulfils this requirement. That is the requirement of 15 percent ductility" says Pettersson.

Pettersson states that position three is based on a large number of creep tests of OFP material, in which no low ductile creep failure has been observed. However, he questions whether SKB has presented sufficient evidence to demonstrate that OFP copper meets their requirements for creep ductility. Pettersson argues that SKB has not convincingly demonstrated this for time ranges and stress levels that are relevant for high-level nuclear waste storage. The different stress dependencies of the two fracture processes, ductile and creep brittle, need to be considered. He also finds it unsatisfactory that a safety barrier function relies on a mechanism which is not fully understood. The effect of phosphorus in copper needs clarification.

2.9 The long-term integrity of the KBS-3 canister, *Allan Hedin*

Allan Hedin, Safety Analyst, SKB, Sweden

In March 2011, SKB applied for a licence to build a final repository for spent nuclear fuel at the Forsmark site in the municipality of Östhammar. The application is for six thousand canisters, each with two tonnes of spent fuel.

The primary safety function of the canister is complete containment. Allan Hedin's presentation summarizes the analyses of the containment potential of the canisters, which are submitted in support of the licence application. He also addresses some issues that have been raised in SSM's regulatory review of the application. The assessment is carried out according to established methodology. Among the key elements that are relevant to canister integrity, Hedin identifies 1) a description of a quality-assured initial state of the copper canister and the cast iron insert, 2) an account of the state-of-the-art knowledge regarding all processes relevant to canister integrity, and 3) an analysis of the evolution of the geological environment and its implications for the repository and in particular for canister integrity.

> "One key element of the methodology is that if there are uncertainties you often address these by making pessimistic assumptions in order to bound the effects of an uncertainty. The assessment time is one million years" says Hedin.

The safety assessment reviews possible failure mechanisms of the canister. At the time of deposition, all six thousand canisters are assumed to be leaktight. This assumption is based on the results of manufacturing and sealing techniques obtained at SKB's canister laboratory.

> "The two principal potential failure mechanisms that we look at in the safety assessment are failure due to corrosion and failure due to mechanical loads" says Hedin.

Canister failure due to corrosion

Hedin states that thermodynamic considerations are the basis for determining what species in the environment have the potential to corrode copper. The extent of corrosion is determined by mass balance considerations or by transport calculations, depending on whether the size of the source of corrodants is known. The corrosion processes included and listed by Hedin are:

- Radiolysis of water surrounding the canister
- Oxygen entrapped in the repository at deposition
- Contaminants in the buffer and deposition tunnel backfill
- Sulphide produced by microbial activity in the buffer and the backfill
- Sulphide in the groundwater
- Oxygen penetrating from the surface under glacial conditions
- A hypothetical case where anoxic water is assumed to corrode copper under hydrogen evolution

The extent of corrosion is calculated and illustrated as expected corrosion depth.

> "For the case where the buffer [bentonite clay] is intact and protecting the canister as expected, the conclusion here is that there will be no failures due to corrosion even in a one million year perspective. There is an erosion process in the buffer that we cannot rule out entirely in the safety assessment, but the buffer material is generally a stable material in Swedish groundwaters. However, if the groundwater has sufficiently low salinity, the buffer may erode, and these are

> conditions that may occur after extended periods of temperate climate or under glacial conditions" says Hedin.

Thus, erosion of the bentonite clay, resulting in direct contact of the canister with groundwater, increases corrosion induced by sulphide in the water. In this case, SKB estimates that the highest sulphide concentrations in the groundwater could cause failure of canisters located in positions with the highest flow rates in the repository after typically hundreds of thousands of years. On average, it is estimated that about one of the six thousand canisters will fail for this reason during the one million year assessment period. In this case, the buffer is pessimistically assumed to be gone from all deposition positions.

> "This shows that the canister in the host rock environment has a considerable containment potential even without the buffer"

Canister failure due to mechanical loads

Two mechanical failure modes are considered: failure due to isostatic load and failure due to shear load. Isostatic loads are caused by the swelling of the bentonite clay and the hydrostatic groundwater pressure. Under glacial conditions, the hydrostatic pressure is estimated to increase from around five MPa to 30 MPa.

> "[There are] no failures due to isostatic load. The cast iron insert is designed to withstand the loads it will be exposed to in the repository" says Hedin.

However, Hedin states that there is a small probability of failure due to shear loads. Although Sweden is located in a tectonically quiet area, large earthquakes cannot be ruled out due to future glaciers.

> "We cannot rule out glacial conditions in the future. As a glacier passes over the repository, you will have a different load situation on the bedrock, and actually we cannot entirely rule out major earthquakes. If that happens, as an effect of that movement you get secondary movements in fractures outside of this major fracture zone. We will not deposit any canister in major fracture zones, but there may be canisters in positions that are intersected by such a fracture outside of the zone. If that happens and the fracture undergoes sufficient displacement, this could cause a canister failure. Radionuclides could be released and travel with the groundwater to the surface to reach the living environment and possibly end up on our dinner plates. This is the type of exposure scenario

> that we are looking at here, and as I said, we cannot entirely rule out this although the probability is very low" says Hedin.

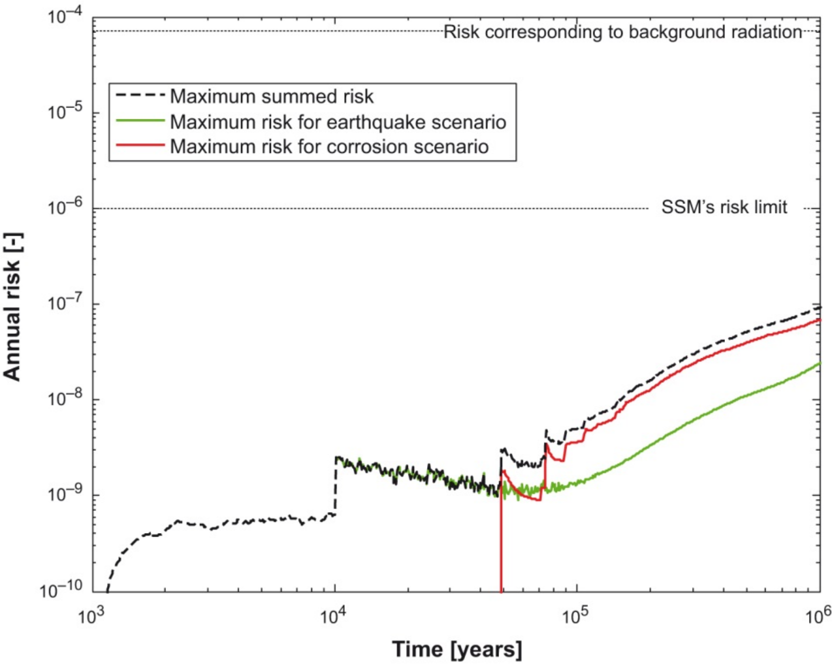
The probability of failure due to shear loads is about one tenth of the probability of corrosion failure.

Conclusion regarding canister failure

Hedin presents the conclusion of the safety analyses. The sum of the maximum calculated risk of canister failure due to shear load and corrosion at Forsmark is below the regulatory risk criterion by a good margin, even in a million year time perspective (Figure 5).

> "As this sum curve is below the regulatory risk limit during the entire assessment period, the conclusion is that you can build a safe repository at the Forsmark site" says Hedin.

Figure 5. Calculated risk for the two contributing scenarios



Source: SKB Art817, Environmental Impact Statement. Interim storage, encapsulation and final disposal of spent nuclear fuel, figure 10:41, page 271

Some issues in the regulatory review of SKB's license application

SSM has requested additional information in a number of areas and Hedin comments on four of these in the last part of his presentation. A previous section of this report summarizes his comment on copper corrosion in pure water. The other issues concern corrosion under dry or semi-dry conditions in the repository, radiation-induced corrosion and creep properties of copper.

Dry or semi-dry conditions could last for about a thousand years in Forsmark. During that time, part of the canister surface will be in contact with a gas phase and the temperatures will be elevated (50-100 °C) for the initial hundred years. Corrodants that are considered under dry conditions include oxygen, nitric acid from radiolysis of air and sulfide. SKB's conclusion based on mass balance and transport considerations is that this corrosion results in limited corrosion depths.

Hedin further addresses "the sauna effect" i.e., evaporation of water at the canister leading to local salt enrichment, which was previously discussed by Peter Szakálos in his presentation. SKB argues that this effect will be weak, if any, due to the fundamental properties of the bentonite clay.

> "The bentonite will absorb – it wants to absorb – any intruding water, and in so doing it will seal the system. The temperature, and this you can calculate, drops rather sharply with distance to the canister, so somewhere there will be a condensation zone and that will be pretty close to the canister so there is a limited water inflow prior to sealing around the canister. We are currently conducting additional tests to demonstrate this" says Hedin.

With regard to radiation-induced corrosion, Hedin says this issue was well covered by Christofer Leygraf and that SKB is funding ongoing experiments at KTH. SKB's conclusion so far is that radiation-induced corrosion has only a minor or negligible effect and does not threaten the long-term safety of the canisters.

> "But we will also look at the long-term corrosion behaviour of radiated samples to see if there are any post-irradiation effects" says Hedin.

Regarding the creep properties of copper, Hedin points out that this was covered by Kjell Pettersson in his presentation and that there is "more work to be done". In December, SKB will also report to SSM on new developments in this area.

Questions and comments for Allan Hedin

> "Have you done any research on the resistance of the repository itself to malevolent intrusion, i.e. deliberate attempts to interrupt the integrity of the repository?" Question from David Lowry (Nuclear Waste Advisory Associates UK)
>
> "We haven't done research on that. It is an area which is difficult to research, I would say. Under Swedish regulations, deliberate intrusion is not included in the safety assessment. But we make sure when choosing the site that it will not be interesting for future generations, but that is more inadvertent intrusion. So we are not doing any specific research on that and it is not really a scientific issue that you can address in that sense" says Hedin.
>
> "I have a few comments and some of them will be touched on tomorrow when I give my presentation. However, the main thing that I would like to point out at this time is that one of the loading cases that you discussed here, you talked about shearing of canisters, you talked about isostatic compaction or compression of them, but the real risk is actually actual tension. This is because of the upward movement of the upper part of the buffer that compresses the internal backfill and brings with it the upper part of the canister, which creates tensile stresses. I will return to that tomorrow," says Roland Pusch (Luleå University of Technology).
>
> "We are aware of this load case of course and that you can get strain from the canister under such situations but let's save it for tomorrow then" says Hedin.
>
> "How strong is the gamma radiation into the [bentonite] clay, does it have an impact?" Question from Roland Davidsson (SERO, Swedish renewable energy organization).
>
> "That has been investigated. Experiments similar to those Christofer Leygraf showed us for the copper have actually been done for the bentonite. No effects have in fact been seen on the bentonite. That is one of the things that we cover in the safety assessment" says Hedin.
>
> "Do you expect water to be present in the canister just before sealing it?" Question from Ron Latanision.

> "The fuel will be dried before that, so the idea is that there will be no water but there will be a trace, you can never say "nothing" so there will be a requirement on the drying process [on how much water that can be accepted i.e., the drying process will determine the amount of water remaining in the canister]" says Hedin.

2.10 Discussion 2 – the long-term safety of the copper canister

Christofer Leygraf, Hannu Hänninen, Kjell Pettersson, Allan Hedin and Ron Latanision (chair)

> "1980, I heard that 'we have the perfect solution to deal with everything'. Then, as we get more and more knowledge, we find out everything was wrong. Over the last twenty years we have learned a lot about this, and in thirty years from now we can perhaps say "it was all wrong". In a hundred years, we may be able to do it a lot better, or in two hundred years down the line. It is very important that we take the right decision now, because half of the radiation in concentrated form will be left when the sun dies. So we have to do better. This is not very good. So, wait for a hundred or two hundred years" says Britta Kahanpää (Milkas).
>
> "It is SKB's responsibility to convince first of all ourselves that we have a safe solution, and when we have done that we will be in a position to submit an application and proceed to the next step in the repository programme, which is what we have done now. We believe that this is enough and the reasons for that can be found in our licence application, which is also what is now being reviewed by SSM. Another thing to add to this is the ethical dimension. One of the basic principles is that those who have benefitted from the nuclear power should also dispose of the waste. This encompasses several generations, but still, the time to do something is now and we believe we have the information necessary to take the next step in the programme. This is not the final step, there will be more steps ahead, but this is a very important step because it is about getting a licence to actually build the repository" says Hedin.
>
> "I have been in this business quite a long time. We wrote the first evaluation report for engineered barriers in Finland in 1979. It was about 200 pages or something. Then as a young engineer, I realized that of course there will be new questions arising all the time. But during the 35 years I have been involved in this, I have realized that all the issues which have been raised, in a few years' time we have been able to solve them, offer a suitable answer, and then new issues arise. So this is a continuous process. We need to find the answers to these

questions, and to my understanding nothing wrong has been done. So we have solved most of the problems up to now. Of course, we have plenty of new problems on the table which have not yet been solved, but I am pretty sure that they will also be solved like the previous ones" says Hänninen.

"We are definitely learning more and more about what goes on, and I think if you compare with the last meeting four years ago there has really been a lot of progress. The problems as I see them [for example issues related to corrosion or to mechanical properties] form a kind of one-dimensional pathways, where we take one step further, we learn something, we raise new questions pathway where we take one step at a time. The problem is that we don't look enough laterally between these different pathways because I think that what we learn from one pathway has an impact on the other ones too. For instance, the effects of radiation on surface topography. We have learned from your [Hedin's] summary that surface condition is very, very important, so if we start with a diamond-polished surface or if we start with a rough surface with craters, we might get completely different results. [Similarly] I can make connections to your [Hänninen´s] problem and the one where we had the combination of gamma radiation and the possibilities of introducing defects in the lattice that can have an influence on hydrogen absorption, and we can go on and on… So I think that actually the number of problems increases exponentially if we take that approach. We can solve them, I am convinced of that, but it is not as simple as just expressing it in one-dimensional issues, in my opinion" says Leygraf.

"As practicing engineers, we are always managing risks. That is the nature of the enterprise. Whether you are building a contemporary automobile or an airplane, you always need to ask the question: What service environment does this service system see? For example, if you are building automobiles today, we know they perform far better than they did years ago. Because engineers have learned, they have progressed and they have improved the quality of the materials we used to build automobiles. It would be very easy I think, if you look at airplanes to make the same type of argument – have there been failures in terms of the materials that have been used for airplanes? Perhaps, but we still fly airplanes and that is the nature of engineering. We build engineering systems and we need to understand the service conditions in which they perform. I think the crux of the issue that you [Britta Kahanpää] are raising, and it is an important issue, is: How confident is this group that we understand the service conditions in which the waste will be put in place? That is a very important question from my perspective. From what I have heard today, I think I would agree with Christofer on this, I think we have learned quite a lot, even in the last four years but I take your point and it is a concern that we need to be very careful about, that is the nature of engineering" says Latanision.

"Certainly there has been a lot of knowledge gained since 1980, but going back to engineering, I think it actually gives me a lot of confidence that the original concept of KBS-2, when we had copper canisters and bentonite buffer and crystalline rock, essentially has not had to be changed, even if, of course, there are aspects of the system like the cast iron insert, details about how you really manufacture bentonite blocks and things like that [which] has evolved over time. But I think most of what we have seen of fundamental challenges, "will the system work?" – after a few years we are usually able to conclude that it was not an issue, whereas in some instances we have seen, okay we have to do some minor adjustments to the design, not in the overall ideas but on some details. So I would say certainly, there have been lots of things learned, but the process as such gives me confidence" says Johan Andersson (SKB).

"First comment is that I have been looking at copper corrosion for very many years and one observation is there has been a lot of work done over the last thirty years and we have tended to focus on work that has been done during the last four-five years and a lot of the information that was developed ten or twenty years ago is still relevant but doesn't seem to get read or understood or appreciated. I would suggest that people look at the whole depth of information that we have generated over the past thirty years and take all of that into consideration. There are some instances today where it wasn't apparent to me that the speakers had done that. The second point I would like to make [is that] I think it is extremely important that when we look at these issues, we understand what the environmental conditions are, [what] the exposure conditions are in the repository. I appreciate that for students wanting to get PhDs, they need to accelerate tests because they need to do an experiment for two or three years and get papers published and that is fine and I understand that. But if it is not possible then to extrapolate those environmental conditions over those times scales to repository time scales, we need to be aware of the repository conditions and make sure that we understand the relevance of accelerated tests to those conditions in the repository, which we appreciate are more difficult in the lab to study because the effects are much smaller. But we need to be aware of what we are doing in the lab and how to extrapolate that to the repository environment" says Fraser King (Integrity Corrosion Consulting Ltd).

"We have a regulator who must ultimately decide whether the conditions in the repository are suitable for the containment material. So there is another layer of enquiry that we haven't talked much about and that is SSM. They have a major role in this exercise of course" says Latanision says.

"I guess my concern is that when we use these highly accelerated conditions, we may be looking at phenomena that are not relevant to the repository and that may raise, for people who are not specialists in that area, issues which under repository conditions are not really issues" says King.

"Just a comment on the last comment. If you consider the presentation on gamma radiation, we definitely are aware of [studies] that were performed thirty years ago and even more, fifty-sixty years. In fact, the largest body of investigations was done in the former Soviet Union, where there is really a lot to learn. We definitely have tried to consider that in the investigations. The problem is the balance. You need to make an accelerate the processes in order to focus on the phenomena in a reasonable time frame so that you start to get a deeper understanding of what really occurs in order to be able to eventually extrapolate to conditions [in the repository]. We saw earlier from Kjell Petterssons presentation, if you don't understand what really goes on at the grain boundary it is very hard to make an extrapolation from laboratory conditions to deep repository conditions. So I think it is a balance, you need to accelerate the tests to some extent, and then the question is to what extent" says Leygraf.

"I perfectly agree, trying to make predictions over enormous time scales is the biggest issue we face. That is why we need this mechanistic understanding and that is why, admittedly, in the early days when we were looking at these issues, we did accelerated tests, which were then difficult to extrapolate to repository conditions. But over the years we learned and we understood that that was the crucial issue to make sure that the mechanism is the same and that we can extrapolate from these accelerated conditions to repository conditions. Again, my concern is that in some cases, perhaps, we are not looking at the same mechanism under these accelerated conditions as the one that will operate in the repository" says King.

"I would like to add to what the previous speaker here said and that is regarding the impact of scale. The scale dependence of the properties of the rock and the canister material, the buffer and everything, we need to consider that. In the laboratory, we test very small pieces of the material but when we come to larger volumes, we have all these defects that accumulate with size" says Roland Pusch (Luleå University of Technology).

"A comment on Allan Hedin, he is obviously very satisfied with the corrosion issues and I wouldn't of course agree with that. For instance, if we can find a solid corrosion product on a ground sample, of course we can guess that if it is electropolished and potentially hydrogen-charged, you will not see that for much longer. So I am just a little bit curious, you feel very confident about the corrosion issues, do you have any more comment on that? We can see a solid corrosion product, doesn't that concern you?" asks Peter Szakálos.

"I am not a corrosion expert, I don't think I have any more comments than on the general level I did it other than, I mean, the point there is that if you have a very clean system, the thermodynamics seem to be valid. So the conclusion one is tempted to draw then is that we are seeing a surface effect, and as I said, that would presumably be a transient phenomenon. But we need to sort this out. I hope you heard me say also that, I mean, we need to understand where the hydrogen comes from before we can close this issue" says Hedin.

"I think you should add what Gunnar Hultquist has said for thirty years: *you have to understand the thermodynamic effect of the presence of hydrogen*; that should be included" says Szakálos.

"We will continue to do the corrosion experiments and hopefully one day we will figure out what the difference is between our experiments" says Mats Boman.

3 THE LONG-TERM PERFORMANCE OF THE BENTONITE BUFFER

Session chaired by Barbara Pastina, Senior Program Officer, Saanio & Riekkola Oy, Finland

3.1 The physical/chemical stability of the buffer clay in a KBS-3V repository, *Roland Pusch*

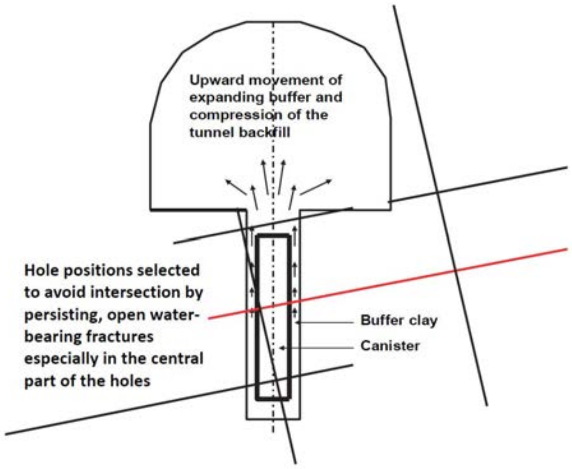
Roland Pusch, Professor Emeritus in Engineering Geology, Luleå University of Technology, Sweden

Rock fractures and stresses on the canister and buffer

Roland Pusch presents an illustration of a section of the KBS-3V deposition tunnel with deposition holes (Figure 6).

"The holes are 8 metres deep and about 1.8 m in diameter" says Pusch.

Figure 6. A section of the KBS-3V deposition tunnel with deposition holes



Source: Presentation by R. Pusch, November 21, 2013

Next, he points out that the surrounding rock has discontinuities that can be either active water conductors or dry. The positions of the holes are selected to avoid intersection by persistent, open water-bearing fractures.

> "Especially in the central part [of the holes], in view of the possibility that movements will occur in the rock along such persistent fractures – they can be up to a hundred metres long. So if one can characterize the rock with respect to the presence of such fractures, one can identify holes that are suitable for depositing canisters. I have pointed out many times that SKB does not have any practical, technical categorization scheme for the various discontinuities in the rock" says Pusch.

Pusch also raises the concern of whether the bearing capacity of the bentonite clay is sufficient for carrying the heavy canister. Could the canister slowly sink down through the bentonite clay and reach the bottom of the hole?

> "In practice one can say that the density planned for the buffer here is a guarantee that such large movements cannot take place" says Pusch.

Pusch adds that the shear resistance of the buffer is also important to consider.

> "If the buffer is very dense and rigid, then a possible shearing along this fracture for instance [pointing at the illustration] could generate critically high stresses in the canister and also cause mechanical destruction of the buffer around it. So one should try to find locations for the [deposition] holes here that are not intersected by critically oriented water-bearing fractures, especially where they intersect the deposition hole at half-height" says Pusch.

Next, Pusch explains that the bentonite clay in the deposition hole is prevented from expanding radially but not upwards. This is due to the relatively soft and displaceable backfill of the tunnel. The upward expansion of the clay generates shear stress along the contact between the clay and the canister.

> "The canister will tend to be lifted in the upper end here, while it is kept firmly in the position down here. So tension stresses will appear in the copper shell. This may not be critical per se but it can have an effect on corrosion, as we discussed yesterday" says Pusch.

Loss of expandability and self-sealing capacity of bentonite close to the canister

Previous investigations suggest that the buffer will be fully water-saturated in three to five years, according to Pusch.

> "In practice, if we look at the background of these values we find that in fact, a more proper interpretation of the data means that it would take 50 to 100 years until the buffer is fully water-saturated."

The properties of the bentonite clay, such as stiffness and heterogeneity, are affected by the rate at which water enters it.

> "In a repository where we have a temperature gradient of say 90 to 100 °C at the canister and 40 to 50 °C at the rock, we have all these processes that change the whole thing in a microstructural way."

The process will lead to a more permeable and less soft clay. Therefore, Pusch concludes that the system becomes stiffer and more permeable than it was to begin with, or than it would have been without a temperature gradient. Cementation by precipitated silica and iron will permanently prevent expansion on wetting.

> "Loss of expandability is important because if we have movements in the rock that create small fractures or fissures in the buffer, they will not be so effectively sealed, self-sealed, as when we have the natural

> system. So these precipitation reactions here [of silica and iron] hinder or prevent a return to a homogenous state. So, close to the canister, we will have a material that is not as good as the original material" says Pusch.

In conclusion, heterogeneity and cementation raises hydraulic conductivity (10 to 100 times) and leads to a loss of expandability and self-sealing capacity.

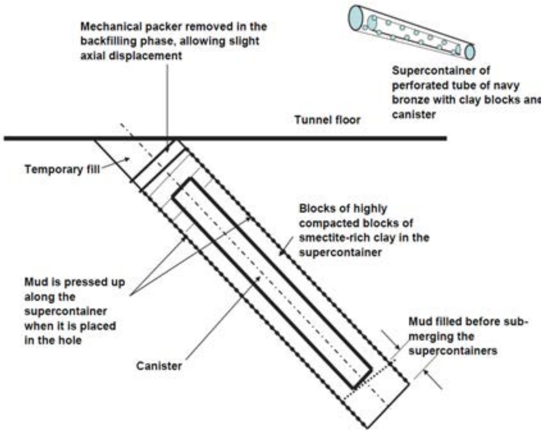
> "This may sound very risky but it is not because the hydraulic conductivity of the original blocks of clay when they are saturated is a hundred times lower than that of the surrounding rock. The clay will still be less permeable than the surrounding rock. One thing bothers me and that is the rock surrounding the deposition holes. According to SKB, the rock around each and every deposition hole will be fractured. The rock will be highly fractured and have an increased hydraulic conductivity. This is of course of no importance if the buffer is still fully intact, but if there is a loss of expandability the bentonite will also lose the ability to seal the fractured rock and isolate the canister from the rest of the system" says Pusch.

Placement of the canisters

Finally, Pusch discusses the difficulties involved in putting the canisters in place, which has to be done by machines. To make the placement of the buffer and canisters safer and simpler, he favors an inclined orientation of the deposition holes (Figure 7).

After the presentation, Barbara Pastina (chair of the session) comments that Pusch has published the above discussion in Environmental Science and Earth Journal this year together with a comment by SKB. Therefore, this debate can also be followed in the scientific literature.

Figure 7. Proposal for inclined orientation of the deposition holes



Source: Presentation by R. Pusch, November 21, 2013

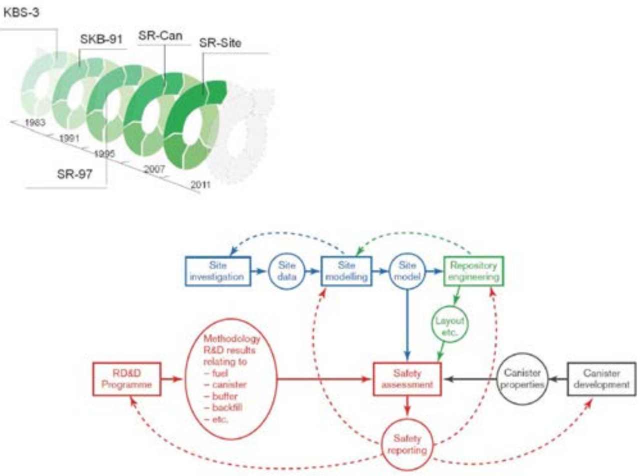
3.2 Production of bentonite components and operational issues, *David Luterkort*

David Luterkort, Specialist Engineered Barrier Systems, SKB, Sweden

David Luterkort describes SKB's safety assessment process. It is an iterative process, which started in 1983 (Figure 8). In brief, results from the safety analyses are fed back into the research and development programme for use in updating and improving the different barriers, canister development, repository engineering as well as site modelling and site investigation.

"The cycle is repeated and the system is improved" says Luterkort.

Figure 8. SKB' safety assessment process



Source: SKB general presentation material 2014 and SKB TR-11-01, vol 1, Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main report of the SR-Site project, Figure 1-4, page 57

Luterkort's presentation focuses on the production and installation of buffer and tunnel backfill, and on how to put the canisters in place.

> "It is very important to be able to show in a reliable way that we can achieve the initial state that we assume in the safety performance assessment and that we can describe it in a very good way. To be able to do this, we need to have very good control of the whole production line, starting with the procurement and buying of bentonite, so that we can define the right requirements on the bentonite and make sure that delivery is satisfactory. Then [follows control of] the whole chain of manufacturing the components – the blocks, the pellets – [and] transporting them into the tunnel and installing them according to the specifications" says Luterkort.

Currently, using standard methods, SKB is producing a large number of backfill blocks for full-scale tests of backfilling in the beginning of 2014. New equipment for putting the blocks in place is also being tested. In addition, installation of the canister by a fully automated deposition machine is being further developed at the Äspö hard rock laboratory.

> "We are also working on buffer design and installation. The objective then is to achieve an efficient and robust installation taking the expected water inflows in Forsmark into account as well as the early evolution of the buffer. This will also define requirements on the logistics in the repository. It is important to make this system work as a whole" says Luterkort.

The choice of locations for deposition holes includes characterization of the bedrock in a number of steps. Luterkort explains that the model of the rock is continuously updated and the locations are chosen on basis of the model. Currently, SKB is working on the practical aspects of this. Luterkort also describes a more sophisticated system for rock characterization than SKB's current one. The system is presented by Posiva in a report and their approach to characterizing the rock is similar to SKB's, using a model that is continuously updated.

Finally, Luterkort presents an illustration of the logistics of the planned deposition sequence, showing how the tunnels are constructed, how the deposition holes are made and how the canisters, buffers, backfilling and plugs are transported.

In the years ahead, Luterkort concludes that the manufacturing, installation and quality control of the buffer, backfill and plugs will be developed in greater detail. The installation of the different components will first be tested separately. Integrated testing will then take place to ensure that the system works as a whole.

3.3 Chemical erosion of bentonite components in the KBS-3V design, *Tim Schatz*

Tim Schatz, Senior Researcher, B+Tech Oy, Finland

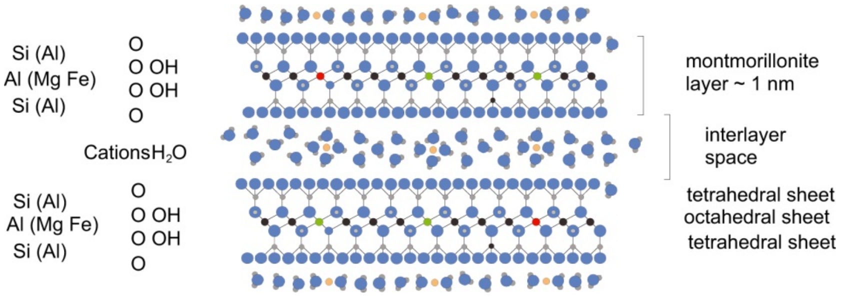
Bentonite consists primarily of the clay mineral montmorillonite, which has substantial swelling ability when in contact with aqueous solutions. In principle, Tim Schatz states, the volumes of the deposition holes in a KBS-3V type repository are fixed and the mass of bentonite balanced. Consequently, a suitable swelling pressure is developed. However, the possibility of transmissive fractures intersecting the holes means that volume-constrained conditions may not be ubiquitous. In such conditions, continued localized quasi-free swelling of bentonite may occur until an equilibrium or –in the case of erosion – a steady state is reached. The density of the clay will decrease as it swells farther into the fracture space, changing from a hydrated solid to a swelling paste to a gel. Thereafter, depending on the composition of the groundwater, the clay may disperse as colloids. The material is considered most susceptible to erosion by flowing groundwater when it is at or near the colloidal transition point.

Dilute water makes the clay more susceptible to erosion

The montmorillonite layers are negatively charged and balanced by cations located between the layers of clay mineral (Figure 9). This structure results in an affinity for water in the interlayer space.

> "The swelling ability of the clay is then strongly dependent on the nature of these compensating cations and also the chemistry of the aqueous phase. In the case of montmorillonites dominated by small, monovalent cations – lithium, sodium, potassium –swelling ability at low ionic strength can be sufficient to produce colloids" says Schatz.

Figure 9. Structure of montmorillonite



Source: SKB TR-09-34, Bentonite erosion. Final report, figure 1.1, page 11

Intrusion of glacial meltwater – i.e., very low ionic strength water – into the repository may thus lead to transformation of the clay mineral into a colloidal phase that is susceptible to erosion.

> "Such low ionic strength groundwater may be observed in temperate periods and has also been observed in Spain, Czechoslovakia and Switzerland."

Experiments on the erosion behaviour of bentonite

To examine the possible erosion behaviour of the bentonite buffer in contact with dilute groundwater, Schatz and colleagues conduct artificial fracture experiments. In these experiments, they can probe buffer erosion under flow-through conditions in relation to buffer composition, groundwater composition and velocity, presence of accessory minerals and fracture geometry (aperture, slope angle).

At higher ionic strengths (10 g/L sodium chloride), the clay material (sodium montmorillonite) extrudes into the fracture quite homogenously and continuously over the course of the experiment, which is one month, approximately.

> "The rate of expansion slows but it does continue to extrude" says Schatz.

However, at lower ionic strengths, for example in de-ionized water, both extrusion and erosion are observed.

> "You do see the same extrusion into the fracture but you also see that the material is being eroded away. In this case the extrusion distance, after approximately I think 120 hours, reaches a steady state. So you have a balance then between erosion and extrusion" says Schatz.

Schatz and colleagues have observed erosive and non-erosive behaviour of the clay under several different conditions. They also monitor the effluent solids content emerging from the fracture.

> "In the case of an erosive test, you can see you are producing quite high concentrations of eroded mass that are coming out of the fracture system, although there is certainly some transient or slowly decaying behaviour of this solids evolution. But in the case of the non-erosive conditions, essentially no effluent solids content above background is observed" says Schatz.

Calculation of average erosion rates under various conditions shows that even small changes in ionic strength lead to changes in average mass loss. Schatz concludes that the erosion process is very sensitive to even small changes in ionic strength. Fracture geometry will also play a role in erosion behaviour.

Schatz also presents data showing that, whether erosion was observed or not, the material that extruded into the fracture in their experiments was relatively impermeable to water flowing in the fracture. This was visualized via dye injection.

In summary, erosion is observed for both sodium montmorillonite and 50/50 calcium/sodium montmorillonite at or below a concentration of ~4.3 mM sodium chloride. However, below this threshold value, erosion is very sensitive to solution composition down to an ionic strength of ~1 mM. Solutions below the concentration of approximately 1mM seem to be purely erosive. Evidence was also found for structural formation and evolution of the eroding material, which may provide an explanation for the cases observed where erosion was attenuated. Such structural formation was only evident in the calcium-containing systems.

Schatz concludes that, in general, the results of their study are in agreement with those of previous studies performed by other laboratories. Currently, Schatz and colleagues continue to study the erosion process in order to clarify the mechanism behind it. There are also ongoing efforts in model development i.e., quantification of buffer mass loss on a repository scale.

3.4 Chemical stability of bentonite and clay stone under repository conditions in the French context: interactions between clay materials and cement, iron and glass

Nicolas Michau, Research Manager, Andra, France

In the French design for the deep repository, there are three clays of interest: the Callovo-Oxfordian clay stone in the host rock, bentonite and clays formed during the life of the repository. The Callovo-Oxfordian clay stone is composed of clay minerals, including illites, and carbonates, silicates and accessory minerals such as pyrites and feldspars.

> "As a backfill, you can have crushed clay stone that is re-compacted in situ" says Michau.

Bentonite is found in plugs for the disposal cells and in seals for galleries and access shafts.

The properties required of the clay materials are homogeneity, low porosity, low permeability and a low diffusion coefficient. Other properties required and listed by Michau are: a high exchange and sorption capacity for radionuclides, the ability to swell with water, plasticity to fill in the voids left in the components and engineered barriers, and durability over time in the repository.

Michau explains that the different clays are exposed to successive alteration processes due to contact with other materials used in the repository, such as concrete or carbon steel, and to conditions during construction, operation and the post-closure period in the repository. An example of the latter is that the clay stone is oxidized during excavation, which may cause corrosion of iron components or alteration of cement and concrete. Next, Michau presents a more detailed overview of different transformation processes in the clays and discusses how potential problems can be minimized. He then proceeds to present the research and development strategy used at Andra in France.

> "As I have showed you, the reactivity of clay rocks and clay materials is quite complex and we need a multidisciplinary approach to get the different results, we [need] to have a different level of understanding. To get the global picture, we decided to assemble a network of scientists working on the same issue that we call "Groups of Laboratories". The idea is to give a global theme to a scientist and then to manage the interfaces between the different groups. For example, we have one group working on glass-iron-clay interaction, one on concrete components and another on thermodynamic characterization of the different phases and then you observe [as illustrated on the slide] that you have a network between the different groups and an exchange of either data or models or methods to get the most out of different experiments. The end result is scale modelling of the repository" says Michau.

To give an example of the size of a group, Michau says that the glass-iron-clay group consists of about twenty laboratories.

Michau stresses that the time scale is important in guiding the research and development strategy and shows an illustration of the time scale involved in the repository project. For example, the end of the dissolution of vitrified waste in a hundred thousand years or more can be compared to the time that has passed since the dawn of civilization.

Next, Michau discusses the advantages and disadvantages of experiments performed in surface laboratories versus underground research laboratories, as well as observation of natural or archaeological analogues.

> "The last tool is modelling of course, because you can extrapolate in time and space. Usually, they [models] are fast and inexpensive but I think [this] is less and less true because the models tend to increase in complexity. The drawback is of course you need a lot of things like models, data, bigger and bigger computers and you need certain [prior] knowledge of the phenomena" says Michau.

It can also be hard to validate the results of modelling.

Finally, Michau provides some examples of recent achievements:

> "We have quite good models for cement degradation, iron corrosion and glass alteration in clay environment. We also have quite good thermodynamic databases for clays and [radionuclides]. We have made some progress in material specifications such as steel grades, cement formulation and even sand composition, because we don't use bentonite alone – it is a mixture between bentonite and sand."

Nicolas Michau has not commented on the above presentation of his contribution at the symposium.

3.5 Performance of the buffer and uncertainty management in the Finnish safety case TURVA-2012, *Margit Snellman*

Margit Snellman, Safety Case Project Manager, Saanio & Riekkola Oy, Finland

In December 2012, Posiva Oy applied for a licence to construct a geological repository for spent nuclear fuel at Olkiluoto in Finland. Posiva's safety case, called TURVA-2012, supports the Preliminary Safety Analysis Report (PSAR 2012) and the licence application. The focus of Margit Snellman's presentation is on the assessment of buffer performance.

The buffer is assessed against a set of performance targets that are defined in the Design Basis report. Different evolutionary processes that may affect the performance targets and target properties are discussed for three time windows: the period of excavation and operation up to closure (about a hundred years), the post-closure period during the next ten thousand years, and beyond ten thousand years over repeated glacial cycles up to a million years.

> "Compliance is mostly based on modelling and of course supported by experiments" says Snellman.

Important processes affecting the buffer and backfill in the beginning, each with associated uncertainties, include excavation-related processes such as rock damage, changes in the in-flow to deposition holes and tunnels, changes in groundwater composition, as well as internal processes such as heat from the canister and swelling of the clay.

> "In the very long term, we have to consider future glaciations" says Snellman.

Consequently, during the post-closure period for example, Snellman states that some buffer and backfill material may be lost through piping and erosion. However, a sufficiently high buffer density will be maintained according to their analysis. The production of sulphide by microbes in the buffer is expected to be low. Nevertheless, it cannot be ruled out in localized zones of low backfill density.

Beyond ten thousand years, chemical erosion of buffer and backfill has to be considered. This would be due to dilute groundwater conditions during ice-sheet retreat and the melting period.

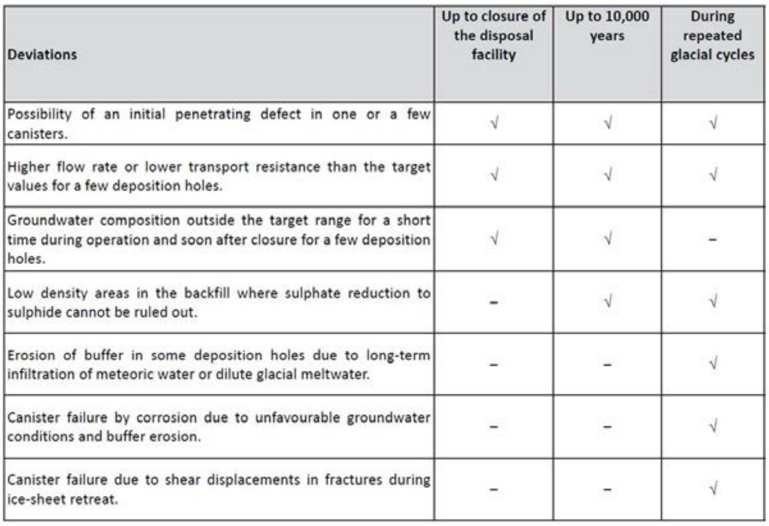
> "According to analysis, no canister failure is expected during the first glacial cycle – not even if the buffer is chemically eroded, as long as the conditions otherwise correspond to the expected evolution. But after repeated glacial cycles for up to one million years, four to five canister failures may occur, or with even more pessimistic assumptions up to a few tens of canister failures" says Snellman.

An overall summary of the performance assessment is presented as a table in the report (Figure 10).

> "What is different from SKB is that we have considered as a deviating condition that we may have an initial penetrating defect in one or a few canisters. We have a different welding method and we have

> performed statistical analysis and made estimates where we came to the conclusion that we have to include this case of initial penetrating defect" says Snellman.

Figure 10. Uncertainties identified in the Finnish performance assessment



Deviations	Up to closure of the disposal facility	Up to 10,000 years	During repeated glacial cycles
Possibility of an initial penetrating defect in one or a few canisters.	√	√	√
Higher flow rate or lower transport resistance than the target values for a few deposition holes.	√	√	√
Groundwater composition outside the target range for a short time during operation and soon after closure for a few deposition holes.	√	√	–
Low density areas in the backfill where sulphate reduction to sulphide cannot be ruled out.	–	√	√
Erosion of buffer in some deposition holes due to long-term infiltration of meteoric water or dilute glacial meltwater.	–	–	√
Canister failure by corrosion due to unfavourable groundwater conditions and buffer erosion.	–	–	√
Canister failure due to shear displacements in fractures during ice-sheet retreat.	–	–	√

Source: Posiva 2012-12, Safety Case for the Disposal of Spent Nuclear Fuel at Olkiluoto - Synthesis 2012, Table 6-1, page 157.

Next, Snellman reviews the treatment of uncertainties in the report. An example of uncertainties is the presence and hydrogeological significance of a damaged zone around a deposition hole. Another example is long-term chemical erosion of the buffer, leading to accelerated canister corrosion.

> ”Radiological consequences in the individual canister failure cases have been analyzed, and multiple canister failures based on the performant assessment have also been included in the analysis and the summary of results, and we can see that we are still below the regulatory guidelines" says Snellman.

Snellman concludes that the number of failed canisters is uncertain and depends for example on assumptions regarding groundwater flow. However, for a single canister failure, the safety margin is great enough that the range of uncertainty can be accepted.

> "We think that the safety case [TURVA-2012] provides sufficient assurance of the long-term safety of the planned repository to justify the start of the construction of the repository and the encapsulation facility. We are aware that we have remaining uncertainties regarding the future evolution of the repository and its surroundings, but the conclusions regarding long-term safety are not affected by these uncertainties and the uncertainties will be diminished further by future R&D [research and development] work by the time of the application for the operating licence" says Snellman.

3.6 Discussion – the long-term performance of the bentonite buffer

Roland Pusch, David Luterkort, Tim Schatz, Nicolas Michau, Margit Snellman and Barbara Pastina (chair)

> "I want to ask about the environmental impact assessments. When you do an environmental impact assessment, you have to have different alternatives, and SKB has only presented one alternative. You ought to have, always, a no-action alternative that means you do nothing, you wait for a future optimal solution. Then you have different alternatives. SKB's alternative is to leave the nuclear waste to the coming generation and they will die in the future [at one point in time, how far into the future I don't know] The best alternative is, you have produced the nuclear waste, a dangerous waste, the best is to convert the radioactive waste into non-radioactive material and you can do that. It's expensive but you can do it and you have to do it if you are humane" says Britta Kahanpää (Milkas).

> "First of all, our ambition is of course to protect the environment and protect the people of the future by means of a safe solution that minimizes radiation exposure from the waste that is produced and will be produced. We think that the KBS-3 method is the best for this purpose and we have argued quite persuasively for this, and we have also discussed a number of alternatives. A no-action alternative is also described [in the environmental impact statement] which is continued storage in bulk, basically. With respect to transmutation, a way of getting rid of the radioactivity, in doing transmutation you create new radioactivity – it is more short-lived but it will be more intense. So, if you look at the total dose rates, we think that direct disposal is the best way" says Olle Olsson (SKB).

> "I have a question for David [Luterkort] from SKB about the verification of the initial state. I think this is quite an important question because SKB set up quite high expectations in that they assume a perfect initial state, no mistakes, no faults whatever. We have

made a formal request for supplementary information but still, I will ask the question. I would like to know if you could say something more about your plans for full-scale demonstration and verification of the whole deposition sequence, including the backfilling of tunnels, under realistic conditions, repository conditions and using remote control and radiation shielding and all these things that you will use during normal repository operation. I know you did mention something about integrated testing but [this is] of course just one aspect. Could you elaborate a little bit on that?" says Björn Dverstorp (SSM)

"I guess what you would say is a perfect initial state. There [are] boundaries, as we have expressed it, a span of densities or something like that, a span of material composition that we have to keep within. In doing that, the production line report is an indication and a start on how we intend to do this and we are working with it in the full-scale tests that we are now conducting. So, as we move towards industrialization of the system, as a part of that, we will develop the quality assurance methods and the quality control methods. We are currently devoting a great deal of effort to these issues," says David Luterkort (SKB).

"We have a sequence of integrated tests that will be more and more complex, starting now with the full-scale test of backfill installation, where we are going to use the robot system. One of the critical elements is to make sure that we can put in the backfill blocks fast enough in order to meet our requirements. The next step will be simultaneous buffer and canister emplacement and this we have described, I think fairly clearly in a way, in the R&D programme. The next integrated test will be when we also put in the deposition tunnel plug. Finally, at some time when we have constructed the repository, or before the application to put it into operation, we have to conduct formal commissioning tests. Then we have to show that the operations, as we describe them in the operating licence, actually work. Then the complete system of the production facility for the production of bentonite blocks, transportation down to the repository, installation, all these steps have to be done with the right organization, with the right tools and, of course, all the quality assurance and quality control procedures to ensure that we actually fulfil the requirements we have in terms of acceptance of deposition holes, the amount of buffer material and its distribution and the proportions of the different materials in the bentonite blocks and so on. So I think we have quite an elaborate plan for doing this integrated testing leading into commissioning tests, as we said, in an answer that we have already given you" says Johan Andersson (SKB).

"I have a question for Margit Snellman from Finland. I am puzzled by your certainty to be able to make predictions for such long time periods in the future. You had a slide where you showed up to a hundred thousand years and a hundred thousand to a million years and I'd be very interested to hear any comment from you on how you can predict over such a long time frame. [I am] particularly curious if it is something that you felt you have been able to do for a long time, or whether at some point you achieved enlightenment that it was possible, or if you were ever doubtful about the possibility of doing this?" says Miles Goldstick (Milkas).

"This is related to the temperate and glacial periods and repetitions of these and this is based on the knowledge we have learned from the past. We know that there have been periodic glaciation and temperate periods and, also, there are a number of available [publications] showing solar periods and CO_2 balances. There is a lot of available information on this and we did have experts involved in this [assessment]. So, I think we are as confident as we can be about this scenario that we have developed. We know for sure that the next glaciation will come but the exact timing of course, we cannot say that precisely, but we know that there will be repeated cycles coming" says Margit Snellman.

"I can say something about the SKB case. We are working with several scenarios, so we have for example a greenhouse scenario where the onset of the first glaciation is much delayed by an assumed greenhouse effect, or enhanced greenhouse effect. We have a number of scenarios, actually, in order to cover the uncertainties that Margit mentions. You don't know exactly what we take as a basis for all this repetition and assumed repetition of the last glacial cycle, but we are not claiming that that is what is going to happen or even that that is the most likely development in the future. But that is one case and we start from that and we look at other cases where we vary the important conditions for repository safety from that. So it's not fruitful to try to say that you can actually predict, it is a very strong word, what will happen in the next one hundred thousand years, but what you need to do is to understand what conditions in the external environment are important and then put bounds on those and look at various scenarios for those. Then you are in a position to say something about safety of the final repository" says Allan Hedin (SKB) says.

"I think the audience here is interested in hearing a comment from SKB related to the statement this morning by Roland Pusch. He mentioned that SKB has no methodology for characterizing fractures and fracture systems in the deposition tunnels and in the deposition holes" says Öivind Toverud (Bromma Geo consulting).

"I will just answer in brief and then leave the rest to Raymond [Munier]. There is a methodology, which is based on updating a model continuously and then choosing a solution based on the model," David Luterkort (SKB) says.

"I had hoped to avoid this question… because I am guilty, slightly. As a matter of fact, once upon a time in my PhD I had an implementation of something similar to what Roland [Pusch] has proposed, but in a more mathematical statistical framework, and it showed that it was more complicated to implement it than to abandon it. As a matter of fact, such a classification scheme requires oversimplification of the complexities of nature to such an extent that we would need to introduce many exceptions to the rules used for the classification and we thought, after careful evaluation, that it was better to abandon it and opt for a scheme of the type that David mentioned earlier, which is similar to the one Posiva uses. Each structure, each hole, each tunnel needs to be evaluated on its own merits and no simplified classification scheme can improve the long-term assessment of safety" says Raymond Munier (SKB).

It is not just theoretical. First of all, we have tried ourselves to do lots of characterization and to understand the near-field rock characteristics of the Äspö hard rock laboratory tunnels. But I would say, perhaps even more importantly, we have been closely followed and collaborated with Posiva and their development of the RCS system that David [Luterkort] was talking about and this is not just a theoretical product, it is actually applied in practice to characterize demonstration tunnels. I think it's a very convincing case, if you happen to read the report, you can find it as a reference to the Posiva safety case, where this detailed modelling and all the capabilities of fracture mapping, geophysics, assessment of pilot hole information together form a very convincing pattern that we are able to find the features that we need to avoid to position the deposition holes and that we also can find the volumes of the rock where it will be okay to do this. We essentially intend to do the same thing at Forsmark, with the exception that part of this kind of modelling and understanding is site-specific, so you need to sort of calibrate these general tools and ideas into what we will actually experience when we go underground at Forsmark" says Johan Andersson (SKB).

"I think from a practical point of view, it is very important for rock engineers to have some tools for simple description of the features that we see there. Hopefully, this [model] will be adapted to this principal in Forsmark" says Roland Pusch.

"That was exactly the point and the thoughts behind sort of how to combine shall we say the more scientific characterization of the fractured rock mass [with] an environment which is essentially to be a construction project and how do you make this work together. So there has been lots of thought behind that" says Johan Andersson (SKB).

"Thank you for the opportunity to follow up. I would like to get back to this certainty in being able to predict for long time periods into the future. If I understood correctly, Allan Hedin said that it wasn't prudent to express certainty. However, SKB is out marketing the KBS-3 project internationally and we are continually getting reports from NGOs in different parts of the world that are saying 'SKB was here and they are saying that this is certain' and we are getting media reports all the time saying 'SKB says we have a certain solution, we have predicted certainly that this is going to be safe for over a hundred thousand years'. As far as I understand, that is the way it is in the application now for the facility up at Forsmark. So, suddenly we have a contradiction here" says Miles Goldstick (Milkas).

"There is no contradiction. What I was saying is that we don't know the future for certain and that is certainly true. Nevertheless, it is possible to put bounds on the consequences that all the future evolutions we can think of would have on repository safety. It is when we do this exercise and find the bounds that we are able to say that the repository will be safe. There is no contradiction in that" says Allan Hedin (SKB).

"Considering the time perspective: Yesterday we started with the definition of what period of time is of interest to SKB and it was one hundred thousand years. Now, the first glaciation followed by de-glaciation – that is a condition that is required for the possible erosion of the buffer – that is within a hundred thousand years. I think you devoted your efforts to quite the wrong thing. What is essential, I think, is to focus on the performance of the buffer and the whole system in the first five to ten thousand years" says Roland Pusch.

"I think we need to study all the time-frames, early, middle-range, long-range" says Barbara Pastina in a final comment.

In November 2013, The Swedish National Council for Nuclear Waste arranged an international symposium, *New insights into the repository's engineered barriers*, to discuss the safety of the final disposal of spent nuclear fuel proposed by the industry.

The Swedish Nuclear Fuel and Waste Management Company (SKB) submitted its license application for a final repository of spent nuclear fuel in 2011. SKB proposes to use the KBS-3 method which consists of 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 purpose of the symposium was to highlight and discuss the function of the engineered barriers for the final disposal of spent nuclear fuel focusing on the environmental conditions in the repository. Recent results of the current research on the engineered barriers such as the copper canister and the bentonite buffer, as well as their interplay with the surrounding rock were presented. The engineered barriers are determining factors to guarantee the long-term safety of the KBS-3 method.

This report is based on audio recordings from the presentations and discussions at the symposium.

KÄRNAVFALLSRÅDET
Swedish National Council for Nuclear Waste

SWEDISH GOVERNMENT
INQUIRIES