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Research

Coupled Transport/Reaction Modelling of Copper Canister Corrosion Aided by Microbial Processes

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SKI Perspective

Background

The long-term corrosion of copper due to reaction with the groundwater sulphide need to be thoroughly addressed in the safety assessment for the KBS-3 concept for the final disposal of spent nuclear fuel. This corrosion mechanism is generally not expected to proceed at rates that may threaten canister integrity, mainly due to the small concentrations of reactive HS^- in the groundwater environment and also due to the mass-transfer limitations imposed by the bentonite buffer. Nevertheless, it is essential to evaluate all conceivable mechanisms that could locally increase the groundwater sulphide content to such an extent that it could affect the overall rates of canister corrosion. The most likely process in this context is the activity of Sulphate Reducing Bacteria (SRB). This report includes an assessment of the impact of SRBs just outside the bentonite buffer. In this study, the microbial activity kinetics has been neglected and rates of sulphate conversion have instead been assumed to be controlled by limiting concentrations of either sulphate or methane (which is the assumed electron donor). Possible side reactions with the generated sulphide have been conservatively neglected.

Purpose of the project

The main purpose of this project is to evaluate conceivable implications of SRB activity in the repository environment. An additional objective is to summarise information concerning groundwater components of relevance for the assessment of potential SRB activity (mainly SO_4^{2-} and CH_4). Long-term trends for the concentration of these components have been considered and are supported by a discussion about different sources and sinks.

Results

The results suggest that the activity of SRBs just outside the bentonite buffer would increase canister corrosion rates, by elevating the gradient of sulphide across the buffer. The calculated rates suggest an accumulated corrosion of 2 mm during 10^5 years. A worst conceivable case was simulated by inserting the highest measured substrate concentration and applying this rate throughout the assessment period of 10^5 years. This suggests an accumulated corrosion of 25 mm.

Future Work

Additional analysis and/or experimental work directed towards SRB activity and the groundwater sulphide geochemistry might be needed. The purpose could be to evaluate whether or not sulphide concentrations could be locally elevated by microbial processes to such an extent that they would have a pronounced effect on canister corrosion. A more detailed understanding of microbial mechanisms and other reactions involving sulphide would be needed. Analysis of a hypothetical case where microbial activity could take place within the bentonite buffer might also be needed to evaluate the importance of assuming no microbial activity in this part of the repository.

Project Information

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Abstract

Copper canister corrosion is an important issue in the concept of a nuclear fuel repository. Previous studies indicate that the oxygen-free copper canister could hold its integrity for more than 100 000 years in the repository environment.

Microbial processes may reduce sulphate to sulphide and considerably increase the amount of sulphides available for corrosion. In this paper, a coupled transport/reaction model is developed to account for the transport of chemical species produced by microbial processes. The corroding agents like sulphide would come not only from the groundwater flowing in a fracture that intersects the canister, but also from the reduction of sulphate near the canister. The reaction of sulphate-reducing bacteria and the transport of sulphide in the bentonite buffer are included in the model. The depth of copper canister corrosion is calculated by the model. With representative "central values" of the concentrations of sulphate and methane at repository depth at different sites in Fennoscandian Shield the corrosion depth predicted by the model is a few millimetres during 10^5 years.

As the concentrations of sulphate and methane are extremely site-specific and future climate changes may significantly influence the groundwater compositions at potential repository sites, sensitivity analyses have been conducted. With a broad perspective of the measured concentrations at different sites in Sweden and in Finland, and some possible mechanisms (like the glacial meltwater intrusion and interglacial seawater intrusion) that may introduce more sulphate into the groundwater at intermediate depths during future climate changes, higher concentrations of either/both sulphate and methane than what is used as the representative "central" values would be possible. In worst cases, locally, half of the canister thickness could possibly be corroded within 10^5 years.

Executive summary

The integrity of the copper canister is important for the safe disposal of spent nuclear fuel in a final repository. Copper can be corroded by several species: under reducing conditions it will be corroded by HS^- to form chalcocite (Cu_2S) or covellite (CuS) (Beverskog and Puigdomenech, 1997). Under oxidising conditions copper can be oxidised o form cuprite (Cu_2O) or tenorite (CuO). In saline water it can be corroded to form copper chloride complexes (Puigdomenech and Taxén, 2000). Copper can be corroded relatively uniformly on its surface by general corrosion. Copper can also be corroded by localised corrosion that attacks only special regions of the canister. Possible fissures or other weak areas of the canister may be susceptible to crevice corrosion. The selective corrosion on welds could occur where welding created a heterogeneous region. Stress corrosion cracking occurs in an aggressive chemical environment when corrosion is coupled by mechanical stress in certain mechanically loaded regions. Pitting is the corrosion in a small area with great depths and usually results in small holes on the copper surface (Taxén, 2002a; Taxén, 2002b). Galvanic corrosion can occur when dissimilar conducting materials are connected electrically and exposed to an electrolyte.

In the spent fuel repository environment, the general corrosion by sulphide will be the most important corrosion process. The non-adherent layer of chalcocite (Cu_2S) or covellite (CuS) formed during corrosion gives little protection to further corrosion. Thermodynamic considerations show that when copper is corroded by sulphide, the cathode reaction can be proton reduction.

The sulphide concentrations in typical groundwaters in crystalline rock are usually very low. Based on this and other hydrogeological and hydrogeochemical observations, the integrity of the copper canister is considered to be much longer than 10^5 years (King et al., 2001). Even though sulphide concentration is generally low in the groundwater at a potential repository site, the sulphate concentrations are usually several orders of magnitude higher. Sulphate reducing bacteria (SRB) can reduce sulphate to sulphide by coupling the reaction with oxidation of organic carbon (Hallam et el., 2004). In the groundwaters at intermediate depths a major source for organic carbon is methane. Methane is believed to emanate from the mantle of the Earth (e.g. Svenson at al. 2004) and can be used by SRB as an energy source. To study the long-term stability of the copper canister against corrosion, we need to address general corrosion of copper canister by sulphide produced through sulphate reduction by SRB.

Sulphate reducing bacteria were directly observed in the groundwater at the site of the Äspö Hardrock Laboratory in southeastern Sweden (Kotelnikova and Pedersen, 1998; 2000) and at the Olkiluoto site in southwestern Finland (Haveman et al., 1999). There were geological, hydrogeological, isotopical as well as groundwater chemical indications of sulphate reduction (Laaksoharju, 1995).

To quantify the extent of copper canister corrosion aided by microbial processes, a coupled transport/reaction model has been developed. The concepts of the model are as follows:

A fracture in the granitic bedrock intersects the deposition hole in a repository. As the bentonite buffer is unlikely to be coincidently damaged mechanically at the fracture opening, groundwater in the fracture will flow surrounding the bentonite buffer. Corrosive species like sulphide will be transported only by molecular diffusion through the bentonite buffer to the canister surface. We assume that sulphate reducing bacteria have colonised at the interface between the bentonite buffer and the rock at the opening of the intersecting fracture. Sulphate will be reduced to produce locally high concentration of sulphide at the interface. Part of the produced sulphide will diffuse through the bentonite to corrode the copper canister, and the rest will be swept downstream by the seeping water. Inside the bentonite buffer, no bacteria are assumed to exist or be active because they are unlikely to survive at places with very low water activity.

The sulphate reducing bacteria (SRB) can completely reduce the sulphate in their vicinity in time scales of years, as has been observed in sea sediments (Jörgensen, 1978). The rate of sulphate reduction by SRB is therefore relatively fast and is assumed to be instantaneous in our model. The corrosion rate will then be limited by the supply of either sulphate or methane, whichever has the lower concentration.

In our sample calculations, a representative "central" value of 1 mmol L^{-1} is used for the concentration of the limiting species for corrosion. This value is chosen based on the observations of both methane and sulphate concentrations in groundwaters at intermediate depths at various investigated sites. It could well represent the observations of the methane concentration at the Äspö site. With this representative value, the maximum depth of corrosion of the canister wall will be a few millimetres over 100 000 years.

The concentrations of sulphate and methane are site-specific and largely variable. The Olkiluoto site in Finland showed some very high methane values, up to 34 mmol L^{-1} (Pitkänen et al., 1996; 1999; 2004). The highest values are found in the deepest groundwaters sampled, at a depth of 860 m. At the repository depth the methane concentration is 10 – 15 mmol L^{-1}. Between 1 μmol L^{-1} and 18.6 mmol L^{-1} of methane in groundwater were found from the Canadian Shield (Sherwood-Lollar et al 1993a; 1993b). The measured methane concentrations in the groundwaters obtained from the Äspö site indicate that levels of up to 1 mM methane exist at about 440 m depth at the Äspö HRL (Kotelnikova and Pedersen, 1998a).

Methane occurs frequently in subterranean environments all over the globe, not only in crystalline rock environments. It is believed that the methane emanates from the mantle of the Earth. Evidences of an ongoing methane-generating process in deep Swedish granite have been published (Flodén and Söderberg 1994; Söderberg and Flodén 1991, 1992). Pockmarks in Baltic Sea sediments were found, indicating gas eruption, mainly of methane, from fracture systems in the underlying granite. To explain the 0.2 Ma interval of extreme global warming marking the start of the Eocene epoch about 55 million years ago and a massive and rapid (during a period of 10 ka) input of isotopically depleted carbon, Svensen at al. (2004) proposed that intrusion of voluminous mantle-derived melts in carbon-rich sedimentary strata in the northeast Atlantic may have caused an explosive release of methane—transported to the ocean or atmosphere through the vent complexes—close to the Palaeocene/Eocene boundary. Clark and Phillips (2001) used $^3He/^4He$ signatures as an evidence of the mantle- and crustal-derived geothermal fluids containing, among others, methane. As the methane is originated underneath from the mantle of the Earth, future climate changes will not be expected to have large impact on its concentrations in groundwaters.

The sulphate in groundwaters in crystalline rock may have different sources. In shallow groundwaters and in groundwaters at intermediate depths, the sulphate may come from possible modern seawater and ancient seawater intrusions (Smellie and Laaksoharju, 1992; Pitkänen et al., 2004).

The $\delta^{34}S$ values in some groundwaters located above a depth of 500 m also show marine signatures of about +20 ‰. The groundwaters at a depth of 470 m have values of $\delta^{18}O$ in sulphate oxygen close to those of the seawater, indicating that the marine water may well be present at the intermediate depths at the Äspö site (Wallin, 1992). The groundwaters located above a depth of 500 m at the Äspö site have been compared to the groundwaters in other investigated areas located peripheral to the Baltic Sea, e.g., Hästholmen, Forsmark, Finnsjön, where influences from both modern Baltic seawater and ancient Litorina water (7 400 – 2 500 years BP, Before Present) might be expected. The Äspö water compares well with the Finnsjön water, indicating they are marine-derived, but has been significantly modified by water/rock interactions and by other salt water sources (Smellie and Laaksoharju, 1992).

Injection of palaeo-seawater due to the isostatic movements in the Baltic Shield could possibly reach depths up to 400 – 500 m. Large amounts of saline waters with a marine origin have been observed in the Canadian Shield at depth of 400 m. The formation of these waters has been explained by seawater freezing, most likely in connection with one or more of the latest glaciations (Fritz and Frape, 1982; Herut et al., 1990). The sulphate observed at intermediate depths at the Olkiluoto site has been interpreted as from palaeo-seawater intrusion by Pitkänen et al. (2004).

Another source is the oxidation of sulphide minerals by the intrusion of the melt glacial water down to the intermediate depths. Signatures of old glacial meltwater has been observed in the groundwater in one borehole (KAS03:129-134m) at the Äspö site. The water showed a $\delta^{18}O = -15.8$ ‰ (SMOW) and $\delta^{2}H = -124.8$ ‰ (SMOW) in combination with an apparent ^{14}C age of 31 365 years (Smellie and Laaksoharju, 1992; Laaksoharju et al., 1999; Emrén, 1999), indicating cold climate recharge. Glacial meltwaters have also been observed at Äspö at various depths in the basement (Smellie and Laaksoharju, 1992; Wallin and Peterman, 1994). The Multivaritate Mixing and Mass Balance (M3) modelling also indicated oxidation of pyrite in association with glacial water intrusion as a possible source for the sulphate in the groundwater (Laaksoharju and Wallin, 1997).

The salt contents of very old deep groundwaters are sometimes extremely high, e.g. with chloride concentrations as high as 47 000 mg L^{-1} at depths of 1700 m at the Äspö site (Laaksoharju and Wallin, 1997) and 100 000 mg L^{-1} at a depth of 1862 m at the Höllviken site (Wallin, 1995). The concentrations of sulphate in those waters are also very high, up to 900 mg L^{-1} at the Äspö site. These saline waters are interpreted as representing a separate, deep, possibly regional groundwater system, which is almost stagnant except when intercepted by deeply penetrating conducting fracture zones.

The sources of the salinity of these waters are debatable with fluid inclusions, leaching of evaporates in sedimentary rocks, paleo-seawater intrusion, as well as rock/water interaction all having been proposed. As the deep groundwaters are usually stagnant the uncertainties related to their possible sources will not concern us much in this study.

The Fennoscandian Shield has been affected by a number of glaciations during the Quaternary Period (2.4 Ma) (Ehlers, 1996). Geological evidences show that these glacial events had a large impact on the topography, sedimentary load and erosion of the shield. The heavy ice load caused extensive isostatic movement of the basement, and it also changed the hydrogeological system that had a large influence on the groundwater formation, and on groundwater chemistry, which may be recognised in the fracture infilling and altered mimerals. Groundwater chemistry may also be influenced by the formation of permafrost (Vidstrand, 2003) and the ice sheet during the periods of glaciation, because part or all of the dissolved species may be freezed out from the ice and be increased in the groundwaters underneath the permafrost or ice sheet. During the retreat of the ice sheet after a glaciation, the meltwater may possibly recharge into the repository depth or more deeply and some sulphide minerals may be oxidised along the pathway of the meltwater (Guimerà et al., 1999). Considerable amounts of sulphate may be brought into the groundwaters.

The global sea level (Hallam, 1984) and the glacio-isostatic changes during the Quaternary glaciation and interglacial stages have altered the hydrogeological and hydrochemical conditions significantly in coastal areas and especially in the Baltic Sea region (Morén and Påsse, 2001) where there would have been co-variation of $\delta^{18}O$ and salinity with sea level changes (Stanfors et al., 1999). When a repository site is immersed under seawater, the saline water with a higher density will descend downward into the groundwater underneath (Westman et al., 1999) and increase the concentrations of sulphate.

The glaciations will occur cyclically in the future. During a time interval of 10^5 years as is considered in our model, a similar recurrence of the last Weichselian glaciation will be highly possible. All the processes mentioned above that have affected sulphate concentrations in the intermediate groundwaters would be very likely to influence the concentrations also in the future.

An overview of the groundwater compositions at different sites has revealed that both the sulphate and the methane concentrations vary largely from site to site, and that future climate changes could possibly increase the sulphate concentration. In addition to the representative value of the concentration that limits the corrosion rate (limiting concentration) used in our model, sensitivity analyses are needed to evaluate the robustness of the modelling results.

In the sensitivity analyses, three different cases are considered. The first case is the representative "central" case already discussed, with a limiting concentration of 1 mmol L^{-1}. This case may well represent the observations at the Äspö site. The second case has a limiting concentration of 4.5 mmol L^{-1} and corresponds to the observations at the Olkiluoto site. The third case has a limiting concentration of 10 mmol L^{-1} and is the worst case conceivable based upon the concentration data at different sites. It can be considered as a "hybrid" case of the sites of Äspö and Olkiluoto, in which the high methane and high sulphate concentrations are hypothetically assumed to co-exist at a single site.

The modelling results show that, while in the representative central case, the largest corrosion depth is only a few millimetres, in the worst case considered, however, more than half of the thickness of the canister wall (50 mm) may be corroded within 10^5 years.

Sensitivity analyses also revealed that the corrosion depth is most sensitive to the limiting concentration of either sulphate or methane, and is sensitive to some extent to the equivalent flow rate, and it is least sensitive to the fracture aperture and the geometry of the canister.

From the modelling results of this paper, the following conclusions can be drawn:

(1) With the representative central values of groundwater compositions measured in granitic bedrocks, after 10^5 years a few mm of the copper canister can be corroded by sulphide locally facing the opening of an intersecting fracture in the bedrock if sulphate reducing bacteria are present.

(2) The modelling results are sensitive to the sulphate or methane concentrations and to some extent to the equivalent flow rate Q_{eq}. The results are much less sensitive to the geometry of the system and the fracture aperture.

(3) The sulphate or methane concentration is highly variable from site to site and there are large uncertainties concerning future evolution of especially the sulphate concentration. Sensitivity analyses of this report indicate that, in the worst case conceivable, more than half of the thickness of the canister wall could possibly be corroded by the mechanism considered in this report.

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1 Introduction

In the Swedish concept of spent fuel repository, the spent fuel will be encapsulated in cast iron canisters that have an outer 50 mm thick corrosion protection shield made of copper. One of the aimed design criteria is that the corrosion life-time of the canister with a high probability should be larger than 100 000 years.

The integrity of the copper canister is important for the safe disposal of spent nuclear fuel in a final repository. With the exception of initial manufacture defects like a small hole on a canister wall, the radionuclide release from a canister will not start earlier than at the time of the canister breach. Such an event could occur either due to corrosion or mechanical failure. With a sufficiently long time of copper canister integrity, the hazardous radionuclides will have more time to decay to relatively less harmful species.

Copper can be corroded by several species: Under reducing conditions it will be corroded by HS^- to form chalcocite (Cu_2S) or covellite (CuS) (Beverskog and Puigdomenech, 1997). Under oxidising conditions it can be oxidised by oxygen to form cuprite (Cu_2O) or tenorite (CuO). In saline water it can be corroded to form copper chloride complexes (Puigdomenech and Taxén, 2000). Moreover, copper can also be corroded to a small extent by nitric acid formed by gamma-radiolysis of nitrogen compounds within the canister and in the moist air in the gap between canister and buffer during buffer re-saturation.

The mechanisms for copper corrosion have also been relatively well established. Copper can be corroded relatively uniformly on its surface by general corrosion. Copper can also be corroded by localised corrosion that attacks only special regions of the canister. Possible fissures or other weak areas of the canister. may be susceptible to crevice corrosion The selective corrosion on welds occurs where welding created a heterogeneous region. Stress corrosion cracking occurs in an aggressive chemical environment when corrosion is coupled with mechanical stress in certain mechanically loaded regions. Pitting is the corrosion in a small area with a relatively large penetration depth- (Taxén, 1996; Taxén, 2002a; Taxén, 2002b). Galvanic corrosion can occur when when dissimilar conducting materials are connected electrically and exposed to an electrolyte.

The rate of copper canister corrosion in the spent fuel repository environment is determined by several factors. As the groundwater in the fractures of the granitic crystalline bedrock at the repository depth is expected to be chemically reducing, corrosion of the copper canister by oxygen will be limited. During the periods of repository construction and shortly after the closure of the repository, oxygen can be trapped in the repository. The duration of those periods are on the order of a few hundred years (Puigdomenech et al., 2001). Moreover, the oxide layers formed, usually a duplex of Cu_2O and CuO, seem to be protective to prevent further oxidation. In pure water, copper will generally not be corroded by protons (Beverskog and Puigdomenech, 1997). The corrosion by chloride might be of importance for the repository, as saline groundwaters are encountered in various sites in Sweden (King et al., 2001). In the repository environment, the most important issue for copper corrosion could be the corrosion by sulphide ions. The non-adherent layer of chalcocite and covellite formed during corrosion has little passive protection to further corrosion. Even though sulphide concentration is generally low in the groundwater of a potential repository site, sulphate reducing bacteria (SRB) can reduce sulphate to sulphide by coupling the reaction with oxidation of organic carbon (Hallam et el., 2004). Total organic carbon levels in the deep groundwaters taken from the Äspö Hardrock Laboratory in southeast Sweden are usually on the order of a few mg·L^{-1} (SKB, 1999). On the other hand, at the Olkiluoto site in southwestern Finland methane concentrations in groundwaters at the repository depth could be as high as 15 mmol L^{-1} (Pitkänen, 2004). Methane is believed to emanate from the mantle of the Earth (e.g. Svensen at al. 2004) and can be used by SRB as an energy source. To study the long-term stability of the copper canister against corrosion, we need to address general corrosion of copper canister by sulphide produced through sulphate reduction by SRB.

In this report, previous works on copper canister corrosion carried out by the Swedish Nuclear Fuel and Waste Management Company (SKB) will be briefly reviewed. Our studies of copper canister corrosion mainly focus on production of sulphide by sulphate reducing bacteria and the subsequent possible corrosion of the copper canister by sulphide. A coupled transport/reaction model is developed to account for the transport of sulphide produced by microbial processes through the bentonite buffer and its reaction with the copper canister. The depth of copper canister corrosion can be calculated with the model and the corrosion rate is compared with the marginal life-time of the copper canister proposed by SKB (100 000 years).

As the concentrations of sulphate and methane are extremely site-specific and future climate changes may influence significantly the groundwater compositions at potential repository sites, sensitivity analyses have been conducted. We will have a broad perspective of the measured concentrations of sulphate and methane at different sites in Sweden and in Finland and some possible mechanisms (like the glacial meltwater intrusion and interglacial seawater intrusion) that may introduce more sulphate into the groundwater at intermediate depths during future climate changes. The impact of the large variation of the sulphate and methane concentrations at sites in the Fennoscandian Shield and the influences of their future possible evolution on copper canister corrosion will be accounted for in our model.

The objectives of this study are:

(1) To summarise the present status of SKB's work on corrosion of copper, and to identify if there are any specific factors that may influence copper canister corrosion which have not been sufficiently analysed;
(2) To develop a coupled transport/reaction model to study copper canister corrosion caused by the sulphide in the groundwater that is reduced from sulphate by SRB;
(3) To make sensitivity analyses with a broad perspective of the measured concentrations of sulphate and methane at different sites in Sweden and in Finland and some possible mechanisms that may introduce more sulphate into the groundwater at intermediate depths during future climate changes.

2 A short review of SKB's work on copper canister corrosion

Corrosion of copper canister was considered in the "Base Scenario" in SR 97 by SKB (1999), Swedish Nuclear Fuel and Waste Management Co. It was identified that an important chemical process in the repository evolution is external copper canister corrosion. Stress corrosion cracking could also occur in both copper canister and cast iron insert. The corrosion could possibly be influenced by radiation effects.

There are several recent technical reports of SKB that deal with corrosion of copper canister. Puigdomenech and Taxén (2000) have compiled thermodynamic data for solids and aqueous species in the system of Cu - H_2O - H^+ - H_2 - F^- - Cl^- - S^{2-} - SO_4^{2-} - NO_3 - NO_2^- - NH_4^+ - PO_4^{3-} - CO_3^{2-}. The main conclusions drawn from the study are: (1) Dissolved sulphide and O_2 in groundwater are the most harmful components from the copper corrosion point of view. Even though HS^- may react with the copper canister quantitatively, the sulphide concentrations in natural waters are usually low due to low solubilities of sulphide minerals, (2) Chloride can have negative effects on copper corrosion. When the Cl^- concentration is higher than 60 g L^{-1}, general corrosion of copper by reduction of protons must be considered.

The above mentioned study considered only the thermodynamic aspects of copper canister corrosion. The possible local increase of sulphide concentration produced through microbial processes like sulphate reduction has not been considered. Local high concentration of sulphide could not be completely ruled out when sulphate reducing bacteria are present (Pitkänen, 2004), and the sulphide thus formed usually can not precipitate, mainly due to the limit of the supply of the metal ions involved.

In the study of pitting corrosion of the copper canister, a mathematical model for the propagation of corrosion pits on copper has been described by Taxén (2002a; b). There is a minimum potential and an upper potential for pitting corrosion to occur. The minimum potential is strongly influenced by the composition of the bulk water. The upper potential is limited by the stability of an electrically conducting cathode material (cuprous oxide) where pitting is possible. As the stability of cuprous oxide against oxidation decreases with increasing pH, pitting of copper is less likely to occur at high pH.

The value of the window margin between the minimum and the upper potentials increases with temperature. Pitting is therefore less likely to occur at higher temperatures.

Of the common anions, chloride is the most aggressive species towards copper. Chloride forms strong complexes with monovalent copper and the chloride concentration is decisive for the value of the minimum pitting potential of copper. Pitting is more likely to occur in waters with high chloride concentrations.

Even though carbonate forms strong complexes with divalent copper, carbonate is more aggressive to copper at higher pH in the bulk water than at lower pH in the water in the pitting hole. Therefore high concentration of carbonate facilitates the general corrosion of copper more than the pitting corrosion. The transport of bicarbonate from the pit increases the transport of acidity from the pit and favours the formation of cuprous oxide in the pit. In this perspective, a high carbonate concentration may increase the value of the minimum pitting potential and decrease the value of the upper stability potential for cuprous oxide. Pitting is less likely to occur in waters with high carbonate concentrations.

Sulphate forms a divalent complex with copper. Sulphate is aggressive in pitting corrosion even though it is inert with respect to general corrosion. Pitting is more likely to occur in waters with high sulphate concentrations.

When the copper that is transported out of the pit is in monovalent form, porous cuprous oxide tends to precipitate inside the pit and pitting growth rate will in general decrease. When copper is transported out as bivalent species, precipitation occurs mainly outside the pit cavity and the pitting growth rate will be higher.

As the author concluded that pitting corrosion of copper is only limited by the corrosion potential, it is therefore extremely important that anoxic conditions prevail in the near-field of the repository. The author also claimed that when chloride contents approaching that of seawater, pitting is possible with high propagation rates at high pH values. Subsequent studies showed that there even exists an upper potential for pitting by chloride. Above this potential limit, propagation of the pit is prevented by excessive precipitation of large volumes of CuCl(s).

As the repository environments are chemically reducing, with the exception of the periods shortly after the closure of the repository and possibly during glacial retreat, pitting corrosion may not be a major threat to the integrity of the copper canisters.

The studies conducted by King et al. (2001) have been aimed at the understanding of copper canister corrosion under expected conditions in a deep geologic repository. Various areas are considered: the expected evolution of the geochemical conditions in the groundwater and of the repository environment, the thermodynamics of copper corrosion, corrosion before and during saturation of the compacted bentonite buffer by groundwater, general and localised corrosion following saturation of the bentonite buffer, stress corrosion cracking, radiation effects, the implications of corrosion on the service life of the canister. The conclusion drawn from the studies is that the original prediction made in 1978 of canister lifetimes exceeding 100 000 years remains valid. Several areas for further studies have been identified by the authors. One of them is the possible microbial activity near the highly compacted bentonite.

Under reducing conditions of the repository environment, sulphate reducing bacteria (SRB) may enhance copper corrosion by reducing sulphate to sulphide. Laaksoharju (1995) has studied the sulphate reduction in the Äspö Hardrock Laboratory tunnel in southeast Sweden. This study showed that sulphate reduction had taken place in the past and is most likely an ongoing process.

The anaerobic SRB can live in marine sediments, in the tunnel sections under the sea and in deep groundwaters. Sulphate reduction is an in-situ process but the resulting HS^--rich water can be transported to other locations. The sulphate reduction takes place more vigorously when the organic content in the groundwater is high. Some bacteria use hydrogen as an electron donor instead of organic carbon.

The author has identified geological, hydrogeological, hydrochemical, isotopic indications of sulphate reduction, as well as direct microbial evidences of the presence of sulphate reduction. Sulphate reduction to sulphate by SRB has also been observed at the Olkiluoto site in Finland (Pitkänen, 2004).

Pedersen (2000) has studied microbial processes related to radioactive waste disposal. The study focused mainly on identification of microbial processes near a final spent fuel repository. Sulphate reducing bacteria have not been specifically considered in this study.

3 General corrosion of copper by sulphide

3.1 Thermodynamic aspects of copper corrosion

In this section, we will consider only general corrosion of copper by sulphide. The reason for this consideration is that the sulphate in deep groundwater with a relatively high concentration may be reduced by SRB. The consequences will be the general corrosion of copper by sulphide.

General corrosion is defined as a uniform corrosion of a metal on its surface. From a thermodynamic point of view, the prerequisite for general corrosion of copper is the existence of oxidising agents that can accept the electrons released from the oxidation of Cu(0) to either Cu(I) or Cu(II). Formation of stable aqueous complexes or stable mineral phases of Cu(I) or Cu(II) will enhance the process of general corrosion. Thermodynamically, in the repository environment, sulphide in the groundwater is the most detrimental species for copper corrosion. The formation of the very insoluble corrosion products like chalcocite, Cu_2S, drives the half-cell potential for copper reaction with sulphide to such a low value that proton can become an electron acceptor:

Anode reaction:	$2Cu(s) + HS^- = Cu_2S(s) + H^+ + 2e^-$	$Eh^o = -0.506$ V
Cathode reaction:	$2H^+ + 2e^- = H_2(g)$	$Eh^o = 0$ V

The overall reaction would be

$$2Cu(s) + HS^- + H^+ = Cu_2S(s) + H_2(g) \qquad Eh^o = 0.506 \text{ V}$$

The upper ranges of the concentrations of H^+, HS^- in the groundwaters in the Äspö area in southeast Sweden are 10^{-8} and $3 \cdot 10^{-5}$ mol L^{-1}, respectively (King et al., 2001). The upper range of dissolved H_2 concentration in both groundwaters in the Swedish granitic bedrock (Kotelnikova and Pedersen, 1998; 2000) and at the Olkiluoto site in Finland (King et al., 2001; Pitkänen et al., 1996; Pitkänen et al., 1999) is $2.2 \cdot 10^{-5}$ mol L^{-1}. With a Henry's law constant of $8.17 \cdot 10^4$ atm/(kmol/kmol) (Perry and Green, 1997), the partial pressure of H_2 can be calculated to be $3.2 \cdot 10^{-2}$ atm. When these concentrations are used in Nernst equation,

$$Eh = Eh^o - \frac{RT}{nF} \ln \frac{[\mathrm{Red}]}{[\mathrm{Ox}]}$$

where Eh is half-cell potential (V),
Eh^o is standard half-cell potential (V),
R is ideal gas constant (8.3143 J K^{-1} mol^{-1}),
T is absolute temperature (K),

n is number of electrons involved in the half-cell reaction,
F is the Faraday constant (96485 C eqv^{-1}),
[Red] is concentration of the reductant (M),
[Ox] is concentration of the oxidant (M).

the anode and cathode potential will be –0.609 and –0.429 V, respectively. The anode potential obtained here is in good agreement with other literature values (Puigdomenech and Taxén, 2000). The total corrosion reaction will have a potential of 0.180 V. The positive sign of the potential implies that the reaction is favoured to proceed in the direction from left to right, i.e., the proton can oxidise the copper when sulphide reacts with Cu^+ to form chalcocite. However, the amount of copper that can be corroded will be limited by the supply of sulphide. The above scoping calculations are based on a sulphide concentration measured in the groundwater. When sulphate reducing bacteria mediate the conversion of sulphate to sulphide more sulphide can become available. Local sulphide concentration could be much higher and the corrosion reaction will be even more favoured thermodynamically, as will be discussed later.

3.2 Kinetic aspects of copper corrosion

Most of the electrochemical reactions proceed only at finite rates. For cathode reactions finite rates imply an accumulation of electron at the electrode and a negative potential change of the electrode. This is called cathodic polarisation. Similarly, finite rates of reactions at an anode result in a deficiency of electron and thus an anodic polarisation. With anodic polarisation corrosion of a metal usually occurs at a potential higher than the thermodynamically predicted potential at a finite rate.

Another kinetic aspect of metal corrosion is passivity. The corrosion rate should generally increase with an increasing potential. For many metals there is a potential range in which the corrosion rate decreases as the potential increases. Passivity is caused by formation of thin, protective oxides or other corrosion-product surface films that act as a barrier to the anodic dissolution reaction (Jones, 1992).

Passive film formation has great significance to the mechanisms of copper corrosion. For the copper canister in a repository, the surface films forming in the repository environment largely determine the susceptibility of copper to the different forms of corrosion (Hilden, et al., 1999). At relatively high chloride concentrations, copper does not form protective solid phases. Copper is therefore more susceptible to corrosion in saline groundwater. The non-adherent layer of chalcocite (Cu_2S) or covellite (CuS) formed during copper corrosion by sulphide has little protection to further corrosion, and copper is corroded by sulphide both through general corrosion and pitting corrosion (Thiery and Sand, 1995).

3.3 Corrosion in the repository environment

Corrosion of the copper canister in the repository environment has been extensively studied by SKB as well as by SKI (e.g. King et al., 2001; Hermansson and Eriksson, 1999). Three main types of situations were identified also by Sjöblom et al. (1995): (1) Under oxidising and low chloride conditions, passivating oxide type of layers may form on the copper surface; (2) Under oxidising and high chloride conditions, the species formed may all be dissolved; (3) Under reducing conditions, non-passivating sulphide type layers may form on the copper surface.

During the extremely long period of repository evolution, chemically reducing conditions prevail. Oxidising conditions may occur during the deposition of the canister and shortly after the closure of the repository. It can also possibly occur during the deglaciation period when surface water from the ice-melt may penetrate into the depth of the canister under a higher hydrostatic pressure of the ice sheet. Modelling results of Guimerá et al. (1999), however, indicated that the minerals containing ferrous iron (such as biotite, chlorite, and pyrite) buffer the redox condition and the redox front will probably not penetrate into the repository depth during an intrusion of glacial meltwater.

Current composition of the groundwater in the Swedish crystalline rocks is a result of interaction and mixture of different waters: the carbonate-rich meteoric water infiltrated from the surface, sea waters from various sources, and saline water (Ca-Na-Cl brine) intruded from underneath under the influence of hydrothermal activity during early Phanerozoic to Precambrian age. Glaciation cycles will influence the salinity of the groundwater, but the salinity will probably not increase significantly (Pitkänen et al., 1999).

The most important process of the copper canister corrosion will probably be the corrosion by sulphide under reducing conditions. As no effective passivating film is expected to be formed by the corrosion products chalcocite or covellite, the only limiting factor for the corrosion is the low concentration of sulphide in the groundwater.

The sulphide concentration in the groundwater surrounding a repository given in SKB's SR97 reports is about 0-0.3 mmol L^{-1} at the closure of the repository. It will decrease to about $5.0 \cdot 10^{-3}$ mmol L^{-1} after resaturation in less than 100 years after closure, and approaches 0-0.03 mmol L^{-1} thereafter. At the Olkiluoto site in Finland, sulphide concentration of about 0.3 mmol L^{-1} has been found. Scoping mass balance calculations show that the copper canister will be corroded to a maximum of 0.2 μm/yr without the resistance of the bentonite buffer, and orders of magnitudes lower with the buffer present, by general corrosion. This implies that the canister life-time is $2.5 \cdot 10^{5}$ years, even without the buffer.

The measured sulphate concentrations in the groundwater are several orders of magnitudes higher than the sulphide concentration. Sulphate reduction to sulphide is kinetically very slow without the assistance of microbes. Purely thermodynamic calculations using the $p\varepsilon^{o}$ value in the literature (Stumm and Morgan, 1996) show that, at Eh = -0.3 V, concentrations of SO_4^{2-} and HS^{-} would be equal at pH = 8.28. When pH becomes higher, the sulphate species will dominate. This pH value is within the measured range of the groundwater and thermodynamically the sulphate/sulphide concentration ratio will be very sensitive to the change of pH. Field observation data obtained from different site investigations show that most of the cases the equilibrium has not been achieved. Locally colonised microbes may catalyse the reaction and bring the reaction of sulphate reduction to equilibrium or near equilibrium. As the sulphide species is highly reactive, it may be difficult to detect locally high sulphide concentrations. However, relatively high sulphide concentrations (0.4 mmol L^{-1}) have been observed at the Olkiluoto site in Finland.

4 Microbial processes in the repository environment

Microbes are unicellular living organisms. All organisms in the domains Bacteria and Archaea are microbes. Most of the branches of the domain Eukarya are microbes as well. Microbes are ubiquitous on Earth as long as there is water and temperature is not extremely low or high. Microbial activity generally increases with the temperature in the range of –15 to 113°C (Pedersen and Ekendahl, 1990; Pedersen, 2001).

Most of the microbes can theoretically survive under the repository conditions, with the exception within a saturated bentonite, where the water activity is probably too low to support colonies of microbes. Some species, however, may not survive. Green bacteria need photosynthesis for their growth and therefore cannot survive deep under the ground surface. Some pathogenic microbes and all obligate parasitic microbes need multi-cellular host for their survival and are naturally absent in the repository environment (Pedersen, 2000).

All known forms of life on Earth require liquid water for growth, although they may be able to exist in a viable resting state when water is unavailable. To grow, most bacteria require a water activity of at least 0.98, which is equivalent to seawater (Brown and Sherriff, 1998). At start the bentonite buffer will have a water activity of 0.75 that eventually reaches 0.96 at a water content of 25%. This water activity should be low enough to exclude all bacteria that do not form spores (Pedersen and Karlsson, 1995).

All microbes require carbon and nitrogen as well as some other elements such as nutrients to build their biomass. They also need energy for their metabolism. The nutrient cycles mediated by living systems indeed make much of the environmental chemistry dependent upon the activities of living systems.

Microbes are capable of using almost any kind of energy that becomes thermodynamically available for biochemical reactions (Pedersen, 2000). In doing so, they usually speed up many redox reactions that are otherwise kinetically slow. Therefore microbes in nature function like catalysts to many environmental reactions. The energy sources for their growth can be organic carbon as well as inorganic reducing species like ferrous iron and dissolved hydrogen. Organic carbon (excluding methane) levels in the deep groundwaters at the Äspö site are usually on the order of a few $mg \cdot L^{-1}$ (Smellie and Laaksoharju, 1992). Methane concentration in Äspö groundwater ranges from 0.02 to 1.0 mmol L^{-1}, which is much higher than the total concentration of the other organic carbon compounds. The methane concentration in groundwater in a Finnish site is on the order of 0.3 to 388 μmol L^{-1} (Pitkänen et al., 1999; 2004). The concentration of ferrous iron in the Äspö groundwater is usually two orders of magnitude lower than that of methane (Smellie and Laaksoharju, 1992). The concentration of dissolved hydrogen in the Äspö groundwater is also one order of magnitude lower than that of methane (Kotelnikova and Pedersen, 1998). Methane is a mobile compound that easily diffuses in groundwater. It is geologically produced and is continuously released from the mantle of the Earth to its crust (Stevens and McKinley, 1995). In this study, we will consider methane as an energy and carbon source for microbial activities.

The most relevant microbes to copper corrosion under anaerobic conditions could be the sulphate reducing bacteria (SRB), which catalyse the reduction of sulphate to sulphide. They may be present in the groundwater, embedded in the interface between the bentonite buffer and the rock wall. If they are indigenous initially in the clay that makes up the bentonite buffer, they may also be present on the side of the bentonite buffer close to the canister wall, because small amounts of water may exist in the interface between the buffer and the canister wall. They will, however, probably not survive inside the bentonite buffer because of the low water activity there.

Sulphate reducing bacteria were directly observed in the groundwater at the site of the Äspö Hardrock Laboratory in Southeastern Sweden (Kotelnikova and Pedersen, 1998; 2000). There were geological, hydrogeological, isotopical as well as groundwater chemical indications of sulphate reduction (Laaksoharju, 1995). Sulphur and oxygen isotope studies also showed evidences of sulphate reduction by SRB to sulphide in the groundwater of deep granitic bedrock (Wallin, 1992).

There are two basic types of biological nutrition that are associated with the carbon cycle. The first involves the fixation and reduction of carbon dioxide to carbohydrate and the oxidation of water to oxygen in the presence of external inorganic energy source or solar energy source like in photosynthesis. This kind of nutrition is called *autotrophy* (self-feeding). Under the subsurface environment near a repository, photo energy is not available for microbes to fix inorganic carbon for their growth. The microbes have to obtain their energy and nutrient solely from geological resources. Both carbon and nitrogen required for cell biomass can be derived from dissolved carbon dioxide (mainly in the form of bicarbonate) and dissolved inorganic nitrogen species. *Heterotrophy* is the nutrition of the reverse process of autotrophy in which organic materials are oxidised to carbon dioxide and water in the presence of oxygen. Under anaerobic conditions of the repository environment, other electron acceptors have to be available for the oxidation of organic carbon.

Growth of microbial culture undergoes several phases (Coulson and Richardson, 1994). The initial phase, the so-called lag phase, represents a period of time in which changes occur only in the internal organisation of the individual cells and there is no apparent development of the number of the cells. The cause of the delay of development can be change in food type or concentration, change in pH or the presence of inhibitor. This phase is important mainly in batch cultures. In continuous cultures the microbes may have already fully adapted to their environment and, after a period of acceleration, are growing exponentially, which is the third phase of growth.

In the exponential period of growth, the growth rate is directly proportional to the amount of the microbes given by Malthus' law:

$$\frac{dX}{dt} = \mu X$$

where X is the "microbial density" or the "biomass concentration", μ is the specific growth rate of the culture.

The concentration change with time will be

$$X = X_0 \exp(\mu t)$$

where X_0 is the initial concentration.

The exponential growth cannot be sustained indefinitely and for one reason or another will lead to the stationary phase. Pearl and Reed (1920) proposed an equation by adding an inhibition term at high biomass concentration:

$$\frac{dX}{dt} = kX - k\gamma X^2$$

where k is the maximal specific growth rate of the culture and γ is the reciprocal of the final biomass concentration as the solution of this equation approaches an asymptote $X_m = 1/\gamma$ as t approaches infinity.

In Monod kinetics, a saturation-isotherm type of equation, similar to Langmuir isothermal adsorption equation, is used to relate the growth rate of a micro-organism culture to the prevailing feed concentration:

$$\mu = \frac{\mu_m S}{K_s + S}$$

where μ is the specific growth rate, S is the feed or substrate concentration, μ_m is a constant known as the maximum specific growth rate and K_s is the Monod constant. The Monod equation is the simplest in a series of different equations used for microbial growth rates. Other more complicated expressions are listed in Coulson and Richardson (1994).

5 Coupled transport/reaction modeling

5.1 Conceptual model

A low corrosion rate of the copper canister is ensured by low concentrations of oxygen and sulphide in the groundwater. Oxygen concentration will be negligibly low during almost all the evolving period of the repository, with possible exceptions if secondary water radiolysis becomes important after a canister failure (Liu et al., 2002). The sulphide concentration in the groundwater in the granitic bedrock is also generally low (King et al., 2001). When SRB exist in the groundwater, it might be possible to have locally high concentrations of sulphide. Should the sulphide be transported to the copper canister surface, the corrosion rate of the copper canister could be significantly enhanced. To quantify the extent of copper canister corrosion aided by microbial processes, we consider the following conceptual situation:

A fracture in the granitic bedrock intersects the deposition hole in a repository. As the bentonite buffer is unlikely to be coincidently damaged mechanically at the fracture opening, groundwater in the fracture will flow surrounding the bentonite buffer. Corroding species like sulphide will be transported only by molecular diffusion through the bentonite buffer to the canister surface.

We assume that sulphate reducing bacteria have colonised at the interface between the bentonite buffer and the rock at the opening of the intersecting fracture. Sulphate will be reduced to produce locally high concentration of sulphide at the interface. Part of the produced sulphide will diffuse through the bentonite to corrode the copper canister, and the rest will be swept downstream by the seeping water. Inside the bentonite buffer, no bacteria are assumed to exist or be active because they are unlikely to survive at places with very low water activity. The conceptual model is schematically shown in Figure 1.

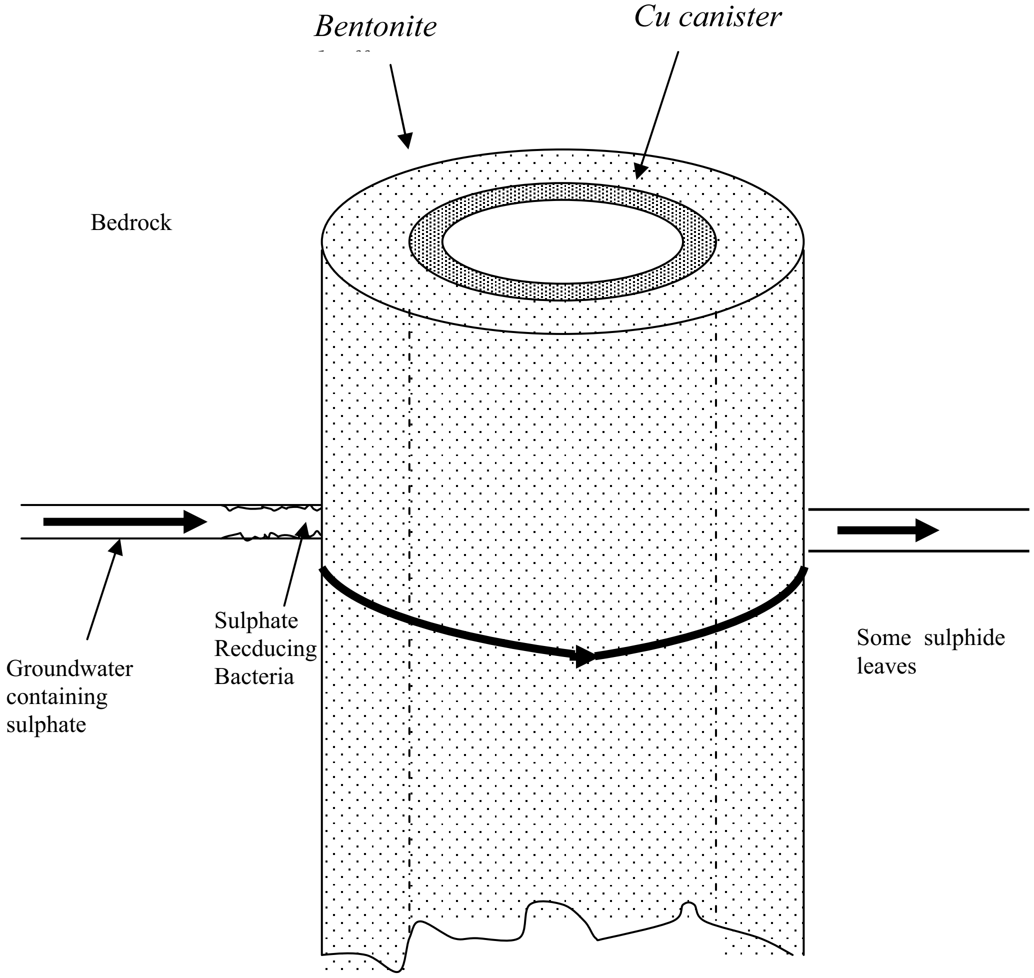

Figure 1. Conceptual model for the coupling of sulphate reduction by microbes and sulphide transport through bentonite buffer to copper canister.

5.2 Modelling of the bacteria aided sulphate reduction

In biologically mediated reactions, the living cells catalyse the reactions through the activity of their enzymes. The enzyme (E) first form a complex with the substrate (reactant, denoted by S), the complex then decomposes to release the enzyme and form the product (P):

$$E + S \Leftrightarrow E\text{-}S \Leftrightarrow E + P$$

The kinetics of this reaction is expressed by the Michaelis-Menten equation:

$$V = V_{\max} \frac{[S]}{[S] + K_M}$$

where V is rate of reaction (mol s^{-1}),
$V_{\max}$ is maximum rate of reaction (mol s^{-1}),
$[S]$ is concentration of the substrate (mol m^{-3}),
K_M is the Michaelis constant (mol m^{-3}).

Biological redox reactions may take several steps of electron transfer towards the final products to maximise the efficiency of the reactions and carry the reactions to an end that usually do not proceed at all without the catalysis of bacteria. For example the groundwater in the granitic bedrock contains significant concentrations of sulphate ions. Reduction of sulphate is inhibited in sterile conditions. However, sulphate reducing bacteria can overcome the kinetic hindrance and generate sulphide, if they are supplied with adequate organic substrates. Methane is an important species (Hallam et al., 2004) since it can serve both as an electron donor and as a carbon source for the growth of the biomass. The concentration of methane in the groundwater is much higher than that of the other competing reducing species. Stoichiometrically, the coupled redox reaction is:

$$SO_4^{2-} + CH_4 + H^+ = HS^- + CO_2 + 2H_2O.$$

There is in general a lack of data for the kinetics of the reactions aided by microbial processes, especially for the microbial activities in groundwater in deep granitic bedrock. In marine bottom sediments, Jørgensen (1978) assumed that one SRB cell reduces $2.5\cdot10^{-12}$ mol SO_4^{2-} 24 h^{-1}, which is $2.89\cdot10^{-17}$ mol SO_4^{2-} s^{-1} $cell^{-1}$ (Mudryk et al., 2000). The same range of reduction rate was also observed in sea bed sediments sampled above the Äspö HRL tunnel (Laaksoharju, 1995). The number of SRB in the Äspö groundwater ranges from 10 to 2400 cells mL^{-1} (Laaksoharju, 1995; Pedersen, 2000). Additional bacteria can be attached to the fracture walls. The sulphate concentration in the Äspö groundwater is $(0.01\text{-}4.2)\cdot10^{-3}$ mol L^{-1}. With these data scoping calculations show that the SRB can probably completely reduce the sulphate in their vicinity in time scales of years, which may be considered to be fast in relation to other processes.

We assume in our following modelling that the rate of sulphate reduction by SRB is fast and is limited by the supply of either sulphate or methane, whichever has the lower concentration. This is equivalent to assuming that the local sulphide concentration will be equal to either the concentration of sulphate or methane. Other reactions involving sulphide ions are neglected, e.g. reaction with dissolved iron. This may be regarded as a conservative assumption which will provide an upper bound of the the influence of SRB activity.

5.3 Modelling transport of corroding species through the bentonite buffer

When the sulphate in the groundwater is reduced to sulphide in the intersecting fracture at the interface between the rock and the bentonite buffer, sulphide-containing groundwater will flow around the bentonite buffer. Part of the sulphide will be transported away by the groundwater flow in the fracture. The remaining will be transported by diffusion through the bentonite buffer to corrode the copper canister.

The sulphide diffuses through the fracture opening into the bentonite buffer. Inside the bentonite buffer it will be transported along both the radial and axial directions of the bentonite buffer. The transport is essentially two-dimensional with cylindrical symmetry. The opening of a single fracture in the granitic rock is on the order of a fraction of a millimetre although it locally can be larger (Neretnieks, 2002). Compared with the vertical dimension of the deposition hole, the fracture is relatively small. The width of the fracture (the horizontal dimension) is usually much larger than the horizontal dimension of the deposition hole. As the fracture opening is small, the concentration or the flux through the opening can be assumed to be constant. The boundary condition on the surface at the outer radius of the bentonite buffer is a constant flux at the area of the narrow fracture opening (which forms a narrow strip surrounding the bentonite buffer), and zero flux in other regions on this surface. At the inner radius of the bentontite buffer, that is also the outer radius of the copper canister, the concentration of sulphide is assumed to be zero because the corrosion reaction rate is fast. The boundary condition for the vertical dimension is that, sufficiently far (a few metres) above or below the fracture opening, the concentrations can be assumed to be zero.

The production of sulphide is determined by how much sulphate can reach the microbial population and it can be described by $N_{tot} = c_0 \cdot Q_{eq}$ in which c_0 is the approaching sulphate concentration (mol m^{-3}) and Q_{eq} is the equivalent flow rate of water in the fracture (m^3 s^{-1}) and can be obtained by solving the diffusion equation for the groundwater flowing around the canister (Neretnieks, 1979; 1985). Part of the products diffuses into the clay. The rest leaves with the groundwater.

We first solve for the concentration profile in the clay. Mathematically the transport equation will be:

$$\begin{cases} \dfrac{\partial^2 c}{\partial r^2} + \dfrac{1}{r}\dfrac{\partial c}{\partial r} + \dfrac{\partial^2 c}{\partial z^2} = 0 & \mathit{for}\ \ (r_{in} < r < r_{out},\ -L < z < L) \\ \dfrac{\partial c(r,-L)}{\partial z} = 0 & \\ \dfrac{\partial c(r,L)}{\partial z} = 0 & \\ c(r_{in}, z) = 0 & \\ -D\, b 2\pi\, r_{out} \dfrac{\partial c(r_{out}, z)}{\partial r} = N & \mathit{for}\ \ -b < z < b,\ \mathit{elsewhere}\ \ 0 \end{cases} \tag{1}$$

where

- c is concentration of the corroding species in the bentonite buffer (mol m^3),
- r is radial dimension of the bentonite buffer (m),
- z is axial dimension of the bentonite buffer (m), and $z = 0$ at the horizontal plane of fracture intersection,
- r_{in} is inner radius of the bentonite buffer (m),
- r_{out} is outer radius of the bentonite buffer (m),
- L is half of the canister length (m),
- b is half of the aperture opening (m),
- D is diffusivity of sulphide in the bentonite buffer, and
- N is the flux of sulphide into the bentonite buffer through the fracture opening (mol m^{-2} s^{-1}).

The equations describe a case where there is a copper canister of length $2L$ is surrounded by clay and is deposited in a borehole. At the middle of the canister there is a fracture in the rock that intersects the borehole. At the mouth of the fracture there is a population of microbes that instantly catalyse the reaction of sulphate and the reducing species. Part of the sulphide formed diffuses in to the clay over the fracture aperture $2b$. $2N$ is the production rate of the part of sulphide that is assumed to diffuse into the clay and further to the surface of the copper canister where it reacts. At both ends of the copper canister it is assumed that no sulphide escapes. For symmetry reasons we need only consider the region $0 < z < L$.

The analytical solution for a very similar case where z extends to infinity is given by Carslaw and Jaeger, (1959; p.221). Neretnieks (1986) solved the above system both for the radially symmetrical case and for a case where the inner and outer radii are similar in size. This simplifies to linear instead of radially converging diffusion. In both models the possible escape of sulphide at the ends of the deposition hole can also be accounted for. The linear model leads to a somewhat simpler solution. The simpler solution with no escape at the ends is given below. For the present application the errors in using the simpler equation are small. Denoting $r_{out} - r_{in}$ by dr, and y the distance from the outer radius inward,

$$c\,\frac{b2\pi\, r_{out} D}{N} = -\frac{b\,(dr-y)}{L} - 2\sum_{m=1}^{\infty}\frac{\sinh(m\pi\,(dr-y)/L)\cos(m\pi\, z/L)\sin(m\pi\, b/L)}{L(m\pi/L)^2\cosh(m\pi\, dr/L)} \tag{2}$$

The rate of copper canister corrosion can be evaluated from the concentration gradient at the surface of the canister. The gradient in the y direction is

$$\frac{\partial c}{\partial y}\frac{b2\pi\, r_{out} D}{N} = -\frac{b}{L} - 2\sum_{m=1}^{\infty}\frac{\cosh(m\pi(dr-y)/L)\,\cos(m\pi\, z/L)\,\sin(m\pi\, b/L)}{m\pi\,\cosh(m\pi\, dr/L)} \tag{3}$$

It may be noted that on the right hand side of the equations only geometric data are involved. Therefore the concentration profile in the region as well as the concentration gradient at e.g. the canister surface can be determined in relative terms.

5.4 Input data

To calculate the rate of copper canister corrosion, several input data are needed in the above model. The inner and outer radii (r_{in} and r_{out} in the equations) of the bentonite buffer are taken to be 0.53 and 0.88 m, respectively (SKB, 1999). The diffusivity of the corroding species in the bentonite buffer is assumed to be $1\cdot10^{-10}$ m^2 s^{-1}. The molar mass of copper and the density of native copper are two constants, with values of 0.06354 kg mol^{-1} and 8920 kg m^{-3} respectively.

Depending on different assumptions of the kinetics of sulphate reduction reaction by microbes, the concentration of the corroding species (sulphide in our case) in the surrounding groundwater, denoted as c_0 in the model, can vary. As has been discussed in Section 4.2, the rate of sulphate reduction to sulphide by microbes is relatively fast, and the concentration of sulphide in the groundwater in the fracture where microbes are assumed to be colonised would be equal either to the concentration of sulphate, or to the concentration of methane (the major reductant for the reduction reaction), whichever has a lower concentration. Other possible reactants like dissolved hydrogen gas, ferrous iron, are expected to play a less important role and have been neglected here.

The sulphate concentration in the groundwater in the Swedish Äspö area ranges between 0.01 – 4.2 mmol L^{-1} (SKB, 1999). The methane concentration in the groundwater in the same area varies between 0 – 1 mmol L^{-1} (Kotelnikova and Pedersen, 1998). In the groundwater at the Finish Olkiluoto site, the concentration of sulphate ranges between 0 – 5.2 mmol L^{-1}, and the concentration of methane varies between 0.004 – 17.9 mmol L^{-1} (Pitkänen et al., 1999). In our sample calculations, a central value of 1 mmol L^{-1} (1 mol m^{-3}) has been used to represent the concentration of sulphate or methane in the approaching groundwater in the fracture. This is the value for c_0.

The equivalent flow rate transferring solute in a fracture, Q_{eq}, is taken as 0.01 $m^3\ a^{-1}$. The fracture aperture is assumed to be 1 mm. The total axial length of a canister is assumed to be 5 m.

The various input data used in the modell are listed in Table 1. They are deemed to be within the range of values that can be expected for a repository and are used as representative “central” values.

Table I **The input data**

Notation	Description	Value
Q_{eq}	equivalent flowrate transferring solute to where fracture aperture of width $2b$	0.01 $m^3\ a^{-1}$
c_o	conc. of corroding species in the surrounding groundwater	1 mol m^{-3}
b	half aperture of facture	0.5 mm
r_{in}	inner radius of bentonite buffer	0.53 m
r_{out}	outer radius of bentonite buffer	0.88 m
L	half canister length	2.5 m
D	diffusivity of corroding species in bentonite buffer	$1 \cdot 10^{-10}$ $m^2\ s^{-1}$
M_{Cu}	molar mass of copper	0.06354 kg mol^{-1}
ρ_{Cu}	density of native copper	8920 kg m^{-3}

5.5 Sample calculations for linear diffusion

Figure 2 shows the relative concentration in the clay. At the mouth of the fracture (the left corner) the concentration related to the total inflow of sulphide is obtained from equation (2) by evaluating at $y = 0$, $z = 0$ which gives $c\,\frac{2\pi\, r_{out} D}{N} = 5.01$.

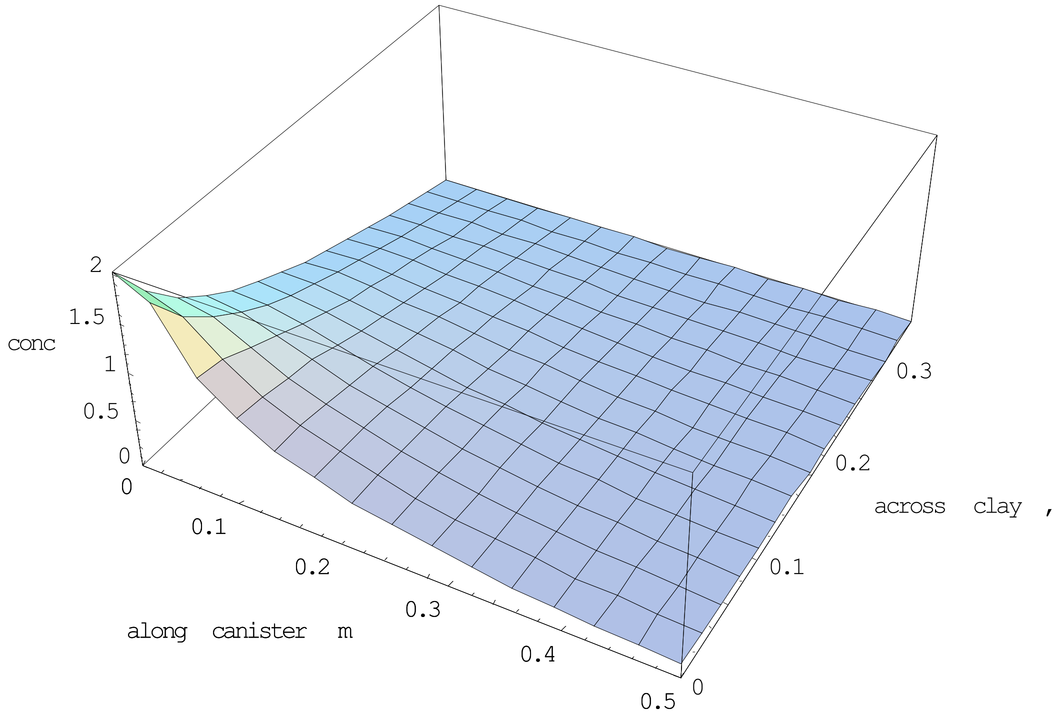

Figure 2. Concentration profile (in arbitrary units) in the clay between the canister and the fracture, obtained from the simpler linear model.

The relative concentration gradient at the surface of the canister is shown in Figure 3. The gradient is relative to the average gradient along the whole surface of the canister. This implies that if we know the average corrosion rate which is obtained from the total flux of sulphide to the canister then the corrosion rate at any location on the canister is directly obtained by multiplication with the relative rate. In this case the rate of corrosion just opposite the fracture in the rock will be 7 times larger than the average rate.

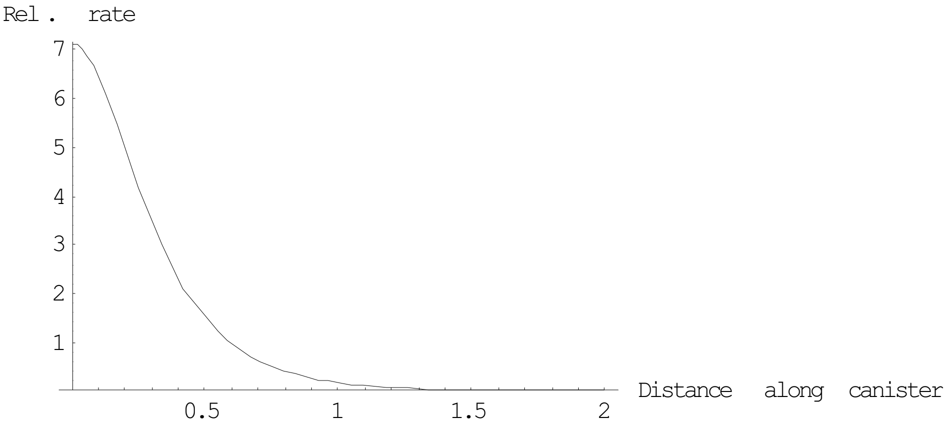

Figure 3. The relative concentration gradient at the surface of the canister, obtained from the simpler linear model.

We now need to determine the rate of supply of sulphide N to the clay. The total amount of sulphide produced is $N_{tot} = Q_{eq}\,c_0$. Q_{eq} is the flowrate of water that is fully depleted of the concentration c_0 of sulphate or methane, whichever is the smaller. Some of the sulphide is carried away with the water $N_{away} = Q_{eq}\,c_i$. The other part N_{clay} goes into the clay. From the above results $c_i \dfrac{2\pi r_{out} D}{N_{clay}} = 5.01$ which gives

$$N_{clay} = c_i \frac{2\pi r_{out} D}{5.01} = N_{tot} - Q_{eq} c_i \qquad (4)$$

c_i and N_{clay} are now obtained to be 0.590 mol m^{-3} and 0.0021 mol a^{-1} respectively. This means that in this example 41% of the produced sulphide enters the clay, and the rest is carried away by the water. The average rate of corrosion can be calculated by

$$R = \frac{2D \left.\dfrac{\partial c}{\partial r}\right|_{r=r_{in}} M_{\mathrm{Cu}}}{\rho_{\mathrm{Cu}}} \qquad (5)$$

where R is the rate of copper canister corrosion (m s^{-1});
D is diffusivity of the corroding species in bentonite (m^2 s^{-1});
M_{Cu} is molar mass of copper (kg mol^{-1});
and ρ is density of copper (kg m^{-3}).

The factor of 2 accounts for that one mole of sulphide can react with 2 moles copper to form chalcosite (Cu_2S). The calculated average value for R is $3.50\cdot10^{-9}$ m a^{-1} which during 10^5 years would lead to 0.35 mm average corrosion and 7 times more at the position directly opposite the fracture i.e. 2.45 mm.

5.6 Sample calculations for radially-converging diffusion

In this subsection, we will present some results of sample calculations for radially-converging diffusion. The solution for the transport equation (1) in cylindrical coordinates is (Carslaw and Jaeger, 1959; p.221):

$$c = -\frac{4N_{clay}L}{\pi^3 bDr_{out}} \sum_{m=0}^{\infty} \frac{F_0(\beta_m r_{in};\ \beta_m r)}{(2m+1)^2 F_1(\beta_m r_{in};\ \beta_m r_{out})} \cos(\beta_m l)\sin(\beta_m z) \tag{6}$$

in which

$l = L - b$;

$\beta_m = (2m+1)\pi/(2L)$;

$F_0(x; y) = I_0(x)K_0(y) - K_0(x)I_0(y)$;

$F_1(x; y) = I_1(x)K_0(y) + K_1(x)I_0(y)$;

and I_0 and K_0 are modified Bessel functions of the first and second kind and of zero order, and I_1 and K_1 are the same functions of first order. Other notations have the same meanings as in the previous sections.

When the concentration at the fracture opening toward the outer surface of the bentonite is designated as c_i, Eq. (6) becomes:

$$c = c_i \frac{\displaystyle\sum_{m=0}^{\infty} \frac{F_0(\beta_m r_{in};\ \beta_m r)}{(2m+1)^2 F_1(\beta_m r_{in};\ \beta_m r_{out})} \cos(\beta_m l)\sin(\beta_m z)}{\displaystyle\sum_{m=0}^{\infty} \frac{F_0(\beta_m r_{in};\ \beta_m r_{out})}{(2m+1)^2 F_1(\beta_m r_{in};\ \beta_m r_{out})} \cos(\beta_m l)\sin(\beta_m L)} \tag{7}$$

From a similar mass balance as shown by Eq. (4), the relation between c_0 (the concentration of the corroding species in the approaching groundwater) and c_i (the concentration at the fracture opening facing the bentonite) will be:

$$c_i = \frac{Q_{eq}}{Q_{eq} - (\pi^3 bDr_{out})/(4L\Sigma_i)} c_0 \tag{8}$$

in which Σ_i is the summation in the denominator of the right-hand side of Eq. (7).

The extent of copper canister corrosion can be evaluated from the concentration gradient at the surface of the canister. The gradient in the r direction is:

$$\left\{ \frac{\partial c}{\partial r} = c_i \frac{\displaystyle\sum_{m=0}^{\infty} \frac{-\beta_m F_1(\beta_m r; \beta_m r_{in})}{(2m+1)^2 F_1(\beta_m r_{in}; \beta_m r_{out})} \cos(\beta_m l)\sin(\beta_m z)}{\displaystyle\sum_{m=0}^{\infty} \frac{F_0(\beta_m r_{in}; \beta_m r_{out})}{(2m+1)^2 F_1(\beta_m r_{in}; \beta_m r_{out})} \cos(\beta_m l)\sin(\beta_m L)} \right. \tag{9}$$

The corrosion depth can then be obtained from Eq. (5).

The concentration profile of the corroding species inside the bentonite buffer with a radially-converging diffusion is shown in Figure 4. The corrosion depth of the copper canister after 10^5 years is shown in Figure 5.

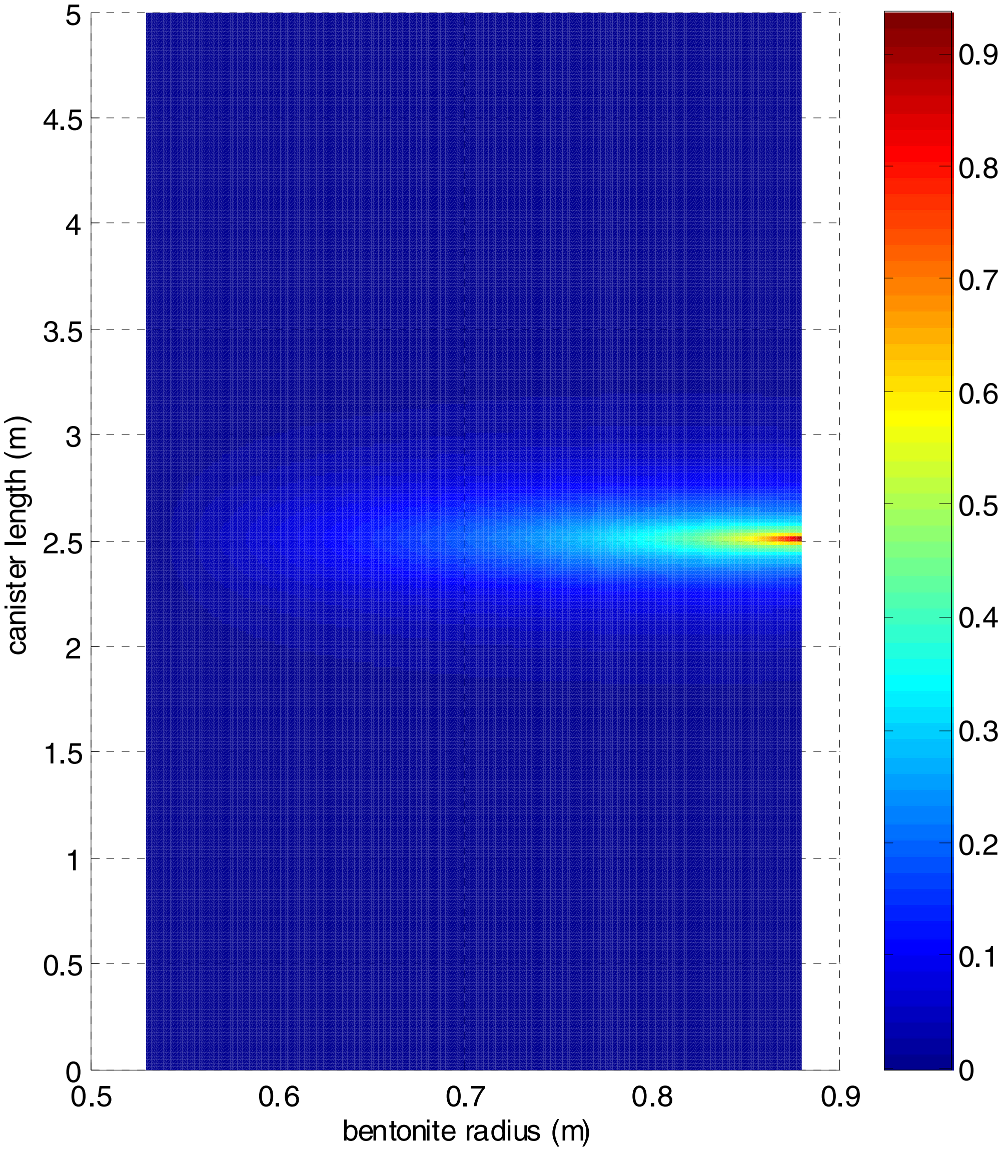

Figure 4. Concentration profile in the bentonite buffer between the canister and the fracture, obtained from the radially-converging model.

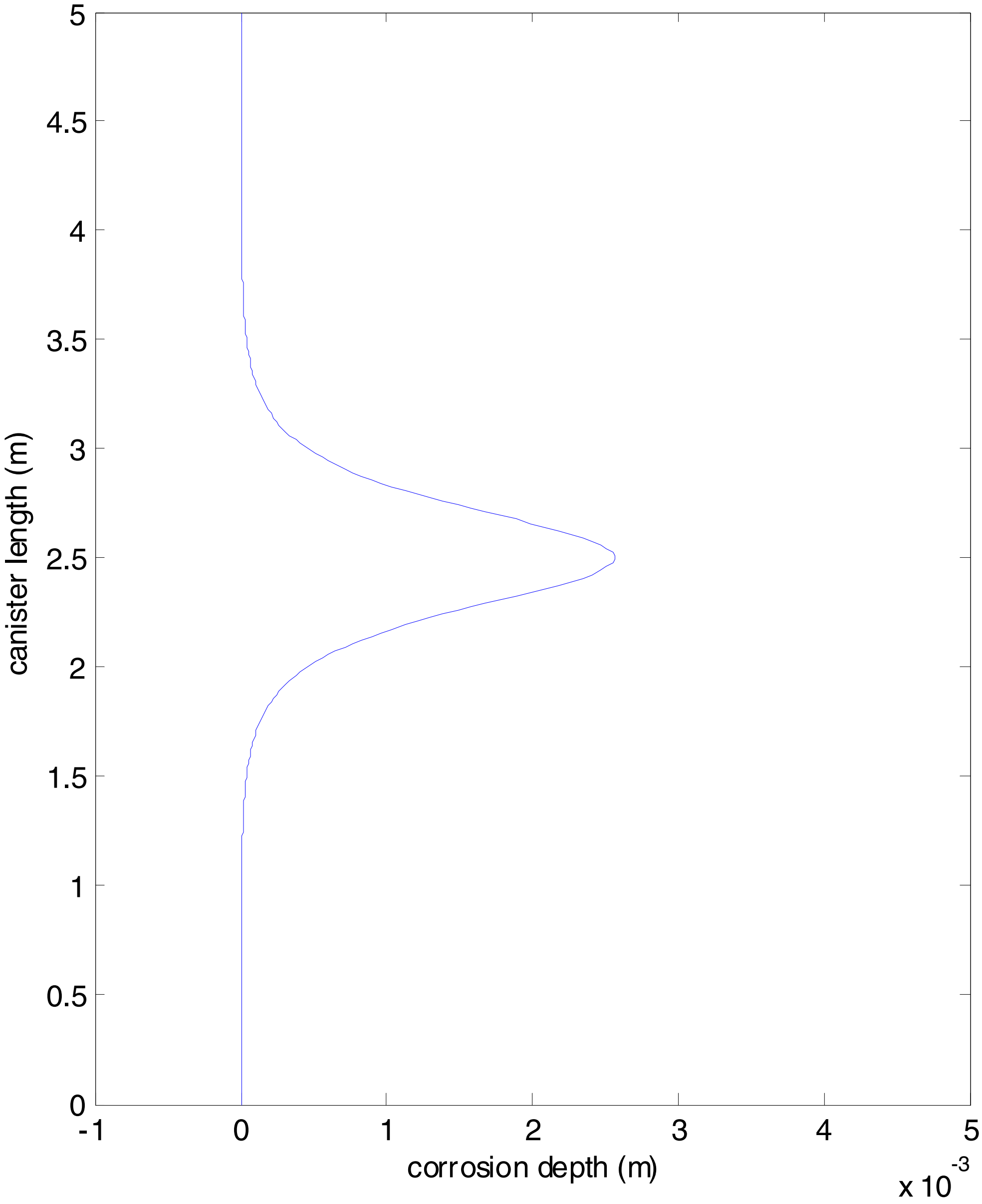

Figure 5. Corrosion depth of the canister wall 10^5 years after deposition, obtained from the radially-converging model.

The maximum corrosion depth is 2.6 mm which is very close to the result obtained from the simpler linear model.

6 Sensitivity analyses

The model presented in the previous sections in this report predicts copper canister corrosion with an assumption that the concentration of the corrodent (sulphate that will be completely reduced to sulphide and methane originated from underneath of the Earth's mantle) in the approaching groundwater flowing in the intersecting fracture is constant. The "representative value" used is a central value for the concentration of the present-day groundwater compositions observed at different sites at the repository depth. The time span that has been considered in the model is 10^5 years. This implies that we have in our model extrapolated the present-day groundwater compositions up to 10^5 years.

As the concentrations of sulphate (Willian, 1995) and methane are site-specific and largely variable (Pitkänen et al., 1996; Kotelnikova and Pedersen, 1998; Pitkänen et al., 1999; Pedersen, 2000) in the Fennoscandian shield, it is therefore important to take an overview of the measured concentrations at different sites. In this section, the hydrogeological conditions of the present-day groundwater systems (especially the groundwaters along the Swedish coastal lines, i.e. circum Baltic Sea) will be presented. We will summarise the data available for the methane and sulphate concentrations at different sites.

Over a period of time of 10^5 years, major environmental changes can be expected. Climatically driven changes such as glaciations, permafrost and changes in sea level will affect the subsurface environment considerably (Andersson, 1998). We will analyse these changes and outline the most important mechanisms that can influence future groundwater composition, and their consequences to our predicted corrosion results. Possible changes (deviations from the present-day situation) of the contribution of the sources of the sulphate within a time period of 10^5 years will be discussed in terms of the influences by the glaciations, permafrost and sea level changes.

The influences of the site-specific and time-dependent concentrations on copper canister corrosion will be explored and the results will be compared with our previous modelling results using the representative values.

6.1 The hydrogeological conditions of the present-day groundwater systems

The present-day climate in Sweden is characteristic of interglacials (warm periods) and is of temperate/boreal type. In areas above sea level (including most part of the Äspö site) the land surface becomes accessible for infiltration of meteoric water. Owing to the humid climate, the groundwater table, and therefore the hydraulic gradient, will follow the topography (SKB, 1999). Within depths of a few hundred metres, regional groundwater flow is generally driven by the hydraulic gradient and the water will finally be discharged into the rivers and the sea. In areas near the Baltic Sea coast, seawater intrusion can also be possible. At greater depths (> ca. 600 m), saline waters of high densities are largely stagnant and only the upper part of them can be influenced by the groundwater flow above them and resulting in mixing of different waters.

Groundwater compositions in the coast area in Sweden: the Äspö site

Different pre- and postglacial events have affected the present-day groundwater compositions at Äspö. However, the effects from the last glaciation and the consequent land uplift are the most recent important events (Laaksoharju and Wallin, 1997).

1. The continental ice melted and retreated and glacial meltwater was injected into the bedrock (13000 BP). The exact penetration depth is still unknown but a depth of several hundred to a few thousand meters is possible according to groundwater flow modelling. Glacial meltwater was mixing with saline water in the bedrock. At the interface a saline groundwater with a glacial signature was found. A non-saline glacial water was present in the upper part of the bedrock.

2. Different non-saline and brackish lake/sea stages covered the Äspö site (13000 BP – 4000 BP). Only a dense brackish sea water such as Yoldia and Litorina seawater could penetrate and affect the groundwater. The Litorina sea stage (8000 to 2000 BP) contained the most saline groundwater and this water was supposed to have the deepest penetration depth. The result was that the glacial and brine groundwaters were mixed with intruding brackish marine water.

3. When the Äspö Island was elevated above sea level (4000 BP) a freshwater pillow was developed. The continuous land rise increased the hydraulic driving force and the groundwaters in the upper part of the bedrock could then be flushed out.

The present-day groundwater compositions at a repository depth are therefore the results of mixing of different kinds of waters (Smellie and Laaksoharju, 1992): (1) recent fresh to brackish near-surface waters (mostly precipitation), (2) modern Baltic Sea water, and (3) deep saline waters. The deep saline waters usually lie > 400 – 600 m below the ground surface and are interpreted as representing a separate, deep, possibly regional groundwater system. The sources of the extremely high salt content of very old deep groundwater are believed to be seawater, fluid inclusions, rock/water interaction and residual igneous/metamorphic fluids.

In a refined multivariate mixing and mass balance model (Laaksoharju and Wallin, 1997), five reference waters were identified: (1) brine, (2) glacial, (3) Baltic Sea, (4) altered marine and (5) meteoric. The composition and origin of the brine water are similar to those of the deep saline waters referred in Smellie and Laaksoharju (1992). The glacial water was the water derived from the melting of the glacial ice sheet. The Baltic Sea water was referred to as modern Baltic Sea water in Smellie and Laaksoharju (1992). The altered marine groundwater has undergone decomposition of organic material due to microbiological sulphate reduction occurring in the marine sediments. This process may have strong impact on the origin and evolution of the groundwater compositions, especially the sulphate concentration, at the repository depth and will be discussed in more detail later in this report. Finally, the meteoric water corresponds approximately the recent fresh and brackish near-surface waters as indicated in Smellie and Laaksoharju (1992).

Groundwater compositions in an inland area in central Sweden: the Stripa mine site

The groundwater compositions in the inland areas in central Sweden can be summarised in the following as were found in the Stripa mine site (Nordstrom et al., 1985):

1. Some of the deeper groundwaters (> 700 m) have usually elevated salinity, up to 700 mg Cl/L,

2. The more saline water at depth has a markedly different water chemistry than the shallow groundwaters, i.e., it is an Na-Ca-Cl-SO_4 type water,

3. The pH increases to the range of 9 –10 with depth,

4. Dissolved inorganic carbon becomes very low with increasing salinity, reaching 9 mg HCO_3/L.

The mixing of different water types in the inland groundwaters is less obvious than that in the coastal groundwaters. The intrusion of modern seawater and the modified marine water does not occur for the inland waters. Although there is a general trend of increasing salinity with depth in the inland water, the salinity is quite variable from one fracture zone to the next. The salinity-depth relation could be better characterised as "heterogeneous" rather than "homogeneous".

Even though the salinity of the deep groundwaters at the Stripa site is much lower than that at the Äspö site, it is improper to draw the conclusion that deep groundwaters in the coastal areas have higher salinity. Both very high and very low salinities are encountered in deep groundwaters of coastal areas, e.g. at the Höllviken site in south-western Sweden extremely high salinity has been found, while at the Klipperås site in south-eastern Sweden, the Fjällveden and the Gideå sites along the east coastal line, the groundwaters are essentially non-saline (Wallin, 1995).

6.2 Methane concentrations in groundwaters in the Fennoscandian shield

The content of methane varies considerably among the studied sites. The Olkiluoto site in Finland showed some very high methane values, up to 34 mmol L^{-1} (Pitkänen et al., 1996; 1997; 2004). The highest values are found in the deepest groundwaters sampled, at a depth of 860 m. At the repository depth the methane concentration is 10 – 15 mmol L^{-1}. Between 1 µmol L^{-1} and 18.6 mmol L^{-1} of methane in groundwater were found from the Canadian Shield (Sherwood Lollar et al 1993a; 1993b). The measured methane concentrations in the groundwaters obtained from the Äspö site indicate that levels of up to 1 mM methane exist at about 440 m depth at the Äspö HRL (Kotelnikova and Pedersen, 1997). In the following we will present the methane concentrations observed in groundwaters in the Fennoscandian shield. Due to the scarcity of the data available, we will mainly focus on the measurement at the Olkiluoto site in Finland and at the Äspö site in Sweden.

Methane concentrations at the Olkiluoto site in Finland

The Olkiluoto site is located in southwestern coastal area in Finland, situated 10 km west of the village of Eurajoki and 13 km north of the town of Rauma. The bedrock surrounding the Olkiluoto site is of Precambrian in age. The oldest rocks in the area are schists and gneisses deformed and metamorphosed during the Svecofennian orogeny 1900 – 1800 Ma ago. Large areas to the east and south-east of Olkiluoto Island are covered with roughly 1570 Ma old rapakivi granites (Vaasjoki, 1977). Therefore at this site there are both igneous rocks of granite and metamorphic rocks of schist and gneisses. The main rock types of Olkiluoto island are, in order of abundance: mica and veined gneisses, migmatite granite, grey gneisses, and diabase. Minor veins and dikes are quartz feldspar gneisses and amphibolites in composition (Pitkänen et al., 2004).

The methane concentrations in groundwaters of different boreholes at the Olkiluoto site are shown in Table 2, together with the total sulphide concentrations and the sulphate concentrations (extracted and re-calculated to millimoles per litre, mmol L^{-1}, from Pitkänen et al., 2004).

Table 2. **Groundwater concentrations of methane, total sulphide and sulphate in different boreholes at the Olkiluoto site**

Borehole/depth (m) /sample #	$S^{2-}_{(tot)}$ [µmol L^{-1}]	SO_4^{2-} [mmol L^{-1}]	CH_4 [mmol L^{-1}]	Min (SO_4^{2-}, CH_4) [mmol L^{-1}]
KR3/443/1	0.31	0.122	2.317	0.12
KR3/860/1	0.31	0.013	34.286	0.013
KR3/860/2	0.31	0.086	33.482	0.0086
KR6/525/1	8.1	0.055	15.214	0.055
KR7/282/1	5.0	3.333	0.0063	0.0063
KR9/470/1	0.31	0.178	10.469	0.178
KR9/498/1	0.31	0.015	15.545	0.015
KR12/365/1	0.31	0.066	5.3794	0.066
KR12/664/1	0.31	0.056	12.3	0.056
KR12/737/1	1.56	0.057	19.7	0.057
KR12/741/1	1.25	0.053	23.134	0.053
KR13/112/1	0.63	2.510	0.157	0.157
KR13/214/1	12.8	4.490	0.027	0.027
KR13/362/1	387.50	1.354	0.6804	0.68
KR13/362/2	384.38	1.250	-	-

The data of concentrations of sulphide and sulphate and methane shown in Table 2 are plotted in Figure 6. It should be noted that Table 2 contains only the data of those borehole waters in which all the sulphide, sulphate and methane concentrations are available in Pitkänen (2004). In Figure 6a, b, and c, the concentrations of sulphide, sulphate and methane are plotted vs. the depths, respectively. In Figure 6d the concentrations of methane are plotted against the concentrations of sulphate.

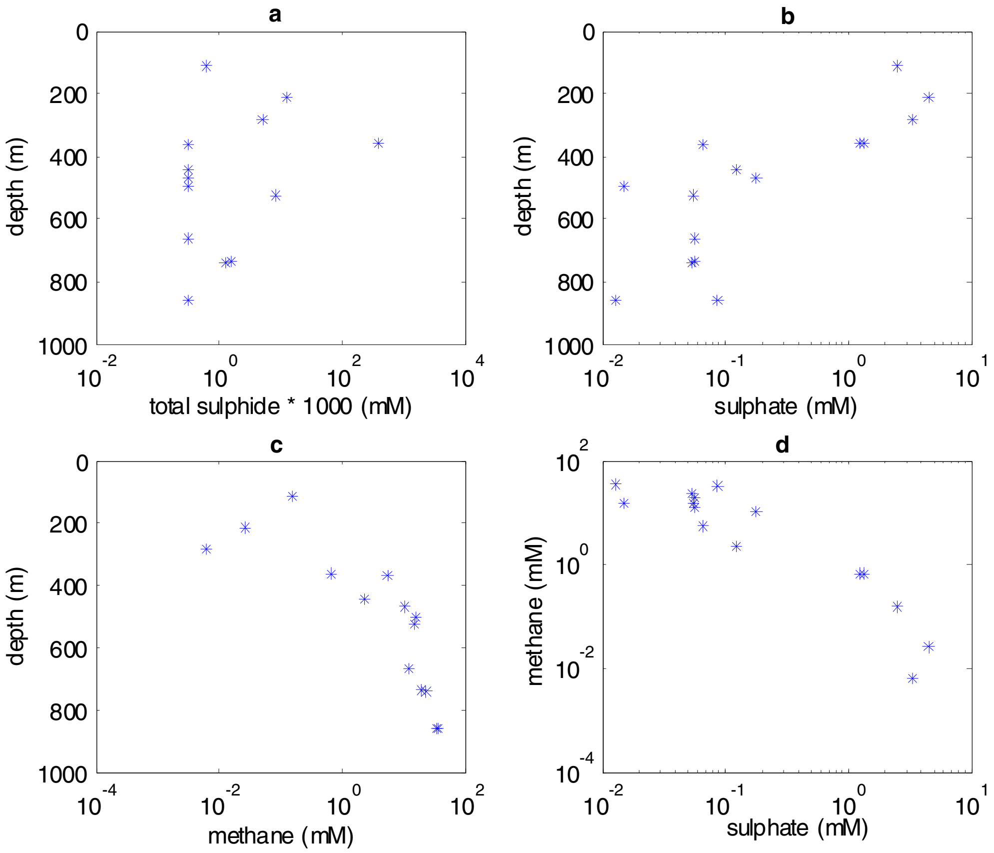

Figure 6. Concentrations of total sulphide (a), sulphate (b) and methane (c) vs. depths, respectively. Concentrations of methane against the concentrations of sulphate (d).

The amounts of total aqueous sulphide ($S^{2-}_{tot}= S^{2-} + HS^{-} + H_2S$ + polysulphides) show a relatively wide range in the Olkiluoto groundwaters (Figure 6a). Small amounts of dissolved sulphide are observed in shallow fresh groundwaters from the overburden and bedrock, indicating anoxic conditions in these groundwaters. The anomalously high concentration observed (387.5 µmol L^{-1}) was analysed at a depth of 362 m in borehole KR13. Other high sulphide concentrations (> 31.25 µmol L^{-1}) were also observed (Pitkänen et al. 1999a) in other boreholes located near to each other. Elevated dissolved S^{2-} concentrations seem to coincide with the transition zone from brackish to saline groundwaters. The sulphate concentrations also show relatively high values in this transition zone.

The sulphate-rich brackish water has been observed between a depth of 100 and 300 m (Pitkänen et al., 1999), indicating an ancient seawater origin. Pitkänen et al. (1996a, 1999) have linked the sulphate enrichment to infiltration from the Litorina Sea based on the following observations: (1) the marine SO_4/Cl ratio and higher salinity of SO_4-rich samples than in present Baltic samples off Olkiluoto island, (2) the typically marine Br/Cl signature, and (3) the low ^{14}C content. Below this sulphate-rich groundwater, the microbiologically catalysed reduction of sulphate results in a dramatic decrease of sulphate concentration. The deep saline groundwaters have negligible contents of sulphate, as they apparently represent methanic redox conditions in which sulphate is reduced (Pitkänen et al. 1996a, 1999; Ruotsalainen & Snellman 1996). This trend of sulphate reduction can also be observed in Figure 6b even though only part of the data are included. The highest sulphate concentration (4.5 mmol L^{-1}) is that at a depth of 214 m. At the repository depth (470 - 498 m) it is 0.015 to 0.178 mmol L^{-1}.

The methane concentrations are relatively high compared to those found at similar depths in groundwaters at other sites in the Fennoscandian Shield, for example, the Hästholmen site in Finland and the Äspö site in Sweden (Havman et al., 1999). The concentration of methane as shown in Figure 6c increases with depth, indicating a possible source coming deeply from the mantle of the Earth. The highest value of the concentration available from Pitkänen (2004) is that at the greatest depth. The value is 33-34 mmol L^{-1} and the depth is 860 m (see the last column of Table 2). At the depth of a repository candidate (around 500 m), the concentrations is 10-15 mmol L^{-1}, which is more than ten times as large as our central representative value used in the modeling in the previous sections. Table 2 also shows the minimum value of either methane or sulphate concentration. Most concentrations are below 0.1 mmol L^{-1}. The highest value is 0.68 mmol L^{-1}.

In our modelling presented in the previous sections it is assumed that the lower value of the concentrations of either sulphate or methane will determine the corrosion rate of the copper canister. From the data of the Olkiluoto site, our representative central value of 1 mmol L^{-1} is lower than the maximum sulphate as well as the methane concentration but higher than the minimum values of min. (SO_4^{2-}, CH_4) shown in Table 2. Should our model be applied specifically for the Olkiluoto site, lower corrosion rate of the copper canister would be expected in any of the waters found at that site.

Methane concentrations at the Äspö site in Sweden

The methane concentrations in groundwaters at the Äspö site are shown in Figure 7 (Kotelnikova and Pedersen, 1998). Compared with the data for the ionic species in the groundwaters, the methane data (and the data of other dissolved gases) are relatively scarce. Most of the data available are related to the microbial studies (Kotelnikova and Pedersen, 1998, 1998a; Haveman et al., 1999; Pedersen, 2000). The maximum value of those data is about 1 mmol L^{-1}, and is considerably lower than those at the Olkiluoto site in Finland.

The sulphate concentrations in groundwaters at the Äspö site are higher than those at the Olkiluoto site, up to 6 mmol L^{-1} at the repository depth (Laaksoharju and Wallin, 1997; Laaksoharju et al., 1999).

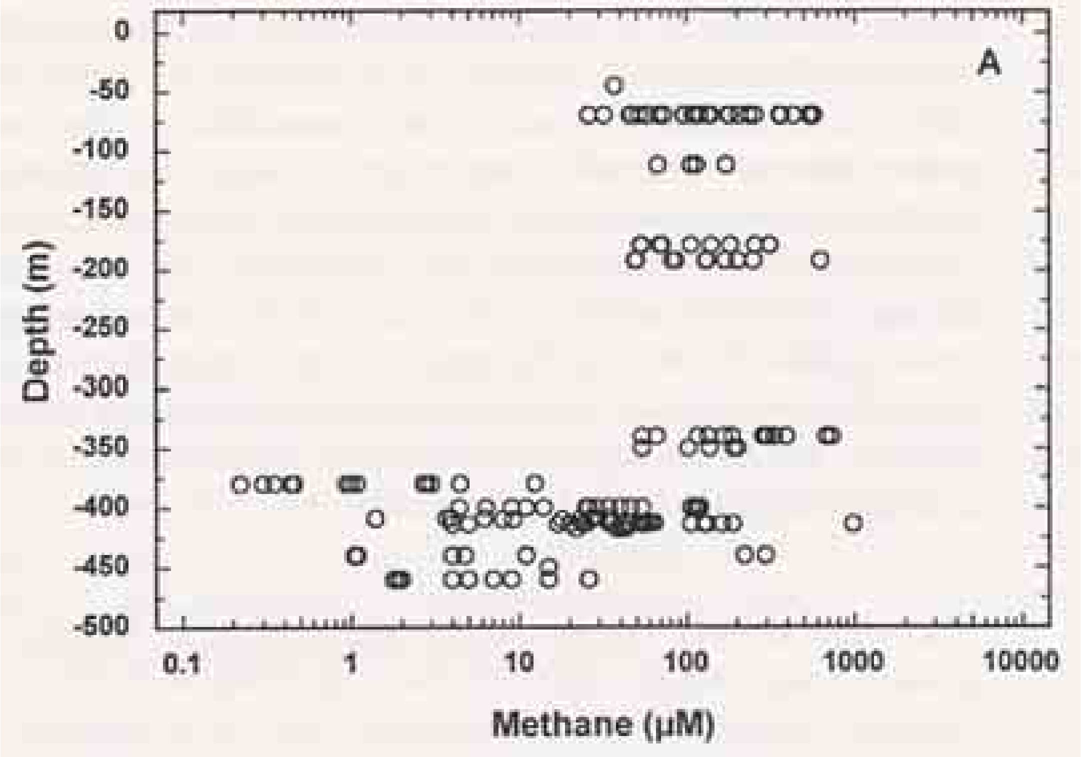

Figure 7. Methane concentrations in the groundwater at the Äspö site at different depths in the granitic bedrock (from Kotelnikova and Pedersen, 1998).

In Table 3 the highest values of concentrations of methane and sulphate at the repository depth at the Äspö site as well as at the Olkiluoto site are summarised.

Table 3. **The highest values of concentrations (in mmol L^{-1}) of methane and sulphate at repository depth at the Äspö site and the Olkiluoto site.**

	at the Äspö site	at the Olkiluoto site
SO_4^{2-} (mmol L^{-1})	6	0.015-0.178[*]
CH_4 (mmol L^{-1})	1	10-15

[*] This value could be as high as 4.5 mmol L^{-1}. See discussions in Section 6.5.

Sources of the subterranean methane

In the following we will present investigation results in the literature concerning the sources of the subterranean methane. The sources of the sulphate in groundwaters in crystalline rocks will be discussed later.

Methane occurs frequently in subterranean environments all over the globe, not only in crystalline rock environments. Evidences of an ongoing methane-generating process in deep Swedish granite have been published (Flodén and Söderberg 1994; Söderberg and Flodén 1991, 1992). Pockmarks in Baltic Sea sediments were found, indicating gas eruption, mainly of methane, from fracture systems in the underlying granite. To explain the 0.2 Ma interval of extreme global warming marking the start of the Eocene epoch about 55 million years ago and a massive and rapid (during a period of 10 ka) input of isotopically depleted carbon, Svensen at al. (2004) proposed that intrusion of voluminous mantle-derived melts in carbon-rich sedimentary strata in the northeast Atlantic may have caused an explosive release of methane—transported to the ocean or atmosphere through the vent complexes—close to the Palaeocene/Eocene boundary. Clark and Phillips (2001) used $^{3}He/^{4}He$ signatures as an evidence of the mantle- and crustal-derived geothermal fluids containing, among others, methane.

Pitkänen et al. (2004) suggested three other possible mechanisms for hydrocarbon (HC) formation in deep groundwaters at the Olkiluoto site: bacterial, thermogenic and abiogenic. Bacterial methanogenesis may proceed either with fermentation of methylated substrates such as acetate or through a carbonate reduction pathway using hydrogen gas to reduce CO_2. Thermogenesis occurs in deeply buried organic sediments in sedimentary basins. Abiogenic sources for HC are formed in hydrothermal systems during water/rock interactions involving the Fischer-Tropsch synthesis reaction based on graphite and hydrogen:

$$C + 2H_2 = CH_4.$$

The mantle origin of the methane in deep groundwaters in crystalline rocks is a more reasonable explanation of the sources of methane. All the other three processes (bacterial, thermogenic and abiogenic) require hydrogen or other low-carbon organics (like acetate). The dissolved hydrogen concentration in deep groundwaters in the crystalline rocks is usually several orders of magnitude lower than the concentration of methane and the acetate concentration probably even lower. The mechanism of mantle origin is also in line with the observations of higher concentrations of methane at greater depths at the Olkiluoto site.

6.3 Sources of sulphate in the present-day groundwaters

In this report we will mainly be concerned with the origin (or sources) and evolution of the sulphate concentration in the groundwater of a potential repository site. In our model the corrosion rate of the copper canister will be limited either by the concentration of sulphate or by the concentration of methane. The methane is derived from underneath of the Earth’s mantle and its supply will possibly not be influenced by the changes of the climate. The sulphate concentration in the groundwater in the water-conducting fractures of crystalline bedrocks is found to be positively correlated with the groundwater salinity. In both the Stripa mine site (a typical inland site) and the Äspö Hard Rock Laboratory site (a typical coastal site), the groundwater compositions change from Ca-HCO_3 type to Na-Ca-Cl-SO_4 type with depth, even though at the same depth, groundwater salinity, and correlated with that the sulphate concentrations, are generally lower at an inland site compared with those at a coastal site.

Sulphate sources in shallow groundwaters – atmospheric fallout and oxidation of sulphides

In the shallow groundwater all sulphate originates in the surface environment from atmospheric fallout and the oxidation of sulphides in the rock matrix. The atmospheric fallout usually contributes a less important portion of the total sulphate, with the exception probably in arid coastal areas (Bao et al., 2004). Under the present-day climate and hydrogeological conditions, atmospheric oxygen penetrates into the underground bedrock with a depth much less than 100 m (Puigdomenech et al., 2001) and deep groundwater is always reducing. The present-day contribution of sulphate from oxidation of the sulphide minerals in the bedrock could be limited and will not be a major source of the sulphate concentration in the groundwater. However, during the period of glaciation retreat and ice sheet melting, oxygen could possibly penetrate more deeply in the fractures of the underground bedrock and may possibly contribute larger portions of sulphate into the intermediate and deep groundwaters. This issue will be discussed later.

Possible modern seawater and modified marine water intrusion at intermediate depths

Another possible source of sulphate in the shallow groundwaters to groundwaters at the intermediate depth (<500 m) is the intrusion of the modern seawater/modified marine water or of the paleo-seawaters. Just during the Holocene Epoch of the Quaternay Period (<10000 years), southern and central parts of Sweden have been invaded by seawater on two separate occasions (Nordstrom et al., 1985).

The isotopic composition of modern oceanic sulphate (Reese et al., 1978; Longinelli, 1989) is relatively constant because of a steady state process between input (river) and output (precipitation and reduction):

$$\begin{aligned}
&\delta^{18}\text{O (in } SO_4^{2-}) = +\,9.5\ ‰\ \text{(SMOW)}\\
&\delta^{18}\text{O (in } H_2O) = -6.9\ ‰\ \text{(SMOW)} \qquad (10)\\
&\delta^{34}\text{S (in } SO_4^{2-}) = +20.0\ ‰\ \text{(CDT)}
\end{aligned}$$

where SMOW stands for Standard Mean Ocean Water and CDT stands for the Canyon Diablo Troilite meteorite.

The δ^{18}O values of the groundwaters in shallow boreholes display a variation between --11 and -7 ‰ (Banwart et al., 1992). These values are between the value of the rainwater at Äspö (–13 ‰) and the value of the water in the Baltic Sea outside Äspö (-6.9 ‰), indicating a mixing of the rainwater and a possible inflow of marine water (Wallin, 1992).

The $\delta^{34}S$ values in some groundwaters located above a depth of 500 m also show marine signatures of about +20 ‰. The groundwaters at a depth of 470 m have values of $\delta^{18}O$ in sulphate oxygen close to those of the seawater, indicating that the marine water may well be present at the intermediate depths at the Äspö site (Wallin, 1992). However, there are no clear evidences that the marine waters have penetrated deeper than this depth (about 500 m). Deeper groundwaters at the Äspö site show other non-marine signatures as will be discussed later.

The groundwaters located above a depth of 500 m at the Äspö site have been compared to the groundwaters in other investigated areas located peripheral to the Baltic Sea, e.g., Hästholmen, Forsmark, Finnsjön, where influences from both modern Baltic seawater and ancient Litorina water (7 400 – 2 500 BP) might be expected. The Äspö water compares well with the Finnsjön water, indicating they are marine-derived, but has been significantly modified by water/rock interactions and by other salt water sources (Smellie and Laaksoharju, 1992).

Injection of paleo-marine water due to the isostatic movements in the Baltic Shield could possibly reach depths up to 400 – 500 m. Large amounts of saline waters with a marine origin have been observed in the Canadian Shield at depth of 400 m. The formation of these waters has been explained by seawater freezing, most likely in connection with one or more of the latest glaciations (Fritz and Frape, 1982; Herut et al., 1990).

At present, a freshwater aquifer has been formed after the Äspö island rose above the sea level. The fresh water flushes out the older water types. The depths to which the waters are flushed out are determined by the prevailing hydraulic driving forces. The land rise gradually increases the penetration depth of the meteoric water until a certain depth was reached where the hydraulic force could not remove the dense saline groundwater. Some of the old signatures of the marine water may have been obliterated by the flushing of the meteoric water or they have been mixed with the flushing meteoric waters.

During the construction of the access tunnel to the Hard Rock Laboratory (HRL) at the Äspö site, altered marine waters were obtained below the marine sediments in the tunnel. Modelling calculations showed that, the disturbance of the tunnel construction could result in rapid seawater intrusion (Laaksoharju, 1995).

As the Äspö site is an area of groundwater discharge, present-day horizontal intrusion of the seawater is minimal. For regions that lie underneath the seawater, vertical marine water intrusion could well be possible by the mechanism of density-driven downward flow.

Sea-bed sediments consist of clay, gravel and organic rich mud. When either modern or paleo-seawater intrudes into the deep groundwater, their compositions may be modified by reactions in the sediments. Microbially mediated sulphate reduction has been inferred to take place in sea-bed sediments (Laaksoharju, 1995). The sulphate concentration in the intruding modified seawater will be lower than that in the original seawater. This may explain the lower SO_4^{2-}/Cl^- ratio of the intermediate groundwater relative to the ratio of the modern seawater (Wallin, 1992; Laaksoharju, 1995). Other inconsistencies of major ion ratios between the groundwater and the seawater have been interpreted as a modification of the seawater when it seeps through the seabed sediments, like the removal of Na, K and Mg from the seawater in exchange for Ca through the ion-exchange processes (Smellie and Laaksoharju, 1992).

Oxidation of sulphide minerals by the intrusion of the melt glacial water down to intermediate depths

When the continental ice formed during glaciation, melted and retreated glacial meltwater was injected in the bedrock. The exact penetration depth is still unknown but a depth of several hundred to a thousand metres is possible (Laaksoharju and Wallin, 1997; Laaksoharju et al., 1999). Ice composition data from the base of the Greenland ice sheet suggests that the meltwaters will be highly enriched in dissolved oxygen, with concentrations at least 3 to 5 times higher than would be obtained at atmospheric equilibrium (Twickler et al., 1986). The high oxygen concentration in glacial meltwater can possibly penetrate into the fractures systems of the bedrock and oxidise the sulphide minerals and produce sulphate.

During sulphate precipitation in the forms of gypsum and anhydrite an isotopic fractionation occurs. After precipitation, the remaining aqueous sulphate is depleted in heavy sulphur isotopes. During microbial processes of sulphate reduction, the light sulphur isotopes will be preferentially reduced and the remaining sulphate in the water will be enriched in the heavy sulphur isotopes (Claypool et al., 1980).

During sulphide and H_2S oxidation, chemical processes will not significantly fractionate the sulphur isotopes (Krouse, 1980; Pearson and Rightmire, 1980) and bacterial oxidation will slightly deplete the ^{34}S isotope.

However, oxidation of pyrite through different kinetic reactions gives different oxygen isotopic signatures of the formed sulphate. The following three reactions have been proposed (Taylor and Wheeler, 1984):

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + SO_4^{2-} + 16H^+ \quad (a)$$

$$Fe^{2+} + \tfrac{1}{4}\,O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\,H_2O \quad (b)$$

$$FeS_2(s) + 7/2\,O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (c)$$

In reaction (a) the sulphate oxygen is derived from the water molecules whereas in reaction (c) it is derived from dissolved oxygen (87.5 %) and water (12.5%). The marked difference in the oxygen isotope composition of atmospheric oxygen ($\delta^{18}O$ = +23 ‰) and meteoric waters ($\delta^{18}O$ = –9.5 to –15.8 ‰) offers the possibility of tracing the origin of the oxygen atoms in the sulphate and investigating the kinetic mechanisms of sulphide oxidation. van Everdingen and Krouse (1985) proposed an empirical equation relating the $\delta^{18}O$ value of the oxygen in sulphate (designated as $\delta^{18}O_s$) and the $\delta^{18}O$ value of the oxygen in water that enters the sulphate by reaction (a) (designated as $\delta^{18}O_w$):

$$\delta^{18}O_s = \delta^{18}O_w\,(0.875Y + 0.125) + (11.5375 - 7.4375Y) \quad (11)$$

where Y is the fraction of sulphate produced by Eq. (a) above.

The glacial meltwater had an oxygen isotope value of about $\delta^{18}O_w = -15.8$ ‰. If it is assumed that the glacial meltwater had the atmospheric oxygen dissolved in it and the dissolved oxygen oxidised the pyrite by reaction (c), Y in Eq. (11) would be zero, and the isotope value of oxygen in sulphate would be $\delta^{18}O_s = 9.56$ ‰. Coincidently, however, this value is also very close to the value of sulphate in oceanic waters (see Eq. (10)). With these data alone it would be difficult to interpret if the sulphate is a result of sulphide oxidation by glacial meltwater or if it has a marine water origin.

The signature of the stable isotopes of oxygen and hydrogen (^{18}O and ^{2}H) of the water indicates that the Stripa deep saline groundwater could be recharged in a cooler climate than the present climate. However, it is very unlikely that glacial meltwaters participated in the formation of the deep groundwaters. These waters are considerably more depleted in ^{18}O than the lowest values observed and only a minor percentage of the deep water could have such an origin (Nordstrom et al., 1985).

Signatures of old glacial meltwater has been observed in the groundwater in one borehole (KAS03:129-134m) at the Äspö site. The water showed a $\delta^{18}O = -15.8$ ‰ (SMOW) and $\delta^{2}H = -124.8$ ‰ (SMOW) in combination with an apparent ^{14}C age of 31 365 years (Smellie and Laaksoharju, 1992; Laaksoharju et al., 1999; Emrén, 1999), indicating cold climate recharge. Glacial meltwater have also been observed at Äspö today at various depths in the basement (Smellie and Laaksoharju, 1992; Wallin and Peterman, 1994). The Multivaritate Mixing and Mass Balance (M3) modelling also indicated oxidation of pyrite in association with glacial water as a possible source for the sulphate in the groundwater (Laaksoharju and Wallin, 1997). The deep saline water, however, has isotopic signatures ($\delta^{18}O = -10.4$ to -8.9 ‰ and $\delta^{2}H = -60.2$ to -44.9 ‰) that are significantly different from the signatures of the cold climate recharge.

The observations of the staple isotopic data of oxygen-18 and deuterium in water at both the Stripa site and the Äspö site showed that the cold climate recharge of water might have penetrated only to the intermediate depth of the groundwater system. It seems that the deep saline groundwaters have not been significantly influenced by such recharges even though some modelling results (Svensson, 1999) and geological observations of amorphous Fe-oxyhydroxides and goethites at great depths at several sites in Sweden (Glynn and Voss, 1996) may suggest that the glacial meltwaters had penetrated to depths of several thousand metres.

The sulphate in deep saline waters

The salt contents of very old deep groundwaters are sometimes extremely high, e.g. with chloride concentrations as high as 47 000 mg L^{-1} at depths of 1700 m at the Äspö site (Laaksoharju and Wallin, 1997) and 100 000 mg L^{-1} at a depth of 1862 m at the Höllviken site (Wallin, 1995). The concentrations of sulphate in those waters are also very high, up to 900 mg L^{-1} at the Äspö site. These saline waters are interpreted as representing a separate, deep, possibly regional groundwater system, which is almost stagnant except when intercepted by deeply penetrating conducting fracture zones.

Wallin (1995) has compared the compositions of the deep groundwater obtained from different locations in coastal as well as inland areas in Sweden. Some of those waters had high concentrations of chloride, but others did not. For example, in the drill hole at Klipperås less than 150 km southwest of Äspö, the water salinity was totally different from that of Äspö. The highest chloride concentration of only 60 mg L^{-1} has been recorded at a depth of 800 m. This indicates that, in regional scales, the compositions of the deep groundwater may be extremely heterogeneous and depend on the specific rock formation and hydrogeological situations at a given site.

The deep saline waters are very old. This is confirmed by the measured $^{40}Ar/^{36}Ar$ and the ^{85}Kr values. The measured ^{36}Cl values indicated a minimum age of 1.5 Ma for the Cl component (Laaksoharju and Wallin, 1997). On the other hand, the ^{18}O of the sulphate and that of the water have not been in isotopic equilibrium. As the time required for such equilibrium is 10^4 to 10^5 years at 25°C (Lloyd, 1968; Mitzutani and Rafter, 1969), Wallin (1992) indicated that a younger water injection is more likely for the intermediate as well as the deep water at Äspö. The situation could also well be that the chloride and sulphate were introduced into the deep saline waters at times longer than 1.5 Ma, some young and possibly meteoric-derived dilute waters intruded into the deep water at later times.

The sources of the salinity of those waters are debatable with fluid inclusions, leaching of evaporates in sedimentary rocks, paleo-seawater intrusion, as well as rock/water interaction all having been proposed.

Fluid inclusions

Fluid inclusions are microscopic droplets of aqueous solution, silicate or sulphide melt, gas or organic materials that occur in most rocks and minerals (Nordstrom, 1985). In crystalline granitic rocks, fluid inclusions occur mainly in quartz crystals (Smellie et al. 2003). In the Stripa site, calculations showed (Nordstrom, 1985) that the percentage needed to mix with fresh groundwater to achieve the groundwater salinity could only be 1-2%. The average values for Br/Cl and I/Cl ratios associated with fluid inclusions and the microfracture fluids obtained from the fluid-inclusion leaching studies are identical to the groundwater ratios. This comparison provides the strongest evidence for the association between fluid inclusions and the groundwater salinity (Nordstrom et al., 1985).

The contribution of fluid inclusions to the groundwater composition is, however, much more complicated than the simple mass balance shows. For the fluid inclusions to be released into the porewater, the hosting quartz crystals must be first broken down by some lithological stresses due probably only to tectonic movements (Smellie et al., 2003). However, as the dominant tectonisation took place before or immediately at the intrusion of the pluton, later break-down of the quartz crystals can be expected to have been minimal. On the other hand, owing to the very small amounts of the fluid in each inclusion, data of chemical analyses on samples in granitic rock have only been available for chloride but not for sulphate, and the contribution of sulphate to the groundwater from the fluid inclusions becomes even more ambiguous. Moreover, the components in the fluid inclusion have to diffuse through the rock matrix to access the fracture system and, depending on the location of the inclusion, it may take extremely long time for them to come to the flowing groundwater. The fluid inclusions of granite at the Stripa site contain sulphate but the concentration is too low to make further determinations of the sulphur isotope data. The ^{36}Cl data of deep groundwaters at the Stripa site showed that the chloride isotopic ratio is much lower than the granite equilibrium ratio and suggested that all of the chloride in solution at depth may not have been entirely derived from the granite (Nordstrom et al., 1985). Even though fluid inclusions in the leptitic basement rock that hosts the intruding granitic rock might be a source of the fluid inclusions rather than the fluid inclusions in the granitic rock itself, the sulphate content of the leptite (about 50 ppm) appears too low to account for a rock origin (Fontes et al., 1989).

Leaching of the granite particles obtained from the Äspö site did not show clear trend of Br/Cl ratio and the ratio varies with particle sizes (Smellie et al., 2003).

Leaching of evaporates in sedimentary rocks

Another hypothesis of the origin of the high salinity in deep groundwaters is the leaching of some ancient evaporates in sedimentary rocks. The strongest evidences for this hypothesis by far are the isotopic signatures of the elements of sulphur and oxygen in dissolved sulphate. The ^{34}S content in the deep groundwaters is significantly lower than those in the shallow groundwaters and those in the waters at intermediate depths. This is interpreted as that the deep water has another separate origin different from those of the shallow and the intermediate waters. The δ^{34}S values of the deep groundwaters are usually around +10 ‰ compared to values around +20 ‰ of the shallow and intermediate waters (Walllin, 1992). The δ^{18}O values of oxygen in sulphate of the deep groundwaters vary between +10 to +13 ‰, considerably larger than the value for modern marine sulphate (about +9.5 ‰). Both the δ^{18}O and δ^{34}S isotopic compositions coincide very well with those of the ancient marine evaporites formed during the Permian Period (290-250 Ma) (Fontes et al., 1989).

Research results obtained from the Stripe mine project (Nordstrom, 1985) indicated that, extensive deposits of Permian evaporite beds are found in large areas in Germany, Russia and Poland and the hypothesis is that some of these may have been eroded and subsequently transported to central Sweden.

No Permian evaporite deposit of halite and gypsium/anhydrite are known in the region of Sweden. However, several episodes of evaporitic sedimentation have taken place in the marginal area of the Baltic Shield (Sonnenfeld, 1984). Paleogeographical reconstructions (Ziegler, 1982) have mapped a Permian gulf in the Olso region. Even though the most important period on a global scale for the formation of evaporites is the Permian Period, sources of other sedimentary deposits as early as during Precambrian (>3500 Ma), Ordovician (510-437 Ma) and Cretaceous (135-70 Ma) have also been observed. Deep (1000 m) subsurface brines are known to occur at Skåne in southern Sweden in Jurassic and Cretaceous (195-65 Ma) sedimentary rocks (Brotzen and Assarson, 1951). Large amounts of the Persian evaporites have been reported in Denmark, Northern Germany and in the southern Baltic sedimentary basins. Minor amounts occur in the UK, France and Poland (Fontes et al., 1989). Regarding the wide-spread occurrence of the Permian evaporites in the northern part of Europe it seems not unlikely that these salts may have been deposited in the Baltic Shield and subsequently eroded.

On the other hand, the Fennoscandian shield has been an area of uplift and erosion since the Devonian (345- 395 Ma) and has not experienced any large depositional environments until the Holocene (Brinkmann, 1969). Moreover, the Br/Cl ion concentration ratio found in halite in Permian evaporites is considerably lower than that in seawater and over an order of magnitude lower than the ratio in the Stripa groundwaters. It is therefore difficult to conclude that the salinity in the deep inland groundwaters like that at the Stripa mine site originates from Permian deposits (Nordstrom, 1985). In addition, sulphate in magmatic and metamorphic environments has similar $\delta^{34}S$ signatures as that in Permian evaporites and the origin of the deep sulphate from this source remains debatable (Andrews et al., 1988). It is more likely that highly saline waters found in deep rocks in Sweden have originated from leaching of sedimentary evaporites during many different periods rather than during only the Permian Period. In addition to the similar isotopic signatures of oxygen and sulphur in dissolved sulphate, the Br/Cl ratio of the Äspö deep groundwaters compares well with that of the Skåne brine waters in Jurassic and Cretaceous (195-65 Ma) sedimentary rocks.

Intrusion of modern and ancient seawaters

Lateral intrusion of modern Baltic seawaters might possibly occur in coastal areas like the Äspö site, but cannot reach inland areas like the Stripa site. Still highly saline waters have been found at depths greater than 500 m at the Stripa site. Moreover, as has been discussed earlier, modified modern seawaters may have reached intermediate depths of the groundwater at the Äspö site, at greater depths the highly saline groundwaters may have different sources other than the modern seawater or modified modern seawater. The deep saline waters found at many sites in the Baltic Shield are not originated from the modern Baltic seawater.

Areas of southern and central Sweden have been invaded by seawater on two separate occasions during the Holocene (10 ka) after the retreat of the last glacial sheet. Approximately 10 000 to 9000 years BP the Yoldia sea covered a large area directly across central Sweden, reaching levels of 150-170 metres above sea level (m. a. s. l.) on the present land surface. Stripa is located just within these limits. It is thus possible that the Yoldia seawater could have infiltrated the Stripa granite. The second invasion of the Litorina Sea came through Öresund, the strait between Sweden and Denmark, and only affected coastal areas (mostly southern and western Sweden), reaching levels of 45-55 m. a. s. l. (Engqvist, 1981). This invasion of the Litorina Sea could not have affected the Stripa area but might have affected the Äspö site and the Olkiluoto site.

The salinity-depth profiles are "heterogeneous" and this suggests an origin other than simple paleo-seawater intrusion (Nordstrom et al., 1985) at the Stripa site. In the deep groundwaters at the Stripa site, the ion ratios of Br/Cl and I/Cl are markedly higher than seawater and modified seawater, the Ca/Mg ratios are 1-2 orders of magnitude higher, and the Mg/Cl ratios are markedly lower. These anomalies cannot be fully accounted for by modern, Holocene, Paleozoic or Mesozoic seawater intrusions (Nordstrom et al., 1985).

The deep groundwaters at the Äspö site also have Br/Cl ratios markedly higher than seawater and modified seawater (Smellie et al., 2003). Even though seawater may have intruded down to the intermediate depths in the coastal areas, it seems extremely unlikely that the deep saline waters originate from either paleo or modern seawater intrusions.

Rock/water interaction

In the geochemical studies of the Stripa groundwaters, correlations of major ions with chloride have been investigated (Nordstrom, 1985). Sodium and lithium cations showed strong linear correlations with chloride, indicating that they might be originated from the same source as chloride. Calcium and strontium also showed good correlations with chloride at high chloride concentrations. But potassium and magnesium did not have obvious correlations with chloride, indicating possible origin of water/rock interactions. The explanation for the potassium (Nordstrom, 1985) was the possible dissolution and precipitation of illite, since the groundwaters were both undersaturated and oversaturated with illite. However, there are uncertainties in the determination of the illite solubility product constant and the measurement of aluminium concentration. Consequently, illite solubility control has not been fully proven. The lack of correlation of magnesium with chloride were attributed to some geothermal processes. Since high temperatures have not occurred at the Stripa site for several millions of years, fluid inclusions might be the possible source for magnesium since it could explain a high-temperature signature in a low-temperature environment.

At the Äspö site evidences of water/rock interactions also exist. The ^{36}Cl values indicate that the age of the chloride in the deep groundwaters is at least 1.5 Ma. The ^{87}Sr values indicate an ion exchange between the water and the clay minerals (Laaksoharju and Wallin, 1997). All the isotopic information implies that the groundwater residence time is long and water/rock interactions occurred and some of the major and minor species may have been influenced by the interactions. The chloride concentrations, especially the sulphate concentrations, however, will not be significantly influenced by such interactions. Their concentrations in the deep saline waters are too high to be accounted for by water/rock interactions when the chemical compositions of the minerals in the granitic rocks are concerned.

6.4 Possible evolution of methane and sulphate in groundwater

In the previous sections and in the first part of this section, we have modelled the copper canister corrosion by sulphide, summarised the highest values of methane and sulphate concentrations at two intensively explored sites and examined the possible sources of methane and sulphate (that is assumed to be reduced to sulphide by SRB) in the present-day groundwaters. In our model we have used a central value of the concentration which is assumed to be the lower one of the methane and sulphate concentrations. In the early parts of this section it is found that it is extremely complicated to identify especially the possible sources of sulphate in the groundwaters.

The groundwaters at shallow and intermediate depths may have different origins compared with the deep saline waters. Complex, changing hydrogeological conditions during the Late Tertiary and the Quaternary glacial and interglacial stages probably caused dramatic changes in groundwater flow and composition (Stanfors et al., 1999). It is believed that such cycles of glacial and interglacial stages will occur in the future, and that they will affect the sulphate and methane content of the groundwater. As it is assumed that the methane in deep groundwaters originates from the mantle of the earth, this source is expected to continue to generate methane also in a distant future. The future climate changes can not be expected to affect this source, but changes of the groundwater flow may affect the transport rates of methane from great depth.

The Fennoscandian Shield has been affected by a number of glaciations during the Quaternary Period (2.4 Ma) (Ehlers, 1996). Geological evidences show that these glacial events had a large impact on the topography, sedimentary load and erosion of the shield. The heavy ice load caused extensive isostatic movement of the basement, and it also changed the hydrogeological system that had a large influence on the groundwater formation, and on groundwater chemistry, which may be recognised in the fracture infilling and altered mimerals. Groundwater chemistry may also be influenced by the formation of permafrost (Vidstrand, 2003) and the ice sheet during the periods of glaciation, because part or all of the dissolved species may be freezed out from the ice and be increased in the groundwaters underneath the permafrost or ice sheet. During the retreat of the ice sheet after a glaciation, the meltwater may possibly recharge into the repository depth or more deeply and some sulphide minerals may be oxidised along the pathway of the meltwater (Guimerà et al., 1999). Considerable amounts of sulphate may be brought into the groundwaters.

The global sea level (Hallam, 1984) and the glacio-isostatic changes during the Quaternary glaciation and interglacial stages have altered the hydrogeological and hydrochemical conditions significantly in coastal areas and especially in the Baltic Sea region (Morén and Påsse, 2001) where there would have been a co-variation of $\delta^{18}O$ and salinity with sea level changes (Stanfors et al., 1999). When a repository site is immersed under seawater, the saline water with a higher density will descend downward into the groundwater underneath (Westman et al., 1999) and increase the concentrations of sulphate.

The last three major glacial events during the Quaternary Period are Elster, Saale and Weichsel. The extreme cold climate during the glacial events at high latitudes affected waters with typical low isotopic (^{2}H and ^{18}O) signatures, whereas the milder interglacials displayed a totally different isotopic pattern (Laaksoharju and Wallin; 1997). Within a glacial cycle temporarily warmer periods are termed interstadials, with a climate similar to Greenland and Antarctica (periglacial conditions).

As the time span considered in our model is 100 000 years, only the situation of the last Weichselian glaciation will concern us. It is also during this period the data from geological, hydrogeological, geochemical and isotopic observations of climate changes are more abundant and more reliable (Puigdomenech, 2001).

Future climate changes have been predicted based on the modelling and observation results of the last Weichsel glaciation (Ahlbom et al., 1991; King-Clayton et al., 1995, Boulton et al., 2001). It is essentially assumed that the same glacial cycle will happen in the future. Our present-day climate is an interglacial, relatively warmer period. Different models of climate change (the ACLIN, Astronomical Climate Index model, see Kukla et al., 1981 and the Imbrie & Imbrie, 1980, model) suggest stadials ("mild" glaciations) at about 20 000, 60 000 and 100 000 years from now. As for the next interglacial period having similar climate like our present-day climate, the Imbrie & Imbrie model suggests that it will occur at ca. 75 000 years while the ACLIN model predicts it being at ca. 125 000 years. All those three stadials may occur both at the Swedish Äspö site and the Finnish Olkiluoto site.

Influences of sulphate concentration by permafrost

During each stadial period the permafrost will cover an area larger than the ice sheet. It is, however, extremely difficult to predict the exact duration, the extent of the influenced area and depth. The salt rejection process during the formation of permafrost will probably introduce a certain amount of sulphate into the intermediate groundwaters at the repository depth. With the extreme difficulties in predicting the permafrost process itself, this additional sulphate cannot be quantitatively described.

Influences by the intrusion of glacial meltwater

The glacial meltwater contains high concentration of oxygen and has a higher recharge rate than the present-day meteoric water recharge. The duration of each period of glacial meltwater recharge is estimated to be about 5000 years (Björck and Svensson, 1992) and the dissolved oxygen concentration to be about 1.4 mmol L^{-1} (45 mg/L) (Ahonen and Vieno, 1994). With these data and typical groundwater flow velocity and compositions of reducing minerals (including pyrite) in the fracture zones and the fractured host-rock, Guimerá et al. (1999) concluded that the redox front caused by the oxygen intrusion will not reach the repository depth, as the crystalline rock contains reducing iron and iron sulphide minerals like biotite, chlorite and pyrite. However, when the pyrite is oxidised, sulphate can be introduced into greater depths than the the location of the redox front and reach the repository depth. Scoping calculations show that the sulphate concentration in the fracture zones could be increased considerably. It is difficult to quantify the eventual increase of the sulphate concentration in the groundwater because of the various uncertainties involved, but a value of a few mmol L^{-1} (a few hundred mg/L) is likely. Moreover, the upconing effect at the wake of the ice sheet during its retreat will also be able to introduce sulphate from the deep saline waters into the intermediate depth where a repository is situated.

Influences by paleo seawater intrusion

The ice of the last glaciation retreated from the area about 11.9 ka ago. Since the ice retreated, the Äspö area and the Olkiluoto area have been covered by both freshwater lakes and brackish sea stages (Björck and Svensson, 1992). Uplift due to isostatic rebound has been going on since the last ice retreated and is still on-going. The island of Äspö rose above the Baltic Sea level some 4 ka ago and the area of Äspö island will be part of the mainland within the next 6 ka (Stanfors et al., 1999).

The Baltic Sea has experienced four major stages with altering freshwater and brackish water during the lasting interglacial (the Holocene, 11.5 ka) period. They are: the Baltic Ice Lake, the Yoldia Sea (10.3 ka), the Ancylus Lake (9.5 ka) and the Litorina Sea (7.5ka) (Westman et al., 1999). The most important impact on the groundwater composition was that during the Litorina Sea stage, since the Litorina Sea contained the most saline water and was supposed to penetrate a greater depth into the groundwater underneath (Pitkänen et al., 2004). Both the Swedish Äspö site and the Finnish Olkiluoto site were under this sea level.

The sulphate concentration in the Litorina Sea water could be as high as 5.5 mmol L^{-1} (Laaksoharju et al., 1999). To penetrate into groundwater at depths the seawater would first seep through the sea sediments and the bacteria and organic matter there may considerably reduce the sulphate concentration and it is uncertain concerning the amounts of sulphate penetrating down to the underneath groundwater. This, however, could be a significant source term of sulphate in groundwaters at intermediate depths during the period the repository site would be immersed by saline seawater again.

6.5 Sensitivity analyses

An overview of the groundwater compositions at different sites has revealed that both the sulphate and the methane concentrations vary largely from site to site. In addition to the representative value of the concentration that limits the corrosion rate (limiting concentration) used previously in our model in this report, sensitivity analyses are needed to explore the robustness of the modelling results.

The selected value of 1 mmol L^{-1} should represent an approximately average value for the concentrations of either sulphate or methane, whichever has a lower value in groundwaters at the repository depth. Due to the limit of the scope of this report, we have only focused on data at essentially two sites: the Swedish Äspö site and the Finnish Olkiluoto site. The methane is believed to be transported upward to the repository depth through the deep groundwater from the mantle of the Earth. The source of the present-day sulphate at the intermediate level of the repository depth is most likely the intrusion of ancient and modern seawater (or modified seawater intrusion), and possibly the product of sulphide oxidation during glacial meltwater intrusion. As the deep groundwater is relatively stagnant, the sulphate in the deep groundwater will probably not influence the concentrations at the intermediate level of the repository depth. The great uncertainties related to the sources of the deep saline waters may therefore not concern us much. Should it be assumed, however, that the sulphate reduction had already occurred in the deep groundwater below the repository depth, the diffusive transport of the sulphide formed up to the repository depth may give an extra contribution of sulphide relative to the concentration that we assumed in our model. The reduction has probably occurred or is an on-going process, at least at the Olkiluoto site, as is indicated by the negative correlation of the sulphate and methane concentrations at different depth shown in Figure 6d.

In Table 3 the highest values of concentrations of methane and sulphate at the repository depth at the Äspö and the Olkiluoto sites are shown. Contrary to the situation at the Äspö site, limiting concentration for copper canister corrosion at the Olkiluoto site becomes the sulphate concentration. Even though the sulphate concentrations at the repository depth is low, much higher concentrations (up to 4.5 mmol L^{-1}) have been observed at depths between 200 and 400 m. Hydrogeological studies often indicate that the groundwater at the intermediate level is dynamic and recharge of groundwaters from above to the repository level is possible. As the sulphate will not participate in other reactions except for the microbially-mediated sulphate reduction, the sulphate will be able to reach the repository depth with the concentration unchanged if they are not reduced by microbes. Moreover, the data presented in Pitkänen are those from different boreholes. The higher concentrations are observed in borehole KR13 and the data for this borehole are available only to a depth of 362 m. For the present-day groundwater sulphate concentration at repository depth, the value of 4.5 mmol L^{-1} seems to be even more reasonable than the lower values presented in Table 3. In one of our case studies below, we will use a limiting concentration of 4.5 mmol L^{-1}.

When the limiting concentration for copper canister corrosion becomes sulphate, large uncertainties will be involved in our model prediction because of the uncertainty of future evolution of the sulphate concentration in the intermediate groundwater as discussed previously in this report. Both future seawater intrusion and the intrusion of glacial meltwater will introduce more sulphate into the intermediate groundwaters. When the deep groundwaters also have high concentrations of sulphate as it is in the case at the Äspö site (up to 10 mmol L^{-1} at depths around 1600 m, see e. g. Laaksoharju and Wallin, 1997), the upconing effect at the wake of an ice sheet retreat will introduce sulphate upward into the groundwaters at the repository depth.

At the two sites we have focused on, one has higher concentration of sulphate (the Äspö site) and the other has higher concentration of methane (the Olkiluoto site). The generally low sulphate concentrations observed at the Olkiluoto site could possibly be of the reason that part of the sulphate in the deep groundwaters have already been reduced by methane catalysed by SRB as the methane concentrations are rather high, and there is a negative correlation between the sulphate and methane concentrations in deep groundwaters. Even though the sulphate concentration decreases with depth, the TDS (total dissolved solid), mainly Cl^- increases with depth (Posiva, 2003), having a similar trend as is observed at the Äspö site. Positive correlation between chloride and sulphate concentrations have been observed in deep groundwaters at various other sites and it would difficult to explain the decrease of the sulphate concentration with depth at the Olkiluoto site if microbic reduction of sulphate is not assumed. Moreover, relatively high sulphide concentrations have also been measured at different depths of the groundwater at the Olkiluoto site. The Äspö site may happen to be a site of low methane emissions from underneath of the Earth’s mantle and the high sulphate concentrations have been preserved. The sulphide produced by sulphate reduction in the deep groundwaters may have precipitated as sulphide minerals or have been transported by diffusion upward into the intermediate levels of the groundwaters. Sulphide in colloid phases has been observed in groundwaters at the Äspö site (Laaksuharju, 1995).

With the limited data available and some sites showing very high methane concentrations while others showing very high sulphate concentrations, it may not be possible to completely ruled out that other conditions could exist for which both concentrations would be high. We therefore considered another extreme case with a limiting concentration of 10 mmol L^{-1}, which corresponds to the highest sulphate concentration at the Äspö site.

In Figure 6 the corrosion depths for three different cases are plotted. The first case (the solid line) is the representative "central" case discussed already in Section 5, with a limiting concentration of 1 mmol L^{-1}. This case may well represent the observations at the Äspö site. The second case (the dotted line) has a limiting concentration of 4.5 mmol L^{-1} and corresponds to the observations at the Olkiluoto site. The third case (the dashed line) has a limiting concentration of 10 mmol $L^{-1}$and is the worst case conceivable based upon the concentration data at different sites. It can be considered as a "hybrid" case of the sites of Äspö and Olkiluoto, in which the high methane and high sulphate concentrations are assumed to co-exist at one single site.

The corrosion depth is calculated by Eq. (5) and is proportional to the concentration of the limiting species (either methane or sulphate) in the incoming groundwater when other parameters in the model are assumed to be constant. The corrosion depth therefore increases approximately 10 times when the limiting concentration increases 10 times, from the representative value of 1 mmol L^{-1} to the worst-case value of 10 mmol L^{-1}. The modelling results show that in the worst case considered, more than half of the thickness of the canister wall (50 mm) may be corroded within 10^5 years.

Other parameters, like the fracture aperture ($2b$) and the equivalent flow rate (Q_{eq}) used in our model have also large uncertainties. Sensitivity analyses for those parameters show that the modelling results are usually less sensitive to their variations compared to the variation of the limiting concentration. When the fracture aperture varies by one order of magnitude, the corrosion depth will hardly change. When the equivalent flow rate varies by one order of magnitude, the corrosion depth will change only by less than 50%.

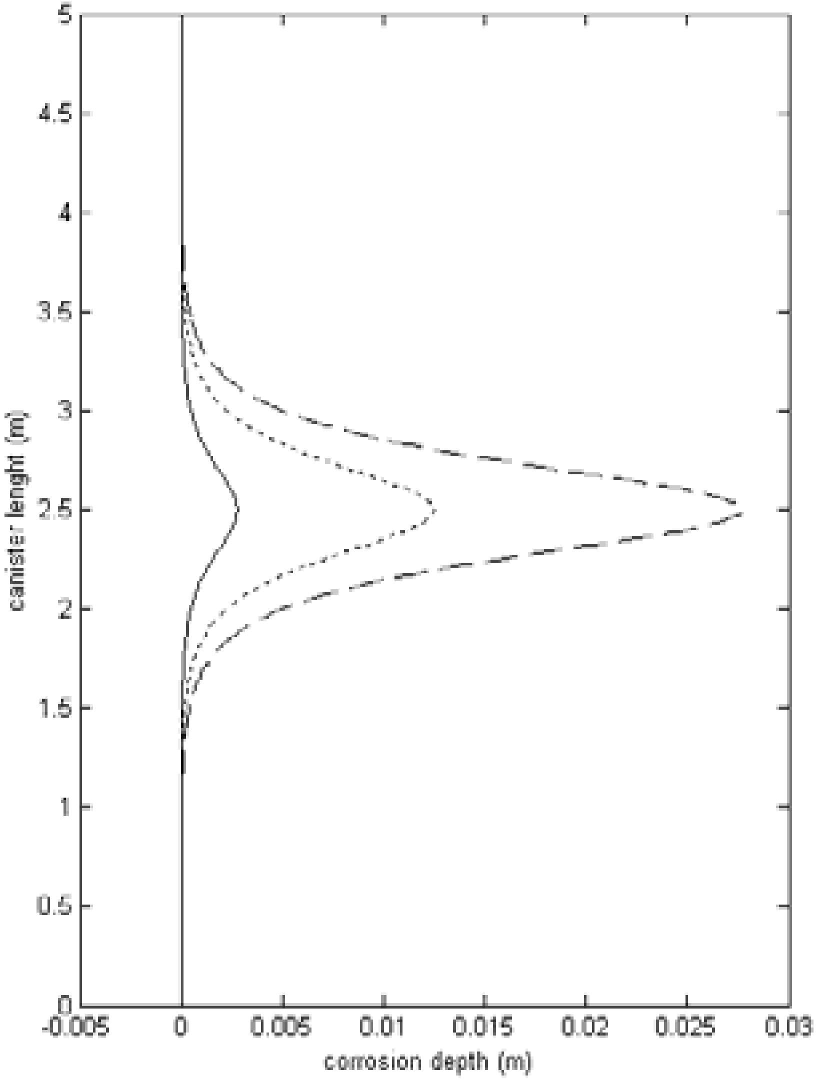

Figure 8. Corrosion depths of copper canister in different cases. Case 1: the solid line, with a limiting concentration of 1 mmol L^{-1} (our representative value), relevant to the Äspö site; Case 2: the dotted line, with a limiting concentration of 4.5 mmol L^{-1}, relevant to the Olkiluoto site, Case 3: the dashed line, with a limiting concentration of 10 mmol L^{-1}, corresponding to a "hybrid"site of both high methane and sulphate concentrations.

7 Discussions and conclusions

We have used a coupled transport/reaction model to address the general corrosion of a copper canister in a final repository for spent nuclear fuel. The corroding species is assumed to be sulphide that is produced through sulphate reduction mediated by microbes (sulphate reducing bacteria, SRB).

Reliable data for microbial reaction kinetics are not readily available for the microbes in deep groundwater but the reaction can be fast. An instantaneous reaction rate has therefore been assumed. This implies that the rate of microbially catalysed reaction is limited by the supply of either sulphate or methane, whichever is lower in concentration. Methane is chosen as an electron donor because it is the dominant reducing species in the groundwater.

In our modelling of the transport of sulphide through the bentonite buffer, any other reactions of the sulphide inside the buffer are neglected. Sulphide generation by SRB has conservatively been assumed to occur as close as possible to the canister, but not in the buffer in which water activity is generally considered to be too low. Generated sulphide may react with ferrous iron to form iron sulphides, but this may be of minor importance because the ferrous iron concentration in the groundwater is usually two orders of magnitude lower than those of methane or sulphate. The availability of ferrous iron from various sources have to be evaluated in more detail in order to determine if its reaction with sulphide have to be considered in future modelling work. The ferrous iron minerals in the bentonite buffer are predominaly already in the form of sulphide minerals such as pyrite. No significant reaction of the sulphide within bentonite can therefore be expected.

In our model the corrosion depth is directly proportional to the concentrations of either sulphate or methane that has a lower value. In our sample calculations, a representative "central" value of 1 mmol L^{-1} is used for the concentration of the limiting species for corrosion. This value is chosen based on the observations of both methane and sulphate concentrations in groundwaters at intermediate depths at various investigated sites. It could well represent the observations at the Äspö site. With this representative value, the maximum depth of corrosion of the canister wall will be a few millimetres.

The modelling results are, however, sensitive to the variations of the concentrations of both sulphate and methane. There are probably significant variations and uncertainties of the concentrations of sulphate and methane in the groundwaters in crystalline rocks. At some sites high sulphate concentrations are observed and at other sites very high concentrations of methane are measured. Future climate evolution may have a limited impact on methane concentration since the methane is believed to be emanated underneath from the mantle of the Earth. The sulphate concentrations at intermediate depths of groundwaters will, however, probably be influenced significantly by several factors like permafrost, seawater intrusion and intrusion of glacial meltwater. It is extremely difficult to quantify the influences and we therefore proceed with sensitivity analyses. The results of sensitivity analyses indicate that, in the worst case conceivable (when the limiting concentration becomes 10 mmol L^{-1}), more than half of the thickness of the canister wall will be corroded within 10^5 years. On the other hand, the modelling results are less sensitive to the variation and uncertainties of the fracture aperture and the equivalent flow rate.

From the modelling results of this paper, the following conclusions can be drawn:

(1) With the representative central values of groundwater compositions measured in granitic bedrocks are considered, after 10^5 years a few mm of the copper canister can be corroded by sulphide locally facing the opening of an intersecting fracture in the bedrock if sulphate reducing bacteria are present.

(2) The results in the example are sensitive to the sulphate or methane concentration and to some extent the equivalent flow rate Q_{eq}. The results are neither sensitive to the geometry of the system, nor to the fracture aperture.

(3) The sulphate or methane concentration is highly variable from one site to another and there are large uncertainties concerning future evolution of the sulphate and methane concentration. Sensitivity analyses of this report indicate that, in the worst case conceivable, more than half of the thickness of the canister wall could possibly be corroded by the mechanism considered.

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