SKI Report 2008:16
SSI Report 2008:06

Review of SKB's Safety Assessment SR-Can: Contributions in Support of SKI's and SSI's Review by External Consultants

March 2008

Statens strålskyddsinstitut
Swedish Radiation Protection Authority

SKi

ISSN 1104-1374
ISSN 0282-4434
ISRN SKI-R-08/16-SE

Foreword

The work presented in this report is part of the Swedish Nuclear Power Inspectorate's (SKI) and the Swedish Radiation Protection Authority's (SSI) SR-Can review project.

The Swedish Nuclear Fuel and Waste Management Co (SKB) plans to submit a license application for the construction of a repository for spent nuclear fuel in Sweden 2010. In support of this application SKB will present a safety report, SR-Site, on the repository's long-term safety and radiological consequences. As a preparation for SR-Site, SKB published the preliminary safety assessment SR-Can in November 2006. The purposes were to document a first evaluation of long-term safety for the two candidate sites at Forsmark and Laxemar and to provide feedback to SKB's future programme of work.

An important objective of the authorities' review of SR-Can is to provide guidance to SKB on the complete safety reporting for the license application. The authorities have engaged external experts for independent modelling, analysis and review, with the aim to provide a range of expert opinions related to the sufficiency and appropriateness of various aspects of SR-Can. The conclusions and judgments in this report are those of the authors and may not necessarily coincide with those of SKI and SSI. The authorities own review will be published separately (SKI Report 2008:23, SSI Report 2008:04 E).

This report compiles contributions from several specific research projects. The separate reviews cover topics regarding the engineered barrier system, the quality assurance, the climate evolution and its effects, and the ecosystems and environmental impacts. All contributions are in English apart from the review concerning ecosystems and environmental impacts, which is presented in Swedish.

Bo Strömberg (project leader SKI)   Björn Dverstorp (project leader SSI)

Förord

Denna rapport är en underlagsrapport till Statens kärnkraftinspektions (SKI) och Statens strålskyddsinstituts (SSI) gemensamma granskning av Svensk Kärnbränslehantering AB:s (SKB) säkerhetsredovisning SR-Can.

SKB planerar att lämna in en ansökan om uppförande av ett slutförvar för använt kärnbränsle i Sverige under 2010. Som underlag till ansökan kommer SKB presentera en säkerhetsrapport, SR-Site, som redovisar slutförvarets långsiktiga säkerhet och radiologiska konsekvenser. Som en förberedelse inför SR-Site publicerade SKB den preliminära säkerhetsanalysen SR-Can i november 2006. Syftena med SR-Can är bl.a. att redovisa en första bedömning av den långsiktiga säkerheten för ett KBS-3-förvar vid SKB:s två kandidatplatser Laxemar och Forsmark och att ge återkoppling till SKB:s fortsatta arbete.

Myndigheternas granskning av SR-Can syftar till att ge SKB vägledning om förväntningarna på säkerhetsredovisningen inför den planerade tillståndsansökan. Myndigheterna har i sin granskning tagit hjälp av externa experter för oberoende modellering, analys och granskning. Slutsatserna i denna rapport är författarnas egna och överensstämmer inte nödvändigtvis med SKI:s eller SSI:s ställningstaganden. Myndigheternas egen granskning publiceras i en annan rapport (SKI Rapport 2008:19; SSI Rapport 2008:04).

Denna rapport består av bidrag från flera separata forskningsprojekt. Dessa granskningar täcker frågor kring tekniska barriärerna, kvalitetssäkringen, klimatutvecklingen och dess effekter, ekosystemen och miljöpåverkan. Alla bidrag är på engelska med undantag av bidraget om ekosystemen och miljöpåverkan som är på svenska.

Bo Strömberg (projektledare SKI)   Björn Dverstorp (projektledare SSI)

SKI Report 2008:16
SSI Report 2008:06

Review of SKB's Safety Assessment SR-Can: Contributions in Support of SKI's and SSI's Review by External Consultants

March 2008

Table of contents

1. Review of the SR-Can project reports with regard to the long term structural integrity of the copper shell of the waste canister.
   K. Pettersson

2. A critical review of issues in the SR-Can report relating to the containment performance of the KBS3-canister
   W. H. Bowyer

3. Status of research on chemical erosion of the buffer
   R. Arthur, W. Zhou

4. Audit of data and code use in the SR-Can safety assessment
   T.W. Hicks and T.D. Baldwin

5. Review of the climate and climate-related issues in the safety assessment SR-Can
   P. Holmlund

6. Future intrusion of oxygenated glacial meltwaters into the Fennoscandian shield: a possibility to consider in performance assessments for nuclear-waste disposal sites?
   P. Glynn

7. Ekosystem och miljöpåverkan: Slutrapport för uppdrag inom SSI:s delprojekt (in Swedish)
   K. Stark

8. Impacts of future glaciations on geochemical conditions at repository depth: Review of SKB’s approach
   A. Bath and H.-P. Hermanson

9. Review of the SR-Can project regarding microbial processes
   R. Hallberg

Review of the SR-Can project reports with regard to the long term structural integrity of the copper shell of the waste canister

Kjell Pettersson

Matsafe AB
Skeppargatan 84
114 59 Stockholm
Sweden

Summary

The SR-Can project reports have been reviewed with regard to the mechanical integrity of the copper shell of the waste canister. The most severe threat to canister integrity has been identified as shear deformation of the canister during a post-glacial earthquake. For the postulated 10 cm shear caused by the design basis earthquake the shell will survive the initial shear. However it is likely that the copper shell will remain under tensile stress for a considerable time after the earthquake. The exact stress levels and time dependencies will need to be determined by improved calculations compared to those performed so far. The persistent stress after the earthquake shear will make failure by creep brittle fracture or stress corrosion cracking possible. SKB has discarded the possibility of creep brittle fracture on the basis that the phosphorus doped copper has a creep ductility of at least 10%. However it is shown in the report that SKB research results so far do not fully support that conclusion. Stress corrosion cracking has also been excluded as a possible failure mechanism by SKB for times later than the first tens of years after sealing of the repository. This conclusion is largely based on threshold values of important parameters determined in very short term experiments compared to canister residence times in the repository. A more quantitative determination of how important aspects of SCC depend on environmental parameters is needed in order to make the conclusions credible. It is also important to consider all possible mechanisms of SCC in more detail than has been done so far.

Sammanfattning

SR-Can projektets rapporter har granskats med avseende på den mekaniska integriteten hos avfallskapselns kopparmantel. Det svåraste hotet mot kopparmantelns integritet har identifierats som den skjuvdeformation kapseln utsätts för i samband med en post-glacial jordbävning. Den 10 cm skjuvdeformation som orsakas av den konstruktionsstyrande jordbävningen kommer inte att leda till att kapselns integritet bryts. Däremot är det troligt att kopparmanteln kommer att vara utsatt för dragspänningar under mycket lång tid efter jordbävningen. Hur hög och långvarig spänningen blir måste bestämmas genom beräkningar som är bättre än de beräkningar som gjorts hittills. Den långvariga spänningen efter jordbävningen kan leda till brott på manteln genom sprött krypbrott eller spänningskorrosionsbrott (SCC). SKB har uteslutit krypbrott baserat på en slutsats att den fosfortillsatta kopparn har en krypduktilitet på minst 10 %. Emellertid visas i rapporten att de forskningsresultat SKB utgår från inte till fullo medger en sådan slutsats. SCC har också uteslutits som ett möjligt brottssätt för tidpunkter senare än de tiotals första åren efter att avfallsförvaret förslutits. Denna slutsats baseras i hög grad på tröskelvärden för viktiga parametrar vilka bestämts i mycket kortvariga experiment jämfört med de tider som avfallskapslarna kommer att förvaras. Det behövs mer kvantiativa data på hur olika aspekter av SCC påverkas av yttre parametrar för att göra denna typ av slutsatser trovärdiga. Det är också viktigt att beakta alla tänkbara former av SCC mer i detalj än hittills.

Table of contents

1. Introduction

In association with its application for building an encapsulation plant for high level nuclear waste, mainly spent fuel, the Swedish Nuclear Fuel and Waste Management Company (SKB) has submitted to the Swedish Nuclear Power Inspectorate (SKI) a preliminary safety assessment of the KBS-3 concept for long term storage of waste canisters in two potential repositories, Laxemar and Forsmark. The safety assessment, called SR-Can, is of a preliminary nature and will be followed by a more definitive safety assessment, SR-Site, when SKB applies for building the final repository. The SR-Can project is reported in a main report [1] which refers to numerous underlying reports where more details of the information used in the safety assessment can be found.

On assignment from SKI the present writer has taken on the task of reviewing the SR-Can project with regard to the properties of the copper used as the outer shell of the waste canister. Previously from about 2002 the present writer has performed research for SKI on copper properties with an emphasis on the creep properties of copper. The work has been documented in several reports [2-5]. Prior to 2002, about 1991-1999 the writer participated in reference groups on canister integrity [6] and canister corrosion organized by SKB. The writer also performed stress corrosion cracking research on copper for SKB [7, 8] as well as some other minor research [9, 10].

The present review will cover the manufacture of the canister, the loads on the canister during the different phases of the storage in the repository with subsequent identification of the largest threat to canister integrity and a discussion on whether or not the conclusios in SR-Can on canister integrity are sufficiently substantiated. Any threats to canister integity from mishaps during manufacture, transport and deposition are outside the scope of the present report.

2. Manufacture of the canister

The copper shell of the waste canister has a length of 4.8 m, an outside diameter of 1.05 m and a wall thickness of 50 mm. Currently the preferred way of manufacturing the shell is to use extrusion. This means that a bottom and lid will have to be welded to the shell. The bottom of the shell is welded to the shell in the shell fabrication plant while the lid is welded to the shell in the encapsulation plant after filling the shell with the canister insert and the fuel elements.

Use of extrusion instead of the previosly contemplated method of welding together two rolled half-shells is a significant improvement with regard to the assessment of the long term integrity of the canister. The latter method would have led to concerns with regard to macroscopic residual stresses induced during the fabrication of the shell. There are no such concerns with the extrusion method and material characterizations of extruded material have not revealed any abnormalities with regard to the microstructure.

Two methods of welding the lids have been suggested, electron beam welding (EB) and friction-stir-welding (FSW). Compared to EB welding the relatively newly developed method of FSWdoes not involve any melting of the material. This ensures a relatively homogeneous structure which in the tests performed so far have been described as similar to the bulk structure [11]. The reported grain size, 75 µm, is somewhat finer than the grain size in the extruded material. Measured residual stresses after FSW are less than 40 MPa. These promising results make it likely that FSW will remain the joining method of choice for shell bottom and lid also in the final version of the KBS-3 concept.

However there is one detail which requires further study. The method of FSW results in severe plastic deformation of the material. During severe plastic deformation recrystallization probably takes place several times. Very often the final result is a very fine grained structure. In fact severe plastic deformation is a method by which nano-crystalline materials can be produced. Xie et. al have shown how a fine-grained microstructure is developed in association with FSW in pure copper [12]. It is by no means clear or even likely that a fine-grained zone in the friction stir welds of the copper shell would have a negative impact on its properties. But it is an unknown entity in this context. Therefore SKB should determine the margin to formation of a fine-grained structure with the use of their selected weld parameters. Unless a sufficient margin is shown to exist it is necessary to determine what impact a fine-grained zone would have on the properties of the weld and its possible effect on canister integrity.

3. Loads on the canister during storage

The time period for which the canister integrity is assessed can be divided into three parts, the first 1000 years, the next 100000 years and another 900000 years [1]. During the first 1000 years it is assumed that the climate is unchanged in the main scenario or possibly subject go global warming in an alternative scenario. The choice of alternative has no impact on the factors which determine the canister integrity.

The loads experienced dring the different periods have been summarized in the SR-Can report on the design basis for the canister [13]. There is also an earlier report on the design basis [14]. The first period is characterized by saturation and swelling of the bentonite. The swelling pressure depends on the bentonite density and is expected to lie in the range 3.4 to 11.7 MPa. The ground water pressure of 5 MPa in Forsmark or 4 MPa in Laxemar is added to the swelling pressure. The resulting compressive stress on the canister shell will make it deform on to the insert. The maximum strain will be about 4 %. Since the deformation occurs in compression there is no concern for failure by creep cracking or stress corrosion cracking. However locally on the canister shell there will be regions of tensile stress. As shown for instance by Karlsson there could be a tensile stress on the inside of the copper lid if there is a gap between lid and insert [15]. This stress is large enough to cause stress corrosion cracking (SCC) but fortunately there is no environment inside the canister which can cause SCC. There is a potential for brittle creep failure but, as will be discussed later in the present report, that although SKB has not demonstrated satisfactorily that brittle creep failure is excluded in phosphorus doped copper other arguments can probably be used to demonstrate that brittle creep failure will not occur under repository conditions. Thus it can be concluded that these loads are no significant threats to the integrity of the copper shell during first 1000 years.

However one point of uncertainty is the non-uniform loads caused by an uneven saturation of the buffer. These loads are discussed first in [14] and later in [16]. In the latter report it is shown that uneven loads from the buffer can lead to considerable stresses on the insert but it is stated that the stresses in the copper shell are below the yield strength of the copper. One of the load cases is said to lead to insert collapse, but is not discussed further. Since details of insert collapse may be somewhat unpredictable shell penetration can not be excluded after insert collapse. This load case thus needs some further elaboration.

The next 100000 years will probably start much the same as the first 1000 years. However with time it is likely that one or more glaciation cycles will occur. The ice cover of up to 3 km will put pressure on the rock which is transmitted down to the repository. The external pressure on the canister will now be so large that there is concern for collapse of the insert. However experiments and calculations have demonstrated that the margin to global insert collapse under the added pressures of buffer swelling, groundwater and ice cover, up to about 45 MPa, is about a factor of 3. Again, since the main stresses are compressive, there is no concern for tensile failure by creep or SCC except in the lid where potentially creep brittle failure could occur.

The most severe challenge to canister integrity comes from the loads which might occur after glaciation. Geological evidence shows that very severe earthquakes, up to about magnitude 8, have occurred in the northern parts of Sweden in connection with previous deglaciations. No similar evidence is available from the parts of Sweden where the repository is expected to be located. Thus in SR-Can it has been estimated that there is a certain probability that earthquakes up to a magnitude of 6 may occur during a deglaciation during the first 100000 years. The earthquake is caused by a sudden shear movement of the two faces of a pre-existing fracture in the rock underground. Such pre-existing fractures may be located close to the repository so that one or more deposition holes are sheared. As far as possible pre-existing fractures in association with the repository will be identified and deposition holes potentially affected by shearing of these fractures will not be used. However there will still be a certain probability for earthquake shear in used deposition holes.

SKB has postulated that the maximum shear which needs to be taken into account in the design of the canister is 10 cm. The resulting stressess and strains in the canister for 10 cm and 20 cm shear have been calculated in for instance [17] and [18, 19]. The calculations show that the canister shell will be subjected to significant plastic deformations. Based on the calculations in [17] the present writer attempted to calculate the stresses in the canister and how they could be expected to develop with time after an earthquake shear [5]. The calculations took creep in copper into account using the model included as an appendix in [5]. The result is shown in Figure 1. The relevant curve is the result for 25 ˚C since it is only during the first 2000 years that the temperatures of the canisters exceeds 25 ˚C. This estimate did not take creep in the bentonite into account. According to [13] the recent calculations by Hernelind takes creep relaxation in the bentonite into account. However on examination of the report by Hernelind [19] there is no mention of taking other creep effects into account than those of copper.

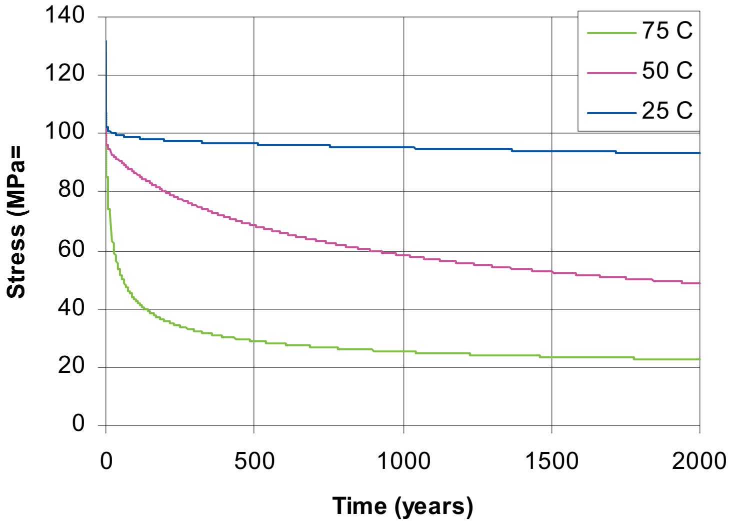


Figure 1. Estimated stress level in canister after an earthquake event at different temperatures.

For the creep of copper Hernelind has used an earlier version of the creep model developed by the present writer [20]. This can be expected to give similar results to that of the most recent version of the model [5]. However Hernelind apparently uses the model in a way that it is not intended to be used. One point of the model is that it treats plastic deformation and creep in a unified manner where pure creep or pure plastic deformation are just limiting cases of the model at slow and fast strain rates respectively. It appears as if Hernelind has retained the concept of a time independent plastic yield followed by a linear strain hardening, which is definitely at variance with the model. Thus his results must be considered to be somewhat uncertain. The particular result that 11 % creep occurs during the “creep phase” also seems somewhat unlikely in view of the fact that the external loading on the bentonite-canister complex remains fixed during that time. There is however no big doubt about the general conclusion from Hernelind’s calculations, that the canister will survive the purely mechanical deformation in association with the rock shear and the following creep deformation. What remains in doubt is whether or not time dependent degradation mechanisms driven by the tensile stress present over a long time period as indicated in Figure 1, will be a threat to canister integrity. The answer to that is no according to SKB. With regard to creep brittle fracture they say that the phosphorus doped copper has an adequate ductility. With regard to stress corrosion cracking they have concluded that the environment is such that no SCC can occur. The next two sections will be devoted to an examination of those two conclusions.

From a canister integrity point of view the next 900000 years of storage will be a repeat of the questions for the first 100000 years. It is possible to speculate that a crack growing slowly due to a stress imposed by an earthquake, but which did not penetrate, might get a new start as a result of a new glaciation cycle. However such speculation seems rather pointless, particularly since the waste has lost much of its radioactivity in that stage.

4. Creep brittle fracture of the phosphorus doped copper

As sometimes pointed out by SKB creep deformation is mainly beneficial since it will lead to reduction of any residual stresses or other stresses which might have been caused by deformations of the canister. There is no loading case which will lead to extensive creep deformation of the canister, except the case calculated by Hernelind [19] which needs to be examined further.

The problem with creep is thus mainly the problem of creep ductility. When a metal fails under conditions of creep, failure usually occurs in one of two possible modes, ductile failure with extensive plastic deformation or intergranular creep fracture with a limited amount of plastic deformation. However most parts of the canister can be expected to be fairly tolerant to brittle creep failure since the main source of tensile stress is the residual stress. This in turn is of the order of the yield strength, about 50 MPa. With an elastic modulus of about 100000 MPa this means that the maximum creep strain which can occur before the stress is fully relaxed is about 0.05 %. However as discussed in Section 3 there may be a sustained tensile stress for long times after an earthquake shear.

Early creep experiments with oxygen free high conductivity (OF) copper resulted in brittle intergranular failures with failure strains as low as 0.3 % [21]. In the same test series there was also a phosphorus-desoxidized copper with about 50 ppm of phosphorus. The experiments showed that this type of copper did not suffer from the low-ductile intergranular creep failure and it was also observed that the creep rates were about 10 times lower than for the OF copper. These observations led to the choice of oxygen free copper with a phosphorus addition (OFP copper) as the material for the SKB waste canister.

Sulphur segregated to the grain boundaries was implicated as the cause of the creep brittle failures of the OF copper. A comparison of OF copper with 6 and 10 ppm of sulphur showed that the latter was very brittle while the copper with 6 ppm S reached about 10 % strain before failure. As to the reason why the presence of P has a beneficial effect on ductility it has been hypothesized that the P in some way competes with S for sites at the grain boundaries so that the grain boundaries in OFP copper therefore contain less S than the boundaries in OF copper [13]. Another suggestion is that P forms a compound with S and in that way passivates the S.

After the choice of the OFP copper SKB has performed an extensive amount of creep testing on the material in various conditions. The material has been tested with different grain sizes, after welding etc. In none of the tests performed has any creep brittle behaviour been observed. It should be noted however that all testing has been performed at higher temperatures and higher stresses than those expected for the canister in the repository. The simple reason for this choice of parameters is that with lower values creep rates will be so low that no results will be obtained. In any case, based on these results and the application of well established extrapolation methods for creep rapture, SKB expresses with confidence that the OFP copper will have an adequate ductility for the application as waste canister shell material, a value of 10 % is used in the SR-Can project.

SKI consultants have examined the problem of creep ductility and have estimated the creep life of the OFP copper [5, 22] based on a theory by Cocks and Ashby [23]. These estimates addressed the actual fracture mechanism for creep brittle fracture as formulated by Cocks and Ashby. In one of the discussions the creep life was estimated to 4 million years. In fact the Cocks-Ashby theory overestimated the life of OF copper so much that it is reasonable to conclude that the Cocks-Ashby model does not apply to OF copper. The use of the Cocks-Ashby theory or other theories of creep brittle fracture is in contrast to the SKB approach where ductile fracture data is used to extrapolate to conditions of lower stress and temperature for an assessment of the possibility of creep brittle fracture. For that approach to be valid it must also be necessary to demonstrate a relationship between ductile creep failure and creep brittle failure.

One of SKB:s main consultants regarding questions of creep fracture has argued at some length in a KASAM report that the OFP copper has an adequate ductility for use as waste canister material [24]. The problem is that the conclusion is based on a series of creep tests in which the specimens have failed in a ductile manner. Why this may be a problem is illustrated in Figure 2. In the Figure, data of the creep lives of OF copper and OFP copper at 215 ˚C have been plotted. It is clear that the creep lives have different stress dependencies for the two materials as would be expected since one of the materials fails with the creep brittle mechanism and the other by ductile failure [23, 25]. For the former mechanism the stress exponent is numerically small, theoretically 1-2 [23, 25] but in the Figure about 6, while for the ductile mechanism the stress exponent will roughly be the same as the stress exponent in Norton’s law, since

$$t_f \cong \varepsilon_f / \dot{\varepsilon} \qquad (5)$$

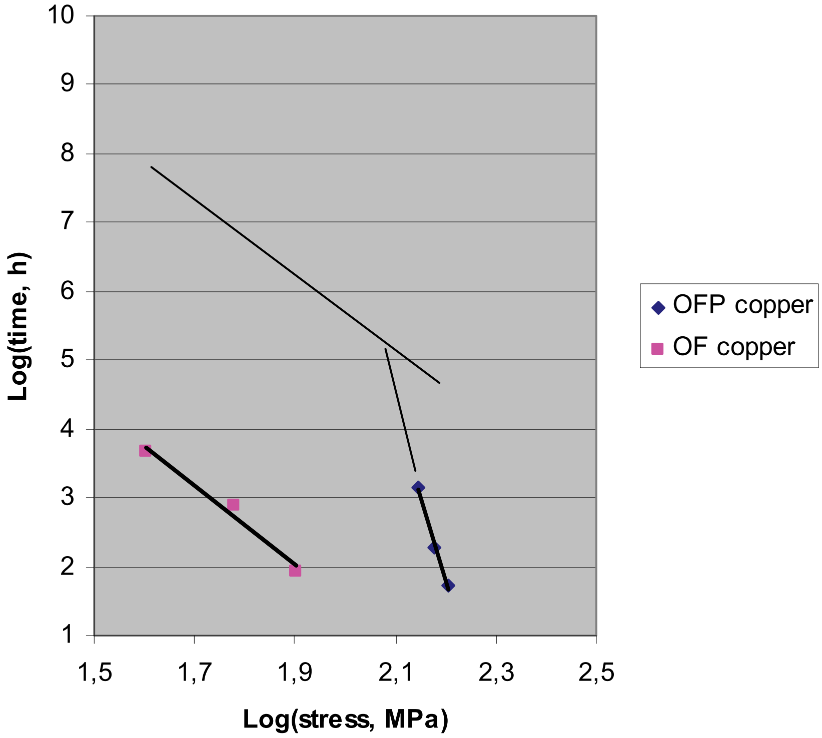


Figure 2. Time to failure as a function of stress for specimens tested in [21].

The thin line parallel with the failure line for OF copper illustrates a hypothetical situation in which the creep brittle mechanism has been decelerated by a factor of 10000, perhaps by the addition of phosphorus. If such a situation existed the creep brittle mechanism would only be accessible by testing for more than 230000 hours at a stress a stress below about 104 MPa. Testing at higher stresses would lead to ductile failures in shorter times. Therefore in our hypothetical situation the creep-brittle mechanism could be at work in OFP copper but it would be inaccessible by practical experiments. If this creep life equation applies to the OFP copper it would have a creep life of just 2000 years at a stress of 50 MPa. In Section 3 we saw that such levels of stress or even higher can be present for long times after an earthquake shear. With regard to creep ductility of the OFP material there is in fact no adequate information available at the present time. It should be clear from the discussion above that the SKB tests on OFP copper tell us little about the relevant ductility. Thus it is currently uncertain whether or not the OFP copper fulfils the specification of 10 % creep ductility quoted in the SR-Can Report [1].

There is however a possibility to produce data on the creep brittle mechanism and that is to use triaxial stress states in which high tensile stresses can be combined with low shear stresses. Thus the creep brittle mechanism which depends on tensile stress will be accelerated in comparison with the ductile mechanism which depends on shear stress. This has to some extent already been done for the OFP copper by Auerkari and coworkers at VTT [26, 27]. They have tested CT specimens of copper at constant load and for a rather long time. The evaluation of the results has been according to the LICON methodology as described for instance by Bowyer [28]. The LICON methodology relies on a time to failure equation which contains a stress intensification factor H and a deformation mode dependent reference stress. Bowyer notes that the equation is purely empirical and expresses that some of the content of the equation must be taken on trust. One important and promising result of the VTT tests on a CT specimen is the relatively low density of creep cavities in the specimen after the test [26]. Another relevant observation was that the density of cavities was about the same on the surface as in the interior after the test. This latter observation might be an indication that stress triaxiality plays a smaller role than expected for nucleation and growth of creep cavities. Finite element calculations showed that after 64000 h of testing the tensile stress at the crack tip still was about 130 - 360 MPa which would be well above the hypothetical failure line in Figure 1. However in view of the fact that this was a cold worked material and just one test it is not sufficient proof that the OFP copper has no creep brittle behaviour.

The preceding discussion has not taken temperature effects into account. The data in Figure 2 concern 215 ˚C. The VTT experiments were performed at 150 ˚C and the critical temperatures for the copper canister is about 15 to 25 ˚C after the earthquake shear [1]. At these temperatures the creep brittle process will be slower. Since it is a solid state process it is reasonable to assume that it is controlled by a solid state diffusion process with its characteristic activation energy. The lowest activation energy for diffusion in copper is that for boundary diffusion which is 104 kJ/mol [29]. If we apply that activation energy to the creep brittle process we can get an estimate of how much longer the creep life would be at constant stress compared to the creep life at 215 ˚C. The data is shown in Table 1.

Table 1

Creep lives relative to the life at 215 ˚C

Temperature ˚C	Creep life relative to life at 215 ˚C
215	1
150	51
100	2710
75	30100
50	486000
25	1.25×10^7

This table indicates that even if the hypothetical situation regarding creep brittlenes depicted in Figure 1 existed, there should be little concern for brittle creep fracture since the creep-brittle process is sufficiently decelerated by the temperature to reduce the risk of brittle fracture. However since this estimate so far is pure speculation it falls on SKB to give it a firmer basis.

It is thus concluded that SKB has not succeeded in demonstrating that the creep ductility of OFP copper is adequate for its purpose. There are however good prospects for making a more convincing case. One way could be to perform triaxial creep fracture tests which may result in useful data. Another way could be to determine the activation energy for the creep brittle process in OF copper which might then result in a credible extrapolation like that shown in Table 1.

5. Can stress corrosion cracking be excluded?

Experience from the light water reactor industry indicates that it is easy to underestimate the risk of stress corrosion cracking of various components. There are about ten different material-environment combinations which from time to time have resulted in serious stress corrosion cracking problems in light water reactors. With few exceptions most of these cases were completely unanticipated in the design and construction of the reactors. It is in the light of this experience that the potential for stress corrosion corrosion cracking of the copper waste canister must be considered quite seriously in the safety assessment of the waste storage system. It also offers a unique scientific and engineering challenge in which behaviour in a million year perspective must be judged based on data from ezperiments which rarely have taken more than a few thousend hours to perform.

A review of stress corrosion cracking information relevant to the problem of storage of waste canister can be found in SKB-TR-01-23 [30], which in turn refers to other reviews pertinent to the problem. Before going into specifics with copper in the repository it is appropriate to deal with a few more general issues. Stress corrosion cracking can be described as the initiation and growth of cracks under the simultaneous influence of a tensile stress and an “aggressive” environment. The quotes on “aggressive” are meant to indicate that quite often some rather benign environments will lead to stress corrosion cracking of certain alloys. Examples are pure water in boiling water reactors which can crack stainless steel, ordinary tap water which cracks alpha-beta brass, and methanol with small amounts of dissolved chloride which cracks unalloyed titanium. There is thus a certain unpredictability about stress corrosion cracking which makes it necessary to explore several different possibilities with regard to possible stress corrosion cracking of the copper canister.

A third important factor in stress corrosion cracking is the material itself. Most alloys can be used in different states. The most common type of state is the level of cold work. As a general rule a harder material is more susceptible to stress corrosion cracking than the same material in a softer state. Thus cold work generally promotes stress corrosion cracking susceptibility. Another possible difference is the grain size. For the effect of grain size it is more difficult to make any general statements. One reason is that some forms of stress corrosion cracks take a path through the grains, transgranular cracking, while other forms take a path in the grain boundaries, intergranular cracking. A third possibility with regard to the state of a material is that it can be subject to hardening mechanisms other than cold work. Again the general rule is that the harder material is more susceptible, but these hardening mechanism might also affect slip behaviour so there is no clear cut relation between hardness and susceptibility. A relatively soft material with planar slip may well be more susceptible than a somewhat harder material with a more homogeneous slip behaviour. Most of these possibilities are of no concern for the copper canister. Only grain size and relatively small amounts of cold work need to be considered.

The most poorly understood aspect of stress corrosion cracking is the initiation of the cracks. One often used model for initiation is that the first step in the start of cracking is the formation of a corrosion pit. The shape of the pit induces a stress and strain concentration which leads to the formation of a crack. Note that this model gives no details about the formation of the crack. One might envisage a slip band at the location of the strain concentration where the intense strain in the band perhaps induces an increased corrosion rate. The shallow corrosion trough at the band gets increasingly sharp until it becomes more and more crack-like. Even if the pit-based model is the most popular initiation model it is clear that stress corrosion cracks often form without pits as a precursor. If the material is subject to slip band formation localized attack where a band cuts the surface can occur on an otherwise smooth surface as well as in the bottom of a pit. However this type of gradual transformation of a corrosion trough to a fully developed crack has rarely been observed. A more common case seems to be that if a surface is observed in differents stages of initiation small cracks suddenly appear without any signs of them at the previous observation. This kind of initiation is not yet fully understood.

For the growth of stress corrosion cracks the theories seem to be more fully developed even if many of the details in the theories require considerable refinement. In TR-01-23 SKB considers four different theories as having relevance for copper in the repository: (a) the film-rupture/anodic-dissolution (FRAD) mechanism, (b) the tarnish-rupture (TR) mechanism, (c) film-induced cleavage (FIC), and (d) the surface-mobility (SM) model.

In the FRAD mechanism crack advance occurs by dissolution following the rupture of a protective film at the crack tip. The protective film is restored while the dissolution current decreases until the plastic strain rate at the crack tip again leads to rupture of the film when a new start of the cycle of dissolution-film repair occurs. If the instantaneous dissolution current density is i then the definition of 1 Ampere as 1 Coulomb/s gives the crack growth rate as

$$\frac{da}{dt} = i\frac{\Omega}{ze} \quad (5\text{-}1)$$

where Ω is the atomic volume, *z* the number of electrons involved in the dissolution of one atom, and *e* the electron charge. If the current density is integrated over the time t_f between film rupture events an average crack growth rate can be expressed as

$$\frac{da}{dt} = \frac{Q_f}{t_f}\frac{\Omega}{ze} = Q_f\frac{\dot{\varepsilon}_{CT}}{\varepsilon_f}\frac{\Omega}{ze} \qquad (5\text{-}2)$$

where Q_f is the integrated current density, ε_f the fracture strain of the oxide and $\dot{\varepsilon}_{CT}$ the crack tip strain rate. The latter parameter is an important part of the model and unfortunately not easy to define. One important aspect of the crack tip strain rate is that the growth of the crack itself is the main contributor to the crack tip strain rate. Thus once a crack has started to move it will be self-sustaining as long as the stress and environment are unchanged. However transients in the applied stress intensity factor may lead to corresponding transients in the crack tip strain rate which may accelerate or decelerate crack growth or even stop it completely.

The tarnish-rupture mechanism is slightly different from the FRAD mechanism in that the crack advances by rupture of the oxide rather than by dissolution following oxide rupture. This mechnism has long been associated with SCC of copper alloys because of the observation of SCC of copper and brasses in so-called tarnishing ammonia solutions. The other two SCC agents identified for copper, nitrite and acetate solutions, also results in tarnish films on the surface and thus the TR mechanism has been proposed for all three SCC agents of copper. The crack growth rate is given by

$$\frac{da}{dt} = C\left(\frac{\dot{\varepsilon}_{CT}}{\varepsilon_f}\right)^{1/n} \qquad (5\text{-}3)$$

where C and n are constants characterizing the kinetics of tarnish growth. Crack growth requires oxidation of the copper to form an oxide which requires the presence of an oxidant. It may be argued therefore that the rate of crack growth in the copper shell will decrease with time and cease when all oxidant has been removed from the canister environment.

The film-induced cleavage model is also based on the rupture of a film at the crack tip. It is assumed that when a cleavage crack initiates in the film it will continue as a cleavage crack a short distance into the underlying metal, a distance which may be of the order of ten times the film thickness. The crack growth rate is given by

$$\frac{da}{dt} = (j + L)\left(\frac{\dot{\varepsilon}_{CT}}{\varepsilon_f}\right) \qquad (5\text{-}4)$$

where j is the length of the cleavage crack in the metal and L the thickness of the film.The film may obviously be an oxide but more interesting perhaps is that it can also be a microporous layer which has been shown to crack in a brittle manner. This type of microporous layer can form in alloys between a noble and a less noble metal. One example is Cu-Zn alloys. In such alloys the Zn may be preferentially dissolved leaving a skeleton of copper behind. The question now of course is whether or not such a microporous layer can form in the relatively pure canister copper. There is in fact one such example where preferential dissolution of copper has been observed where dislocations emerge on the surface. Considering the high density of dislocations at a crack tip it does not seem impossible that such a mechanism may be of importance in copper.

SKB has listed about twenty cases of SCC in the three environments known to cause SCC in copper in TR-01-23. Most of these cases can be ascribed to one of the three mechanisms described above. A fourth mechanism to which no case of copper SCC can be ascribed is the so-called surface mobility mechanism. This mechanism focusses on the stress at the crack tip which is of the order of the yield strength of the material. This stress serves as a driving force for removing atoms from the tip which can be expressed as a deviation from the equilibrium vacancy concentration in the material. Thus there will be a vacancy concentration gradient which will result in vacancy diffusion from the crack tip on the crack surfaces. The resulting crack growth rate is

$$\frac{da}{dt} = \frac{D_s}{L}\left[\exp\left(\frac{\sigma\Omega}{kT}\right) - 1\right] \qquad (5\text{-}5)$$

where D_s is the surface self diffusion coefficent and L a diffusion distance, typically 10^{-8} m. This mechanism could obviously work without an environment but then the surface self diffusion is too slow. The role of the environment is that it provides surface adatoms with higher diffusivities than that of the pure metal. An important aspect of the surface mobility model is that crack growth never ceases since the surface diffusivity is always non-zero.

SKB has identified the following requisite factors for SCC:

- Potential
    - Evidence for threshold potential for Cu
- pH
    - Evidence for threshold E/pH for Cu
- Temperature
    - Increasing susceptibility with increasing T in nitrite
- Appropriate chemical species
    - For pure Cu, only NH_3, nitrite, and acetate known to cause SCC
- Alloy composition
    - Added P may have marginal effect
- Strength of the material
    - Creep expected to rapidly relieve crack-tip stress
- Stress
    - Loads >yield but will be dominated by compressive stresses

A number of investigation support the observation of a pH-dependent threshold potential for SCC. The observations can be summarized in that the potential for SCC must always be above the Cu_2O/CuO equilibrium line. Thus SCC always occur above the potential for film formation of copper. A further pre-requisite is that the concentraion of the deleterious species must be above a certain value. An interesting observation is that increasing chloride content leads to a decreased susceptibility to SCC. The reason is that chloride promotes active dissolution and prevents film formation. This leads to the following criteria for SCC according to SKB [13, 31]:

1. The values of E_{CORR} and pH at the shell/environment interface must be within the range of thermodynamic stability of a duplex Cu_2O/CuO film.
2. NH_3, NO_2^-, or OAc^- must be present at the container surface at the same time as the Cu_2O/CuO film is stable.
3. the $[NH_3]$, $[NO_2^-]$, or $[OAc^-]$jmust be within the appropriate ranges for SCC.
4. there must be insufficient Cl^- present to inhibit SCC.
5. there must be sufficient tensile stress to support crack initiation and growth, and
6. the susceptibility to cracking may also be affected by temperature.

Based on these observations SKB has chosen a decision tree approach to the prediction of SCC in copper canisters. This rather branchless tree is shown in Figure 3.

SKB has also modelled how the environment around the canister will develop with time. The CCM-SCC.0 model [31] is based on the reaction mechanism for uniform corrosion with addition of prediction of interfacial pH. The result of the base model and sensitivity studies is that E_{CORR} and pH will exceed the Cu_2O/CuO threshold at most for a period of 3.3 years.

The CCM-MIC.0 model calculates the concentrations of ammonia, nitrite and acetate as the result of microbial activities in the canister environment. 12 types of microbes, 3 types of organic matter and 6 electon acceptors are taken into account. The calculations show that the concentration of the deleterious species increases to steady state levels in a few years but these steady state levels are well below values where they could be harmful. The reasons for these low values are that there is a general lack of microbial activity and also that ammonia, nitrite and acetate are consumed by other microbial processes. In addition the lack of an oxidizing environment make the possibility of SCC quite remote.

These analyses by SKB seem to imply that in order for SCC to occur it is necessary that an oxide film can form on the surface. Thus SCC could only occur as long as oxidants were present in the repository which would be at most a few tens of years. This short time for SCC also makes it more acceptable that the experiments on which these criteria are based in most cased have lasted just a few hundred hours or less. However it is also fair to ask on what basis the mechanisms which do not require an oxide film are discounted. These mechanisms are the surface mobility mechanism proposed by Galvele and the film-induced cleavage mechanism observed by Sieradzki and Kim in which the brittle film is formed by localized attack on dislocations. The answers to these questions are not found in any of the reports on which SR-Can is based. However at a joint SKI/SKB workshop on the mechanical integrity of the canister held in 2006 SKB consultant F. King gave the following answers.

With regard to the reference to the critical potential of the Cu_2O/CuO E/pH criterion SKB answered that this criterion does not mean that an oxide film must be present, it simply reflects a E/pH condition associated with all known cases of SCC in copper.

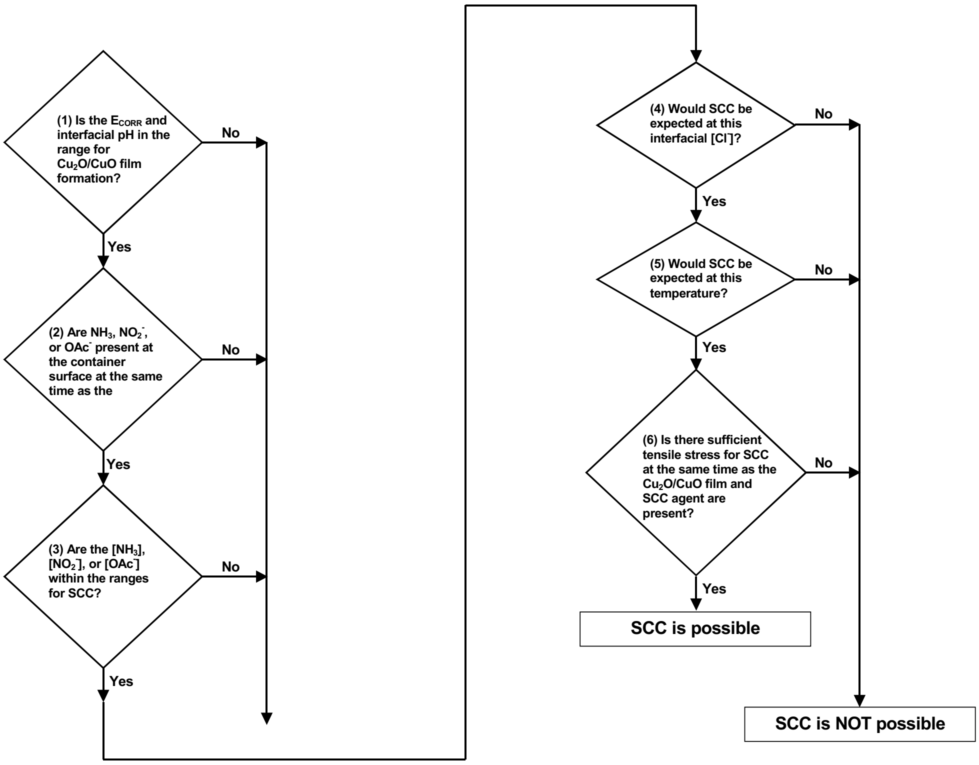


Figure 3. The SKB decision tree used for the prediction of SCC of copper canisters

With regard to the surface mobility mechanism SKB referred to a recent publication by Galvele and coworkers which has demonstrated the SCC in copper may occur at the Cu/Cu^{2+} equilibrium potential [32]. Thus SKB has determined that the potential of the canister is below this threshold potential and concluded that it poses no problem for the canister. However the publication by Farina et. al. does not imply that the Cu/Cu^{2+} equilibrium is a critical potential for SCC by the surface mobility mechanism, it is merely a statement that SCC will occur at that potential with Cu^{2+} ions in solution.

With regard to the observations by Sieradzki and Kim SKB has noted that the nano-porous surface later necessary to initiate a brittle crack could only be produced at extremely high dissolution rates, rates equivalent to corrosion rates of > 350 µm/year. At lower corrosion rates no cracking has been observed regardless of strain rate. Since the high rates necessary for the mechanism to work widely exceeds any dissolution rates possible for the canister SKB has concluded that the film-induced cleavage mechanism due to preferential attack on dislocations is no threat to the canister.

These answers as well as the criteria SKB has produced are not fully satisfactory. They seem to be based on an either/or philosophy. If a certain experiment results in SCC it is clear that under conditions similar to those of the experiment SCC will occur. If on the change of a parameter SCC does not occur we have found a range of immunity. This has been done for several parameters by SKB using experiments which have been run for a few hundred hours at the most. This a philosophy relying on the existence of threshold values for the different important parameters. But there is little scientific basis for the existence of threshold values. Threshold values are often the result of testing within too limited an interval of one or more parameters or the result of a poor experimental design. An example of the latter would be determination of a K_{ISCC}, a threshold stress intensity factor value for crack growth, by loading a fracture mechanics specimen to a prescribed displacement and then monitoring at which K value crack growth stops. However even if there is no K_{ISCC} and the crack growth was described by the relation

$$\frac{da}{dt} = CK_I^n \qquad (5\text{-}6)$$

the experimenter would note as K_{ISCC} the value of K which results in a growth rate of about 10^{-9} mm/s since he would not note any significant crack movement for weeks or months at that rate. But in 10000 years this rate would correspond to 300 mm of crack growth. So the mere fact that a threshold was seemingly determined would not in such a case guarantee absence of crack growth in the long term. A better approach must be to determine relations which have the character of eq. 5-6 which then can be used for extrapolations. If the equations so determined has a mechanistic basis it would make extrapolations more credible. It is therefore recommended that SKB in the forthcoming review of its previous conclusions regarding SCC [13] strive to formulate quantitative relationsships on the influence of various parameters which permit extrapolations to repository conditions, in particular to canister condition after an earthquake shear.

6. Conclusions

The examination of the SR-Can project reports has led to the following conclusions:

- The margin to extreme grain refinement during friction stir welding needs to be assessed and the consequences of extreme grain refinement needs to be determined.
- The most severe threat to canister integrity is the 10 cm shear deformation in connection with a post-glacial earthquake.
- The canister survives the earthquake but persistent tensile stresses after the earthquake may lead to failure by creep or SCC.
- SKB needs to improve the calculations of how stress depends on time after the earthquake.
- The SKB conclusion that creep brittle fracture can be excluded needs to be better substantiated.
- The SKB conclusion that SCC can be excluded for times later than the first few tens of years after sealing of the repository needs to substantiated by arguments which do not wholly rely on threshold values.
- SKB needs to consider all possible SCC mechanisms in more detail than in the SR-Can project.

7. References

1. Hedin, A. E., ed. *Long-term safety for KBS-3 repositories at Forsmark and Laxemar - a first evaluation. Main Report of the SR-Can project*. 2006, SKB.

2. Pettersson, K.
   Models for creep and creep fracture in copper
   in *SKI Workshop on Long-term Integrity of the KBS-3 Engineered Barrier System*. 2002: Stockholm.

3. Pettersson, K.
   Further development of a constitutive model for the plastic deformation and creep of copper. SKI project 14.9-020902:02184.*Matsafe AB, Dec 2003*

4. Pettersson, K.
   Extrapolation of power law creep properties of copper to temperatures of interest for nuclear waste storage.*Matsafe AB, Dec 2004*

5. Pettersson, K.
   Development of a constitutive model for the plastic deformation and creep of copper and its use in the estimate of the creep life of the copper canister.*SKI, SKI Report 2007:12, Dec 2006*

6. Nilsson, F., ed. *Mechanical integrity of canisters*. Vol. SKB Techical Report 92-45. 1992, SKB.

7. Pettersson, K. and Oskarsson, M.
   Stress corrosion crack growth in copper for waste canister application.
   The scientific basis of nuclear waste management XXIII. 1999. Boston: Materials Research Society, pp. 95-101.

8. Pettersson, K. and Oskarsson, M.
   A study of stress corrosion crack growth in copper for nuclear waste canister application.*Dept. of Materials Science and Engineering, KTH, TRITA-MAC-0611,*

9. Pettersson, K.
   A constitutive model for the plastic deformation and creep of copper.*Dept. of Materials Science and Engineering, KTH, TRITA-MAC-0589,*

10. Pettersson, K.
    A study of recrystallization in copper.*Department of Materials Science and Engineering, KTH, TRITA-MAC-0594,*

11. Kapsel för använt kärnbränsle. Svetsning vid tillverkning och förslutning
    SKB Rapport R-06-04, September 2006

12. Xie, G. M., Ma, Z. Y., and Geng, L.,
    Development of a fine-grained microstructure and the properties of a nugget zone in friction stir welded pure copper.
    Scripta Materialia. 57(2007) pp. 73-76.

13. Kapsel för använt kärnbränsle. Konstruktionsförutsättningar.
SKB Rapport R-06-02, September 2006

14. Werme, L.
Konstruktionförutsättningar för kapsel för använt kärnbränsle.*SKB, R-98-08,*

15. Karlsson, M.
Mechanical integrity of copper canister lid and cylinder.*SKI, SKI Report 2003:5, Jan. 2002*

16. Fuel and canister process report for the safety assessment SR-Can.*SKB, TR-06-22, October 2006*

17. Börgesson, L., Johannesson, L.-E., and Hernelind, J.
Earthquake induced rock shear through a deposition hole. Effect on the canister and the buffer.*SKB, TR-04-02, December 2003*

18. Börgesson, L. and Hernelind, J.
Earthquake induced rock shear through a deposition hole. Influence of shear plane inclination and location as well as buffer properties on the damage caused to the canister.*SKB, TR-06-43, October 2006*

19. Hernelind, J.
Earthquake induced rock shear through a deposition hole when creep is considered - first model. Effect on the canister.*SKB, R-06-87, August 2006*

20. Pettersson, K.
A constitutive model for the plastic deformation and creep of copper.*KTH, Dept of Materials Science and Engineering, TRITA-MAC-0589, Dec 1995*

21. Henderson, P., Österberg, J.-O., and Ivarsson, B. G.
Low temperature creep of copper intended for nuclear waste containers.*Swedish Institute for Metals Research, IM-2780, Oct 1991*

22. Bowyer, W. H.
Creep deformation and fracture processes in OF and OFP copper.*SKI, SKI Report 2005:18, October 2004*

23. Cocks, A. C. F. and Ashby, M. F.,
On creep fracture by void growth
Progress in Materials Science. 27(1982) pp. 189-244.

24. Sandström, R. and Rydell, N.
Extrapolation av egenskaper hos kapselmaterial
SOU 2001:35, 2001

25. Kassner, M. E. and Hayes, T. A.,
Creep cavitation in metals
International Journal of Plasticity. 19(2003) pp. 1715-1748.

26. Auerkari, P., et al.
Uniaxial and multiaxial creep testing of copper.*VTT, SKI Report 2003:06,*

27. Holmström, S., et al.
Long-term integrity of copper overpack - intermediate report 2006.*VTT, VTT-R-11268-06, 28 Nov. 2006*

28. Bowyer, W. H.
Multi-axial creep and the LICON methodology for accelerated creep testing.*SKI, SKI Report 2006:33, May 2006*

29. Frost, H. J. and Ashby, M. F.
Deformation mechanism maps. 1982, Oxford: Pergamon Press Ltd.

30. King, F., et al.
Copper corrosion under expected conditions in a deep geological repository.*SKB, TR-01-23, 2001*

31. King, F. and Kolar, M.
Preliminary assessment of the stress corrosion cracking of used fuel disposal containers using the CCM-SCC.0 model.*Ontario Power Generation, 06819-REP-01300-10103-R00, March 2005*

32. Farina, S. B., Duffó, G. S., and Galvele, J. R.,
Stress corrosion cracking of copper and silver, specific effect of the metal cations. Corrosion Science. 47(2005) pp. 239-245.

2

A critical review of issues in the SR-Can report relating to the containment performance of the KBS3-canister

William H Bowyer

Meadow End Farm
Tilford, Surrey
England

Summary

The sections of the Main Report of the SR-Can project related to containment performance of the KBS-3 canister have been studied in conjunction with the background reports which it cites. The study has taken the form of a critical review of the safety case related to containment by the canister.

The report acknowledges that further work is required and is in progress. The cases of acceptance criteria for defects in the insert, creep relaxation following rock shear and non destructive evaluation (NDE) procedures for the insert and the copper shell are cited.

Useful tools have been developed for deterministic analysis of the response of the canister to isostatic pressure and to rock shear. A probabilistic tool has been developed in order to assess the sensitivity of the canister to failure as a result of material property and manufacturing quality variations or variations in the expected environmental conditions.

Much has been learned by the application of these tools to date. Unfortunately the mean mechanical properties for copper and cast iron which were used were inappropriate. They were too fast for the isostatic load case and too slow for the rock shear case. In addition the statistics related to the properties of the cast iron were inadequate. The sensitivities of the predictions to the standard deviations in the mechanical properties indicate that care must be taken to provide reliable data for variations in mechanical properties both within and between casts for the insert.

Both analyses need to be repeated using better data. Some minor refinement of the models may be appropriate. It is also necessary to extend the rock shear case to test for sensitivity to manufacturing and material property variations and to consider the case of rock shear during the glaciation periods.

Table of contents

1. Introduction

SR Can is a safety assessment project. This project is a preparatory step for an assessment intended to support a licence application for a final repository in Sweden.

It is forecast that 9,000 tonnes of nuclear waste will arise from the Swedish Nuclear programme. This will correspond to roughly 4,500 canisters for disposal in the repository. The concept discussed in SR Can is based on 6,000 canisters in order to allow for uncertainties in the future of the Swedish Nuclear Power programme.

The purposes of the safety assessment SR Can are as follows:

1. To make a first assessment of the safety of potential of KBS-3 repositories at Forsmark and Laxemar to dispose of canisters as specified in the application for the encapsulation plant.
2. To provide feedback to design development, to SKB's R&D Programme, to further site investigations and to future safety assessment projects
3. To foster a dialogue with authorities that oversee SKB's activities, i.e. The Swedish Nuclear Power Inspectorate, SKI, and the Swedish Radiation Protection Authority, SSI, regarding interpretation of applicable regulations, as a preparation for the SR Site project.

To this end SKB have provided a report (SKB TR-06-09) entitled, "Long-term safety for KBS-3 repositories at Forsmark and Laxemar-a first evaluation, Main report of the SR Can project". In view of the long title it will be referred to in the rest of this report as "the main report". It stresses (page 45) that the purpose of the main report is to investigate the safety of the system as it is specified at this stage, and to give feedback for further developments to that specification.

This report is prepared as a contribution to the thinking of SKI in their response to the main report.

It is specifically concerned with the isolation performance of the canister and it is presented as a critique on the opinions expressed by SKB in the main report.

The methodology of the main report includes identification of "safety function analysers for isolation" (page 183). These are criteria which must be met if the nuclear waste is to remain isolated.

For the copper shell a single criterion is given that is that the thickness of the copper shell shall remain greater than zero over the entire canister surface. This written as $d_{\min}^{Cu} > 0$

For the insert two criteria are given,

The first is that the isostatic pressure at the buffer canister interface should be less than the isostatic collapse pressure of the canister, represented by:

$$P_{Isostatic}^{Canister\,/\,buffer\ interface} < P_{Isostaticcollapse}^{Canister}$$

and the second, the rupture limit of the canister must exceed the shear stresses to which it exposed represented by:

$Rupture\ limit^{Canister} > Applied\ Shear\ Stress$

These will be considered in the following sections.

The method adopted for this report is to accept the cases given above for review and to follow the main report in page order for each case. The review will examine the views expressed in the main report, the identified background reports and the conclusions drawn from them.

2. Description of the canister

2.1. Materials design and manufacture

The canister consists of an inner container, the insert, of cast iron and an outer shell of copper. The cast iron is designed to give mechanical stability and the copper shell is designed to provide corrosion protection in the repository. The copper shell is 50mm thick and the cylindrical canister has a diameter of 1.05m and a length of 4.8m. In section 4.2.4 (page 84) of the main report it is claimed that “the uncertainties in composition for the canister materials is small”.

This claim is valid for the copper shell but misleading for the cast iron.

The copper shell is produced in an OFHC (Oxygen Free High Conductivity) copper material with added Phosphorus (20 –70ppm) and sulphur content controlled to less than 8ppm. Owing to the methods of manufacture the copper will be of essentially uniform composition over large production batches.

Four methods are claimed as “possible” for production of the copper shell.
Only one has proved satisfactory, that is extrusion of seamless tube to which forged tops and bottoms are welded using friction stir welding. The tops and bottoms are produced by hot forging from the same stock material as the tube. The other methods cited have not been shown to work in a satisfactory way.

The cast iron is the subject of a specification on microstructure and mechanical properties (Andersson et al., SKB TR-04-23). It is specified as spheroidal graphite cast iron in order that it should meet a minimum ductility requirement of 7%.

With the production methods used for cast iron it is to be expected that some segregation of alloying elements and some loss of alloying elements by volatilisation will occur during casting. This will lead to differences in metallurgical structure and mechanical properties through the castings. The quality of the castings therefore depends to a large extent on the judgements and experience of the foundryman.

Whilst guidelines on composition to achieve a given microstructure are available, it is normal to interpret the guidelines together with guidelines related to the size of the casting and the casting practice employed. A consequence of this is that foundrymen in different foundries may, according to the particular practice employed in their foundries, take different views on the ideal composition to aim for. Thus a tight specification on composition could well lead to differences in quality in different foundries. It is fair to say that within a specific foundry uncertainty on overall composition should be small but segregation in the casting and alloy losses during melting and casting are very difficult to control.

In the extreme case variations in structure arising from the above difficulties can lead to variations in ductility from >20% to < 1%. And this has been observed in the SKB programme.

As far as can be ascertained this effect has so far not been adequately investigated. It appears that only three castings have been examined and the level of investigation of each has been scant. The data should be strengthened by further testing.

Two versions of the insert are produced. A boiling water reactor (BWR) version which has 12 fuel channels and a pressurised water reactor (PWR) version which has four fuel channels.

The fuel will be placed in the canister in the encapsulation plant. The insert will be closed by a steel lid and secured with a bolt. The insert is sealed at atmospheric pressure in an atmosphere of at least 90% noble gas. The maximum permissible quantity of water in the canister is 600 grams.

Welding of the lids and bottoms for the copper canister will be by friction stir welding (FSW; SKB R-06-04), non-destructive testing (NDT) of the welds has been studied (SKB R-06-05) - both these publications are preliminary and they are in Swedish, the information in them is therefore not available to non-Swedish speakers. Further work is in progress.

It is necessary to examine the justification for the selection of FSW and also to comment on the NDT performance. For this the full reports will be required and it will be necessary for them to be presented in English.

The initial state aspects of the canister which have been identified as critical to safety are

1. The copper canister tightness, in particular the quality of the sealing welds and
2. The strength of the cast iron insert, affected by the quality of the casting process.

2.2. Acceptance criteria for casting defects

These criteria are not yet available. Work has started but no publications in English are yet available.

It is observed that the outer peripheral region of the insert can be inspected by ultrasonic examination using the pulse echo technique. This is likely to be the case.

It is also observed that the volumes between the fuel channels can be inspected by ultrasound using the transmission method. This is much less likely. The bond between the cassette steelwork and the cast iron has been shown to be incomplete in some of the early cases. It is to be expected that poor bonding here will be more the rule than the exception. The reason is that the relatively low melting point and casting temperature of the cast iron will limit the degree of bonding between the steelwork and the cast iron. The absence of a metallurgical bond will lead to strong reflection of ultrasound at the steel-iron boundary. This would be very likely to mask the effect of reflectors in the volume under inspection.

2.3. Acceptance criterion on eccentricity

An eccentricity limit of 5mm is required. This may be very difficult to achieve, even throughout a single casting. The casting temperature may not be high enough to form a metallurgical bond between the iron and the steel but it will be high enough to cause softening of the steel sufficient to enable some movement under the influence of unbalanced forces occurring during pouring of the iron. It is acknowledged that this difficulty could lead to specification of an increase in the wall thickness of the insert.

3. Safety function analysers for isolation

3.1. Minimum copper thickness

The data report (SKB TR-06-25) points out (page 51) that it is assumed that the copper shell has no load bearing function and is used only to provide corrosion protection. Thus the initial copper coverage is only important when calculating the corrosion resistance of the shell. The design thickness of the shell is 50mm but if volumetric defects are present it could be less than that. It is recognised that defects could occur anywhere in the shell but it makes a judgement that they are more likely to occur in the welds. Following this judgement full non destructive evaluation (NDE) has been made on 20 welds made by the FSW process on full size lids and short lengths of copper tube. The NDE was followed up by destructive examinations to verify the NDE results (this work is reported in SKB R-06-05, in the Data report (SKB TR-06-25) and in the main report).

The Data Report quotes a statistical analysis which “indicates that the maximum defect size in a 4500 unit production run would be 4.8mm with a 95% confidence limit of 7.8 mm.” The main report quotes the same source as the data report and gives a maximum observed defect size of 4.5mm. These statements are confusing and inconsistent. It is possible that this difficulty has arisen in translation and that the intended meaning was as follows, the largest observed defect was 4.5 mm, the 95% confidence limit for a 4500 unit production run was 4.8mm and the maximum expected in the 4500 unit production run would be 7.8mm.

The difficulty in this section is compounded by the “input from experts” in the Data Report (page 53.). They say that the measurement errors in the NDE must be added to the statistically modelled defect size distribution to yield an estimated maximum defect size of 10mm, presumably in the 4500 unit production run.

Finally the judgement by the SR Can team (page 53-Data report) is that 99% of canisters will have no defects greater than 10mm and the remaining 1% will have no defects greater than 15mm. The minimum allowable thickness for the copper shell is 35mm in order to provide the required corrosion life. The SR Can team also indicate that more data is required in order to assign probabilities to any event breaking any of the acceptance criteria. We have to conclude that the judgement of the team is no more than a well educated guess.

In the Main report (page 85) the authors recognise that the estimate that 1% of canisters leaving the encapsulation plant will have defects as large as 15mm in the weld zone is crude and that the maximum permitted size of defects is 15mm. They also make the point that such defects would be very unlikely to be missed by NDE. No comment is made concerning the need to examine for forging defects.

The point regarding NDE is well taken. However, whilst the welds may have a higher number of defects than the bulk material, experience tells that when forging defects occur their size will be distributed about a different and higher mean than the estimated maximum for welding defects. There is no mention of NDE of forged lids and bases in the past or intended examinations in the future.

The minimum initial copper thickness is cautiously assumed to be 40 mm for all canisters sealed under normal operation. Normal conditions are defined as conditions where observable parameters are within the specified “process window”. The value of 40 mm corresponds to the design thickness of 50 mm, less an allowance of 10 mm which in the judgement (crude estimate) of the SR Can team is sufficient to include defects in 99% of cases.

The maximum allowable defect size is 4.5 mm (see Data Report section 4.2). It is indicated that detection of defects of this size would lead to no corrective action. This suggests that 4.5 mm is the lower reliable detection limit and that any defect detected would lead to corrective measures or rejection. It seems that the SR Can team are aware that further work needs to be done in this area and it may well be in progress.

3.2. Isostatic load on the canister

The main report (page 184) asserts that “A probabilistic study based on statistics of measured material data from real canister inserts has shown that the probability of failure is insignificant (~2×10^{-9}) for a baseline case with an isostatic pressure of 44 MPa.” This is a very important result and it is therefore necessary to examine the analysis in detail, including the background work on which it was based.

The study was carried out by Dillström (SKB TR-05-19) and it depends on a considerable amount of data derived from mechanical testing, material studies and deterministic finite element analyses carried out by others. The next section will consider this background information.

3.2.1 Background data for the probabilistic analysis

Yield strength, elongation to fracture and UTS- in tension

JRC (Petten) and The Swedish Foundry Association each carried out approximately 50 tests from each insert and they obtained similar results.

The minimum values in the material specification (SKB TR-04-23) were 240 MPa proof stress (0.2%), 370 MPa ultimate tensile strength (UTS) and 11% ductility. The

Swedish Foundry Association comment that although some tests indicated satisfactory properties none of the castings provided properties which were consistently within the specification.
A closer examination of the experimental data from JRC reveals that the minimum proof stress of 240 MPa was almost always exceeded. The specified fracture strain was almost always met on material from insert I25 but was only met on specimens from the bottom of insert I24 and never met by material from insert I26. The specified ultimate tensile strength was rarely met.

Factors identified by the Swedish Foundry Association as influencing the absolute values and the variability of the measured properties included,

1. the presence of slag inclusions and flotation (flake) graphite causing low UTS and ductility at the top of the casting and
2. poor graphite shape coupled with high pearlite content causing low ductility generally.

Andersson et al. (SKB TR-05-17) refers to the JRC work. The authors point out that it is reasonable to infer from the detailed tensile test results that low strain to fracture values were caused by casting defects. JRC had made a detailed study of the specimens used in the test programme. They concluded that there is a clear trend for decreasing fracture strain with increasing effective defect size. The major contribution to reducing fracture strain was made by large slag defects but relatively minor contributions were associated with clustered graphite nodules, higher pearlite contents and quality of the graphite nodules.

It is suggested by Andersson et al. and by Dillström (SKB TR-05-19) that the "observed variations in mechanical properties (particularly ductility) between and within casts is remarkable". I do not agree, the quality of the graphite and the pearlite content are influenced most strongly by chemical composition in the cast and cooling rates. Both chemical composition and cooling rates will vary significantly within and between casts as a consequence of the complexity and large size of the casting coupled with variations in casting conditions between and within foundries. Slag defects are very difficult to avoid in castings of the size under consideration and it is common for them to be segregated towards the top of the casting. The explanations for variations in mechanical properties presented by the Swedish Foundry Association and JRC are entirely plausible. It should not be assumed that these defects and the associated variations in properties will be reduced with increasing experience in canister production. It is important to answer the questions, "is the variability observed in the three castings examined representative of the worst case and is this level of variability acceptable"? Further work will provide the answer.

Yield strength, elongation to fracture and UTS - in compression

Mechanical properties in compression were measured by JRC only. The resulting data was reported to show much less variability than the tensile property data. This was attributed to the relatively low sensitivity of compression test data to the presence of defects when compared with tensile test data. However, it appears that 144 tests were conducted on tensile specimens by JRC and these specimens included longitudinal and transverse specimens from a wide distribution of positions in the castings. Seven tests were conducted on compressive specimens. They were all longitudinal specimens taken from the outer rim of the castings at the top. Three were taken from casting I24, three from casting I25 and one from casting I26.

The mean values of 0.2% proof stress in compression and compressive stress at the specified minimum strain to failure in tension were 270 MPa and 478 MPa respectively. These values were selected for the probability analysis on the basis that local collapse is dominated by compressive properties (principally the proof stress) and that the measured tensile properties were dominated by manufacturing defects which would be inactive in a compressive stress field.

No statistical data is provided for compressive properties of the cast iron. Minnebo (2004) reports the results of three compressive tests each on material from inserts I24 and I25 and one test from material on insert I26. These were on longitudinal specimens, all taken from the outer wall of the canister at the top. There is no direct evidence that these positions are representative of the insert as a whole but instinct suggests that they would provide the best results. Minnebo (2004) provides true stress–true strain curves for both tensile and compressive specimens taken from similar positions in each insert.

It is noted that the 0.2% proof stress values were the same in tension and compression for each case. It is entirely likely that if compression tests had been taken from a range of positions in the castings, using transverse as well as longitudinal specimens, the variability of results with position in the casting would mirror the variability observed in tensile tests.

Statistical treatment of mechanical test data

Minnebo (2004) reports a statistical treatment of tensile mechanical property measurements on specimens from all three inserts. Although a very large number of specimens were tested (144), interpretation of the results is not easy because they included 20 different specimen batches and each batch had a unique identity. Each identity included an insert reference (I24, I25 or I26), a specimen location (top or bottom), a specimen size (large, medium or small), a specimen orientation (longitudinal or transverse) and test temperature (room temperature or 0ºC). It is unsurprising that this test series has failed to provide complete statistically significant conclusions regarding the effects of the variables examined. It was demonstrated that there was a significant difference in the mean values of proof stress between the top and the bottom of insert I24. On the other hand it was also demonstrated that longitudinal and transverse specimens from the top of insert I26 and transverse specimens from the bottom of insert I26 formed part of a single population. The mean proof stress in this group was 313 MPa and the standard deviation of the mean was 7 MPa. The mean ultimate tensile strength was 399 MPa and the standard deviation was in the range 22 to 26 MPa.

No statistical treatment was reported for the compressive test data.

It is recognised that the probabilistic analysis had to use the data that was available and this was clearly not ideal. In an ideal case the learning from the work reported above would have been used to design experiments to collect statistically meaningful data for the variability of mechanical properties in tension and in compression both within and between casts. It would certainly have used more than three casts and many more than the approximately 50 specimens from some of the casts. Bearing in mind that the compressive test data was used in the probabilistic study, the statement in the main report which describes the probabilistic study as “based on statistics of measured material data from real canister inserts”, can not fail to erode the confidence of the reader in the study as whole.

Deterministic analyses of plastic collapse

Erixon of ÅF-S (SKB TR-05-17, Appendix F) carried out finite element analyses to model plastic collapse and fracture of the insert in order to provide input data for the probabilistic analysis. He used a material model for cast iron with different compressive and tensile properties.

His parameter set included a range of values for the outer radius of the canister (to simulate the effect of eccentricity of the cassette ($\delta_{cassette}$)), the corner radius of the fuel channel (r_{corner}) and the 0.2% yield stress and ultimate strength of the cast iron. He used an ultimate strain of 10% in both compression and tension.

The material model allowed for differences in compressive and tensile properties and the analyses indicate that using very small values for yield stress and ultimate stress in tension has no influence on the results. In view of this, the scatter in tensile test results, the comparatively lower scatter in the compression test results and the expected small difference between tensile and compressive properties in sound material it was decided to use the compressive test results only in the analyses.

The results from the deterministic analyses were as follows,

1. The stress-state of the insert is mainly compressive and when the pressure is below ~30 MPa. It is dominated by stress concentrations at the corners of the fuel channels nearest to the outside of the canister. Increases in pressure above this level leads to an increase in plastic flow until local collapse of the ligament occurs. The dominating parameters controlling the collapse are external pressure and eccentricity of the cassette. It is confusing to refer to the localised onset of plastic deformation described in the report (SKB TR-05-17) as collapse. The illustrations provided and the development of localised plastic strain which is described do not correspond with the failure of integrity implied by the word collapse. Examination of the illustrations suggests that true collapse does not occur until the condition described as final collapse is reached. An alternative view of the observations is that centres of plastic response are predicted to occur in the insert, at or below the working stress. This implies that the safety factor is no more than 1. It is unknown in the writers experience for an engineering structure to be designed to operate under conditions where a substantial volume of the structural material is stressed above its yield stress.

2. The dominant stress component in the process of plastic collapse is the largest principal stress in compression and this is the component which follows the corner of the cassette, i.e. perpendicular to the radius. The path of this stress component is selected (among others) for the probabilistic analysis.

Deterministic analysis of initiation of crack growth

Information for this part of the probabilistic analysis was also obtained from the deterministic stress analyses referred to above.

The information was as follows.

1. The analysis indicates that there are tensile regions close to the corners of the fuel channels which are nearest to the outside of the insert. The size of these regions increase with applied pressure, and with increases in eccentricity of the cassette and decreases in corner radius.
2. The maximum principal stress in tension is located within the material when pressure is less than ~ 45 MPa and at the inner surface when it is greater than ~ 45 MPa or when the eccentricity is greater than 5 mm.
3. The magnitude of the maximum principal stress is very sensitive to pressure level in the range 40-50 MPa and the analysis reveals the paths along which the maximum principal stresses lie. These paths have been selected for the probabilistic analysis.

Fracture toughness

Values were derived from tests made by JRC (Petten) and KTH

The JRC tests yielded more conservative results than KTH and therefore the JRC results were used.

The reasons for the discrepancies between the JRC and KTH values is not explained.

The JRC tests measured J_{1c} but K_{1c} was required by the analysis and the conversion from J_{1c} to K_{1c} was made using the formula

$$K_{1c} = \sqrt{J_{1c}\frac{E}{\left(1-\nu^2\right)}}$$

where E=172 and ν=0.3

Values for J_{1c} from the JRC work were not available but working backwards from the given value of K_{1c} yields a value for J_{1c} of 37 /kNm^{-1}.

Defect distribution

The conclusion that fracture strain is controlled by the defect distribution requires that a defect size distribution is included in a probability of crack growth calculation. Unfortunately the paper which fully describes the derivation of the defect size distribution is not available. Reference to SKB TR-05-17 and SKB TR-05-19 leads to the following interpretation.

A series of necessary assumptions are made in order to construct a model.

Failure strain distributions are available for three canisters.

It has been assumed that failure strain may be controlled by penny shaped cracks and their size distribution in a given reference volume.

An elastic-plastic finite element analysis was performed using a commercial FE code in order to model the reduction in failure strain with defect size. The tensile specimen was modelled as an axisymmetric body with a transversely oriented penny shaped crack. An existing model was selected to describe the constitutive behaviour of the material. The parameters in the model were *fitted* using the room temperature tensile test measurements on the specimens from the canisters. J-integral values were then calculated for different crack lengths. From these results it was possible to derive fracture strain versus defect size relationships for prescribed values of fracture toughness.

Relationships were derived for the three canisters using the measured mean values of fracture toughness. Two of these are presented by Andersson et al. (SKB TR-05-17) and the measured values of fracture strain and defect size for the individual specimens from the corresponding canisters are included for comparison. In general the fit with the model treatment is good and conservative estimates of fracture strain are provided for defects exceeding 3 mm in length. For smaller defects, elongation at fracture is overestimated by the model. The proposed reason for the discrepancies are that when large crack like defects are present they dominate the fracture behaviour whilst when the crack like defects present are small, other factors such as high pearlite content or graphite clusters or poor graphite quality have a noticeable impact on fracture strain. This is consistent with the observations made by JRC when they compared tensile test results with the results of microscopical examination of the failed specimens.

An important observation on this result is that for the real situation where crack like defects in the casting are likely to be large the predictions are conservative. On the other hand only three castings have been examined and these are from different foundries. It reasonable to suggest that these foundries had a strong commercial interest in performing well in these trial castings. It is not reasonable to assume that these castings represent the worst case, or even the general case, which might arise in production. It is possible that improvements in practice may lead to consistently better quality over time but it is not reasonable to expect this. These comments apply both to slag inclusions and to the other defects which have been mentioned. There is no indication at this stage concerning the level of variability which might arise for defects in either category.

3.2.2 Probabilistic analysis

Aims of the analysis

This study was conducted in order to evaluate the effects of material and production variables on the probability of in service failure by local collapse or growth of crack like defects not detected by NDE.

It is stressed by the authors that the local collapse criterion is considered because this allows no release. Total collapse occurs at much higher pressure. Only after total collapse will release occur.

The aim of the probabilistic analysis was to determine,

1. The probability of local plastic collapse and
2. The probability of initial crack growth from a defect not detected by NDE.

This writer is not qualified to comment on the mathematical processes, the following comments are made on the assumption that they will be validated by others.

Probability of plastic collapse

The results indicate that the probability of plastic collapse for the ideal input parameter set (p = 44 MPa, r_{corner} = 20 mm, and $\delta_{cassette}$ = 0.) is very low at 1.4 x 10^{-21}.

This result must be viewed in the light of its sensitivity to the input parameters. It is independent of defect population as the collapse mode is in compression. It is very sensitive to eccentricity of the cassette, the cassette corner radius and the applied pressure. These sensitivities are illustrated in table 1 below.

Table 1. Sensitivity of probability of plastic collapse to cassette eccentricity, cassette corner radius and pressure.

Pressure MPa	Corner radius mm	Eccentricity of cassette mm	Probability of plastic collapse
44	20	5	7.53x 10^{-10}
44	20	10	0.27
44	20	15	1
44	15	0	2.3x10^{-5}
44	20	0	1.4x10^{-21}
44	25	0	2.4x10^{-41}
42	20	5	1x10^{-14}
42	20	10	1x10^{-2}
42	20	15	1
50	20	0	1x10^{-4}
50	20	5	1

It is clear from these results that if local plastic collapse on a grand scale is to be avoided when the pressure reaches 44 MPa the cassette eccentricity must be controlled to less than 5 mm and the corner radius must be 20 mm or more. The given probability of failure for this combined case is 7.53 x 10^{-10}. The sensitivity to eccentricity is extreme, at zero eccentricity the probability of collapse is $10^{-21,}$ at 5 mm it is 7.53x10^{-10} and at 10 mm it is 0.27. Corner radius may not be difficult to control but eccentricity of the cassette is difficult to control (owing to the effect of the casting temperature on the material of the cassette and the turbulence of the molten material during casting).

The sensitivity of probability of plastic collapse to variability in mechanical properties of the cast-iron is examined for the case of zero eccentricity of the cassette and 20 mm corner radius and pressures in the range 40 to 50 MPa. (Dillström, SKB TR-05-19 p.28) The results show that:

- For a standard deviation of 10 MPa the probability of local plastic collapse at 44 MPa is $\approx 10^{-8}$.

- For a standard deviation of 15 MPa the probability of local plastic collapse at 44 MPa is ≈ 4 x 10^{-3}.
- At a pressure of 50 MPa the probability of local plastic collapse increases from 10^{-4} at a standard deviation of 6 MPa to ≈ 8 x 10^{-2} at 15 MPa.

These probabilities should be compared with a probability of 1.4x 10^{-21} (table1 above) for the case of 20 mm corner radius and zero eccentricity where the standard deviation is zero.

Unfortunately the case considered here is the best case which is very unlikely to occur because zero eccentricity of the cassette over the entire volume will be impossible to achieve.

The difference in probability of plastic collapse for the two cases, pressure 44 MPa, corner radius 20 mm and cassette eccentricity of zero or 5 mm when the standard deviation in the properties is zero, is a factor of 10^{11} (see table 1 above). This comparison suggests that when a standard deviation of 10 MPa is applied to the values for mechanical properties, probability values for plastic collapse with a corner radius of 20 mm, an eccentricity of 5 mm and a working pressure of 44 MPa (given as 7.53×10^{-10} in table 1) would be increased by a very large factor (between 1 and 1.3×10^{10}). This, in the view of the writer is very serious. A standard deviation in proof stress of 10 MPa or less in any casting of this nature cannot be guaranteed and should not even be suggested, on the basis of results from three compression tests. There is no evidence that an eccentricity of 5 mm max. can be achieved. This suggests that the condition described as localised plastic collapse could have a high probability for a large number of canisters. This would be unacceptable in any conventional safety critical application.

To be useful this information on the effects of standard deviation in mechanical property values needs to be provided for real cases and for the extreme cases. When this is considered together with the uncertainty surrounding the compressive mechanical properties used in the analysis (as discussed in section 3.2.1 above) there is a strong case for obtaining better mechanical property data from a larger number of castings. The analysis could then be re-run for realistic cases with credible data including reliable standard deviation values. There are no major difficulties other than cost in carrying out this further work. It may even be planned.

Probability of the initiation of crack growth

Similar analyses have been performed for the probability of the initiation of crack growth at an existing flaw. The results presented indicate that at 44 MPa applied pressure a corner radius of 20 mm and zero eccentricity the probability of initiating crack growth at a flaw is 1.98×10^{-9}. Eccentricity of the cassette has a very strong influence on the results. Changes from the value above to 6.17 x 10^{-7} and 1.78 x 10^{-3} are calculated for eccentricities of 10 mm and 15 mm respectively. For eccentricities exceeding 15 mm the probability of crack initiation is said to be very large.

The probability of crack initiation is also sensitive to applied pressure as illustrated in table 2 below (these data are taken from SKB TR-05-19 page 12 table 4-3).

Table 2. Probability of crack initiation from an existing flaw as a function of applied pressure and cassette eccentricity for a 20 mm corner radius

Pressure MPa	Probability of crack initiation			
	Cassette eccentricity 0 mm	Cassette eccentricity 5 mm	Cassette eccentricity 10 mm	Cassette eccentricity 15 mm
40	2.01×10^{-9}	2.05×10^{-9}	1.24×10^{-8}	4.81×10^{-5}
44	1.98×10^{-9}	2.04×10^{-9}	6.17×10^{-7}	1.78×10^{-3}
45	1.99×10^{-9}	2.04×10^{9}	1.67×10^{-6}	4.42×10^{-3}
50	3.11×10^{-9}	2.16×10^{-8}	3.11×10^{-3}	2.00×10^{-3}

The above analysis considered a mean value in the defect depth distribution of 0.7 to 1.9 mm. (presumably a conservative selection to match with the peak level in the tensile stress field). A sensitivity analysis was performed to examine a range of depths from 0.7 mm to 5 mm. This indicated that when eccentricity was zero and pressure was 44 MPa the effect of defect depth in this range was zero. When eccentricity was 10 mm and pressure was 44 MPa, the probability of crack initiation increased from 10^{-10} for 0.7 mm depth to 10^{-9} for 5 mm depth.

A crude extrapolation of the data presented suggests that increasing crack depth to 5 mm would lead to increases in probability of crack initiation at 44 MPa to at least 6.17×10^{-6} and 1.78×10^{-2} for eccentricities of 10 and 15 mm respectively. It is clear that 10 and 15 mm eccentricities are prohibited by the very small safety margin in working pressure which they provide.

No data is presented on the sensitivity of the probability of crack initiation at a pre-existing flaw for pressures exceeding 50 MPa.

Inspection of the trends for increases in pressure from 40 MPa to 50 MPa which is given (SKB TR-05-19 figure 4-7 page 30) indicates that for increases in pressure above 45 MPa the probability of initiation of crack growth increases rapidly with increasing pressure.

Table 1 and the associated text shows the extreme sensitivity of probability of local plastic collapse to eccentricity of the cassette. Table 2 shows the sensitivity of the probability of crack initiation to eccentricity of the cassette. Comparing tables 1 and 2 it is clear that the probability of local plastic collapse is connected more sensitively to cassette eccentricity than initiation of crack growth at a flaw is. It is likely therefore that for all practical cases local plastic collapse will be more probable to occur than crack initiation at an existing flaw.

No data is presented for the effects of standard deviation in the mechanical properties on the probability of crack growth from an existing flaw.

Dilström (SKB TR-05-19 page32) points out that local plastic collapse is the first stage of collapse and will not result in a leak. He proposes that final collapse (sufficient to cause a leak) should be defined as the point where the maximum deflection of the canister is 50 mm. And that this should be regarded as the failure criterion. The weakness of this is that it assumes that 50 mm deflection will occur for all cases at lower stresses than initiation of cracks at existing flaws. This has not been demonstrated or even claimed in any of the literature which has been made available.

3.2.3 Final collapse

Several exercises have contributed to the view of final collapse pressure for the canister. Erixon (SKB TR05-17 appendix F), reports many finite element analyses. His results (appendix 4 to appendix F) indicate that the maximum stress in the insert is close to the proof stress of the cast iron at a pressure of 15 MPa when the onset of local plasticity occurs. The results indicate a gradual increase in the size of the plastic zone at constant stress as the pressure is raised from 15 MPa to 45 MPa. At 45 MPa the peak strain in the insert is predicted to be 1.2%, the minimum strain in the plastic zone is taken as 0.2%. This provides a credible view of the evolution of events leading to plastic collapse in a conventional test.

Calculated final collapse pressures are given by Dillström (SKB TR-05-19 page32). They are based on a *deterministic* finite element analysis using the compressive stress-strain curve and a deflection of 50 mm in the canister wall. The total collapse pressures quoted by Dillström are given below; they were derived using a deterministic analysis with zero eccentricity of the steel cassette.

1. 104 MPa for the cast iron insert alone
2. 118 MPa. for the cast iron insert plus the copper barrier
3. 130 MPa when the steel cassette and the copper barrier were included in the model

Mock-up canisters with full thickness copper and cast iron walls and at full diameter but ≈1/7 full height, were pressure tested in an isostatic press (SKB TR-05-18). They failed at pressures circa 130 MPa. which is close to the calculated value when the copper barrier and the cassette are included.

This is comforting, particularly as the agreement with measured collapse pressures is so close to the predicted value. However there are several areas of discomfort.

1. The failure pressure of the mock up canisters should have exceeded the predicted values for full size canisters, owing to the end effects on the 1/7 height models.
2. The particular canister modelled had zero cassette eccentricity. This case will be very rare in practice and properties of the canister are extremely sensitive to cassette eccentricity.
3. The analyses assumed and the confirmatory tests ensured that uniform pressure continued to be applied on the canister after the initial plastic collapse. It appears to be unlikely that the initial event in the real case would cause the canister and the bentonite to part company. However it is demonstrated by Börgesson et al. (SKB TR-06-43), that under conditions of rock shear, separation of the buffer does occur and that under these circumstances the stress system on the canister is modified. It is suggested that the combined effects of rock shear and isostatic pressure on the canister should be investigated.

4. The material models employed by Erixon (SKB TR-05-17 appendix F) and by Dillström (SKB TR-05-19) do not include any rate sensitivity of mechanical properties and the pressure tests on canister were made at conventional loading rates. The proof stress and work hardening rates will certainly be rate sensitive in the time-scale of repository service. This will affect the pressure at which the onset of plasticity occurs as well the extent of the plastic zone and the stress distribution within it.
5. If following 1 and 2 above the final collapse pressure is confirmed at or near 104 MPa then the safety factor on the system will be of order 2. This is quite low for a material like cast iron even for a proposed *conventional* life span.
6. The possibility of initiation of crack growth at existing defects has been tacitly assumed to require a higher pressure than deflection of 50 mm requires. This assumption deserves further consideration.

3.2.4 Conclusions by the SR Can team

On page 502 (the main report) under Conclusions related to canister strength the text (paragraph 2) states that the results (in the probabilistic study) show that, " In all cases where crack growth occurred to a significant extent, local plastic collapse occurred at a smaller load. Therefore only the latter is discussed in the following". In "the following" it goes on to say that under certain circumstances the probability of plastic collapse is unacceptably high and goes on to consider total plastic collapse.

It summarises the information which is referred to and commented in section 3.2.3 above and concludes, "These calculations and experimental studies indicate that a total collapse of the canister, leading to possible release of radionuclides will not occur until the pressure has reached a level of 90 to 100 MPa".

The rejection of crack growth as a failure mechanism was because local plastic collapse is predicted to occur before significant crack growth. No work is reported which explores whether or not significant crack growth occurs before *final* collapse. For this reason as well as the reasons given earlier the conclusion is premature.

3.2.5 Additional comments by the reviewer

1. It is accepted that a baseline case is needed and that some conservative assumptions have been made in the consideration of this case. It would be helpful to have a critique of the assumptions used in the analysis. In particular the assumptions of uniform hydrostatic pressure, the absence of a rate sensitivity in the mechanical properties of the materials, the absence of an influence of defects on the evolution of the stress fields and the failure to consider combined effects of hydrostatic pressure and rock shear.
2. The case considered is idealised as far as stress is concerned. How likely is that a uniform isostatic pressure will occur in any part the repository? The sensitivities of the probabilities which have been calculated lead to an intuitive view that small departures of the stress system from the ideal could have large impacts on the probability of plastic collapse. Is it possible to extend the probability analyses to consider the stress fields which may occur and the probability that they will occur.

3. The material model used does not have rate sensitivity. It includes a specified proof stress and a work hardening rate. The evolution of the plastic region during plastic collapse will depend on these parameters and they will be rate sensitive in the time scale under consideration. Is this likely to have a significant impact on the model predictions?
4. How sensitive are the predictions on crack growth, to the assumption of a single crack and to the assumed defect distribution.
5. It is concluded that the eccentricity of the cassette must be controlled to a maximum of 5 mm. This will be very difficult to achieve consistently in the foundry. Would it be better to use a slightly larger diameter insert?
6. The probability exercise has been conducted using data from three castings; each made in a different foundry. It would be surprising if the values of mean mechanical properties and defect distributions in any one of these were representative of the values and distributions which would be achieved in serial production. Bearing in mind the predictions related to standard deviation of mechanical properties within casts, how sensitive are the probability predictions to standard deviations of the means between casts.
7. It would help develop confidence if an analysis was made to determine the probability of total plastic collapse as a function of applied pressure, taking into account,
    - more credible mechanical property data, including good statistics on variability and the effect of deformation rate,
    - the various sensitivity analyses that have been performed for local collapse,
    - the possibility of crack growth occurring before final plastic collapse.
8. Consideration should also be given to modelling the effects of rate sensitivity to the evolution of the stress and strain fields in the component and the effects of this on the pressure for the onset of plastic collapse.
9. As the tools for these additional studies are developed it is likely that time will not be a prohibiting factor.

3.2.6 Additional conceptual uncertainties identified by the SR-Can team.

In this section (SKB TR-06-09 page 502) the SR Can team acknowledges that the statistical basis for the probabilistic analysis is rather limited.

It must be recognised that there *is no* probabilistic analysis for the total plastic collapse pressure which has evolved as the failure criterion (rather than the local collapse pressure which is the subject of a probabilistic study) during the SR Can study. There is neither any acceptable statistical basis for the data used in the deterministic analysis which has been used for the final collapse pressure calculations.

The work which has been done is based on three castings, all of which were out of specification. One was further out than the others and consequently its properties were disregarded. Björkegren (SKB TR-05-17 Appendix C) has pointed out that the higher level of Mn in cast I26 is responsible for the higher pearlite content and that this in turn is responsible for the lower toughness in this material. This is probably correct but he has not suggested the limits on chemical composition which might be acceptable, or measures which might be employed to assure that the composition and structure of the castings are consistent through the casting. It is possible that this information can only be obtained by experience.

The second paragraph (under conceptual uncertaintiesm, SKB TR-06-09, page 502) refers to consequences of idealised geometries used in calculations and claims that they are negligible up to pressures of at least 60 MPa. This is claimed on the basis of work which is "on going" and has not been published. Preliminary work is referenced but it is only in the Swedish language.

The third paragraph explaims that a simple bi-linear elasto-plastic model used for cast iron and the copper. This is claimed as conservative because the deviation from using the stress-strain curve is small up to 60 MPa. This is unlikely to be the case when rate of application of stress is considered. The rate will be very slow for the onset of glaciation and the work hardening rate will be lower than the rate used as will the proof stress. As far as can be ascertained the rate effects have not been investigated.

The final paragraph indicates that no conceptual uncertainties that challenge the results of the work on hydrostatic pressure have been identified. This would appear to be a premature conclusion.

3.3. Shear

3.3.1 Background

Borgessön and co-workers have carried a series of investigations into the properties of bentonites and the effect of rock shear on the canister over the last 20 years. The investigations have been used to develop a model for the behaviour of bentonite under repository conditions and an integrated model of the deformation of the bentonite and the copper iron canister under earthquake conditions. Rock shears of up to 20cm have been considered.

Each successive phase of the work has involved evolution of the model in the light of earlier experience and reports at each stage have summarised the lessons from the earlier work. It is therefore only necessary to consider the two most recent TR reports (SKB TR-04-02 and SKB TR-06-43) and a recent R Report (SKB R-06-87) prepared by Jan Hernelind (as a member of the Börgesson team).

In SKB TR-04-02, earlier work is described which measured the shear deformation resistance and the relationships between swelling pressure and void ratio, shear strength and swelling pressure, and shear strength and shear rate for sodium bentonite.

The shear deformation tests provided results which fitted well with an elasto-plastic model of shear deformation.

The relationships referred to were all modelled in preparation for the current work. They showed that shear strength of bentonite increases strongly with increases in bentonite density and that shear strength increases by 10% for each decade increase in strain rate. The shear rate investigation ranged from conventional shear rates up to rates of 6m/sec. It was claimed that the model fitted well with experience at the rate of 1m/sec. which is of interest to earthquake resistance studies.

Data for studies on the effects of rock shear were taken from this earlier work. In addition, properties of copper and cast iron were taken from the work of Andersson et al. (SKB TR-04-23). An elasto-plastic model with proof stress and work hardening rates based on the conventional strain rate Andersson et al. data (SKB TR-04-23) was used.

3.3.2 Shear normal to the canister axis

Calculations were made in two steps, first the swelling pressure was applied and then the shear force after the 1 mm gap had closed. The shear was normal to the axis of the canister and it continued until a displacement of 20cm was achieved. The shear rate was 1m/sec and eight calculations were made (viz.densities of 1950, 2000, 2050, and 2100 kg/m^3, and two positions ¼ and ½ distance from the top of the canister).

An additional calculation was made for the reference case (bentonite density 2,000kg/cm^3) because it was observed that tensile stresses developed on the passive side of the canister. The boundary between the canister and the bentonite will not support tensile stresses and the initial model tied the canister to the bentonite. The revised calculation used contact elements which allowed the bentonite and the canister to separate.

The result for the reference case (asymmetric shear at density 2000kg/m^3) is dealt with in detail. The results indicate that a peek strain on of 4.4% arises at the surface of the insert and that this strain arises at a point some distance from the shear plane (approximately 1m) and towards the centre of the canister. For the copper the peek plastic strains are higher at 8% near the shear plane and much higher near the lid. In this case (the copper) the peek strains are not displaced towards the centre of the canister. This implies that there is relative movement of the insert and the copper shell.

The additional case using contact elements showed that the bentonite and the copper separate on the side where tensile forces were predicted. Strains in the copper on the compressive side and in the cast iron were little altered.

The high strains near the lid of the copper shell are due to the design of the lid and difference in stiffness of the lid and the cylindrical section; they should not concern us at this point. The difference in deformation patterns between the insert and the copper is interesting and it should be informative.

Experience tells us that at very high rates of shear, damage is concentrated at the shear plane. The difference in the location of the peek strains in the insert and the copper has to be related to the differences in mechanical properties of the bentonite, the copper and the cast iron. In the calculations allowance has been made for the rate sensitivity of the bentonite properties but none has been made for the rate sensitivities of the properties of the copper or the cast iron.

In the extreme case of a very high shear rate there would be no plastic deformation in the copper or the iron because their elastic limits would be raised to their fracture stresses. For this case all damage would be concentrated at the shear plane. For the case under consideration the shear rate will be somewhere between the properties measured in a standard test (as used in these calculations) and the extreme rate properties. This sensitivity should be explored.

The peek strains calculated are the average strains in the most highly strained elements and they may be underestimates for this reason. It is important to know how the strain varies within the elements at the most highly strained regions in order that the true peek strain can be estimated. It would be informative to explore the effects of using a finer mesh in the analysis of the deformed regions.

The calculations using contact elements indicate that separation of the copper and the bentonite occurs and that the contact elements provide a useful refinement to the model. This observations has implications for the combined case of isostatic loading and rock shearwhich has been referred to earlier (sections 3.2.3 and 3.2.4).

The overall result series from this work indicate a strong sensitivity of maximum strain in the copper and the iron to bentonite density. At 20 cm shear displacement and 2050kg/m^3 bentonite density the peak calculated strains in the copper and the iron are 16% and 11% respectively. Bearing in mind this and the above comments it is recommended that further analyses should be undertaken using a finer mesh in the critical regions and properties of the copper and cast iron measured at appropriate strain rates.

3.3.3 shear planes at 22.5° and 45° to the canister axis

In this work (SKB TR-06-43) both sodium bentonite and Calcium bentonite were considered. All earlier work considered sodium bentonite alone.

Calcium bentonite has both a higher swelling pressure and higher strength than sodium bentonite at a comparable density. For the interesting range of densities both swelling pressure and strength are doubled compared with values for sodium bentonite.

Shear angles of 22.5º, 45º and 90º were examined for both bentonites at densities of 2000 and 2050 kg/m^3.

Contact elements were used to enable sliding and separation between the various materials in the system.

When sodium bentonite is used the strains of less than 1% were calculated for all cases in the iron except the 90º at 2000 and 2050kg/m^3 where values were 1.7% and 3.6%. These were similar to cases where contact elements were not included. For all 22.5º and 45º strain in the iron was less than 1% and strain in the copper tube was always less than 5%.

With calcium bentonite strains were always much higher than with the sodium bentonite.

The reason for testing calcium bentonite is obscure as it appears to be ruled out on the basis of swelling pressure. It is also less satisfactory under shear as it happens.

The much lower strains predicted for shear angles of 22.5° and 45° are surprising and they suggest that further angles for central shear planes as well as other shear plane positions should be examined in order to establish the pattern of variation which may arise.

The main report suggests that as the specification for the copper is 30% and for the iron is 7%, at 10cm shear both are well within specification, it also claims that the worst case, 19% and 4% at 20 cm shear is still within the ductility limit of the copper it makes no comment on the iron. In view of the high strain rates used it is necessary to check the mechanical properties of both the copper and the cast iron at appropriate rates. When the evolution of the model is completed it would be appropriate to consider the effects of variation in mechanical properties and manufacturing tolerances which will occur.

3.3.4 Creep relaxation of shear strain.

Specification is for a creep ductility of 10%. Hernelind (SKB R-06-87) included creep relaxation in his a study which was only on 2000 kg/m^3 bentonite with normal shear planes on the centre line and at ¾ height. The results suggested that 7.6%shear relaxation would occur in the copper for the 10cm shear case and 11.5% for 20cm shear case. This is too close for comfort and they hope to refine the creep model.

4. Conclusions

1. The claim that uncertainty on composition of the insert is small does not recognise that the specification is on microstructure and not composition. Neither does it recognise that a considerable inhomogeneity of composition is inherent in the production process. The variability of properties either within or between casts has not been adequately investigated at this stage.
2. The data on defects in the copper shell is confused, contradictory and confined to the weld region. Defects arising from the forging process are likely to be fewer than weld defects but more severe. It is not clear that these have been investigated.
3. Acceptance criteria for casting defects in the liner are not available. Claims that ultrasonic examination of the outer shell should be satisfactory are very likely to be true but similar claims for the volumes between the fuel channels are much less likely to be true.
4. A requirement of 5 mm max. on cassette eccentricity in the insert will be difficult to maintain in serial production.
5. Analytical tools have been developed for both deterministic and probabilistic analysis of initial plastic collapse and the initiation of crack growth at existing defects in the canister. A tool has also been developed for deterministic analysis of the response of the bentonite canister system to rock shear.
6. Application of the probabilistic analysis to the liner concluded that local plastic collapse will always occur at a lower pressure than initiation of cracks at defects.
7. Concerns that the sensitivities of probability to local collapse to mechanical properties and quality have led to the adoption of a less stringent failure criterion. That is total plastic collapse (defined as a 50 mm deflection in the insert). This has not been the subject of a probabilistic analysis and therefore its sensitivities have not been explored. A deterministic approach suggests that the pressure for a 50 mm deflection is approximately 100 MPa. No reports are available describing work to

check whether or not initiation of cracks at existing flaws will occur in the pressure range 44 MPa to 100 MPa.

8. The total collapse analysis was deterministic and made no use the sensitivity analyses available in the probabilistic analysis. It has no foundation in the statistics of mechanical properties.
9. Both probabilistic and deterministic analyses made for the isostatic loading case assumed that the bentonite and the canister remained in contact throughout the deformation process. If true plastic collapse occurs some separation might be expected.
10. Data on mechanical properties of the liner material provided for probabilistic analysis was statistically inadequate. Too few castings were tested. No statistics were measured for the compression case which was the one used, and the strain rates were not compatible (too rapid) with the strain rates likely to occur in service.
11. The only valid results on isostatic loading are the deterministic results and they provide no information on sensitivity to material and production variables.
12. Whilst probability of local plastic collapse is predicted to be very low for the reference case, sensitivities to cassette eccentricity and variations in mechanical properties are extreme. This and the poor quality of the input data on mechanical properties limits confidence in the results of the analysis.
13. It appears that initiation of cracks from existing defects is unlikely to occur at lower stresses than local plastic collapse. The actual probabilities for crack initiation is however subject to all the uncertainties arising from poor input data referred to in 10 above.
14. The probability exercise has provided valuable hindsight and there is a strong case for taking the lessons which it provides to plan a further study based on sound mechanical property statistics.
15. A series of studies have provided a valuable insight into the effect of rock shears of up to 20cm on the resulting mechanical processes in the canister and the bentonite. Care has been taken to understand and allow for the effects of shear rate on the bentonite, but no attempt has been made allow for the effect of shear rate on the response of the iron or the copper (shear rates will be much more rapid then rates used for the data provided). This needs to be done in order to build confidence in the analysis.
16. It would be helpful to explore the sensitivities of the shear response of the canister to variations in canister and bentonite properties. This requires a better knowledge of the variations in the properties of the materials and of the quality of manufacture.
17. It would also be informative to consider the case of combined hydrostatic pressure and rock shear.
18. A preliminary exercise to examine creep relaxation has demonstrated that further study will be appropriate.

5. References

Minnebo, P; Statistical Analysis of Engineering Tensile Properties of Nuclear Waste Canister Insert Material, EUR21487EN, Joint Research Centre of the European Commission, 2004.

SKB R-06-04, Svensk Kärnbränslehantering AB; Kapsel för använt kärnbränsle. Svetsning vid tillverkning och förslutning, Svensk Kärnbränslehantering AB, Stockholm, 2006.

SKB R-06-05, Svensk Kärnbränslehantering AB; Kapsel för använt kärnbränsle. Oförstörande provning av kapselkomponenter, Svensk Kärnbränslehantering AB, Stockholm, 2006.

SKB R-06-87, Hernelind, J; Earthquake induced rock shear through a deposition hole when creep is considered - first model. Effect on the canister and the buffer, Svensk Kärnbränslehantering AB, Stockholm, 2006.

SKB TR-04-02, Börgesson, L; Johannesson, L-E; Hernelind, J; Earthquake induced rock shear through a deposition hole. Effect on the canister and the buffer, Svensk Kärnbränslehantering AB, Stockholm, 2004.

SKB TR-04-23, Andersson, C-G; Eriksson, P; Westman, M; Emilsson, G; Status report, canister fabrication, Svensk Kärnbränslehantering AB, Stockholm, 2004.

SKB TR-05-17, Andersson, C-G; Andersson, M; Erixon, B; Björkegren, L-E; Dillström, P; Minnebo, P; Nilsson, K-F; Nilsson, F; Probabilistic analysis and material characterisation of canister insert for spent nuclear fuel. Summary report, Svensk Kärnbränslehantering AB, Stockholm, 2005.

SKB TR-05-18, Nilsson, K-F; Lofaj, F; Burström, M; Andersson, C-G; Pressure tests of two KBS-3 canister mock-ups, Svensk Kärnbränslehantering AB, Stockholm, 2005.

SKB TR-05-19, Dillström, P; Probabilistic analysis of canister inserts for spent nuclear fuel, Svensk Kärnbränslehantering AB, Stockholm, 2005.

SKB TR-06-09, Svensk Kärnbränslehantering AB; Long-term safety for KBS-3 repositories at Forsmark and Laxemar - a first evaluation. Main report of the SR-Can project, Svensk Kärnbränslehantering AB, Stockholm, 2006.

SKB TR-06-25, Svensk Kärnbränslehantering AB; Data report for the safety assessment SR-Can, Svensk Kärnbränslehantering AB, Stockholm, 2006.

SKB TR-06-43, Börgesson, L; Hernelind, J; Earthquake induced rock shear through a deposition hole. Influence of shear plane inclination and location as well as buffer properties on the damage caused to the canister, Svensk Kärnbränslehantering AB, Stockholm, 2006.

3

Status of research on chemical erosion of the buffer

Randy Arthur
Wei Zhou

Monitor Scientific, LLC
Denver, Colorado
U.S.A.

Summary

This report assesses the status of research and modeling that is being carried out on behalf of SKB to determine whether chemical erosion of the buffer in a KBS-3 repository for spent nuclear fuel could occur to such a extent that repository safety would be adversely affected. Such erosion is possible if the constituent clay minerals in bentonite are suspended as colloids and transported away from the deposition holes in flowing groundwater. Erosion of at least 6% of the initial dry mass of bentonite could generate advective conditions in the buffer. This is a potential concern because such conditions could enhance the transport of corrodants to the canister's surface, thereby increasing corrosion rates.

Our assessment considers 1) how the potential issue of buffer erosion is handled in the SR-Can safety assessment, 2) numerical mass-balance models of buffer erosion developed by SKB, 3) an alternative, preliminary reactive-transport model developed in the present study, and 4) descriptions presented at a recent workshop on SKB-sponsored research projects involving various aspects of buffer erosion. Based on these sources of information, we conclude that important uncertainties in current conceptual models of buffer erosion exist and can be grouped into categories related to: 1) formation and stability of clay colloids, 2) buffer-groundwater interactions, 3) colloid transport, and 4) hydrogeology and hydrochemistry of glacial meltwaters. Although these uncertainties may be difficult to address in a comprehensive and timely manner, it is possible that they can be prioritized and reduced sufficiently to help establish credible bounds on buffer erosion rates.

Table of contents

1. Introduction

A contributing factor to risk in the main scenario of the SR-Can safety assessment of the KBS-3 disposal concept for spent nuclear fuel involves corrosive canister failure as a result of chemical erosion of the bentonite buffer by contact with dilute glacial meltwaters (SKB 2006a). It is believed that buffer erosion may occur if the constituent clay minerals in bentonite are suspended as colloids and transported away from the deposition holes in flowing groundwater[1]. Erosion of as little as 1200 kg of bentonite from a deposition hole (about 6% of the initial dry mass) could generate advective conditions in the buffer (Börgesson and Hernelind, 2006). This is a potential concern because such conditions could enhance the transport of corrodants to the canister's surface, thus increasing corrosion rates (SKB 2006a). Assuming pessimistic hydraulic conditions at the Forsmark site, for example, and using cautious assumptions regarding sulfide concentrations and deposition hole acceptance criteria, SKB estimates that buffer erosion could lead to the failure of some tens of canisters over an assessment time frame of one million years. Calculated risks for both the Laxemar and Forsmark sites are, however, below the regulatory risk limit during the first 100,000 years of repository evolution (SKB 2006a).

This report assesses the status of new and ongoing research and modeling that is being carried out on behalf of SKB to help reduce uncertainties in the general knowledge base on buffer erosion. The objectives of the report are to provide a commentary on SKB's research program that can be used to assist SKI in its review of the SR-Can safety assessment report, and to help track future progress toward resolving this potential issue. Much of the information considered in this report was presented at the "Workshop on Bentonite Erosion (IV)", which was held in Stockholm on June 13, 2007[2]. Presentations made at the workshop are especially useful for the present study because they provide an informative and timely snapshot of the status of current work being carried out by SKB on buffer erosion.

The report is organized as follows. Section 2 describes how the concept of buffer erosion is handled in the SR-Can safety assessment (SKB 2006a). Conceptual and numerical modeling approaches that have been used by SKB to estimate erosion rates are then described in Section 3. Section 4 provides a summary of the presentations given at the workshop noted above. The main conclusions of this study are summarized in Section 5.

---

[1] Buffer erosion may also be induced by shear forces exerted by flowing groundwater at the buffer-groundwater interface, and by hydraulic forces acting on the buffer during saturation (piping). These physical processes are not considered here. They are evaluated by Börgesson and Sandén (2006) and Liu and Neretnieks (2006).

[2] It is anticipated that the results of much of the research summarized in these presentations will be formally presented in SKB's RD&D Programme 07 to be published in 2007 (see SKB 2006a).

2. Treatment of buffer erosion in SR-Can

An equation used in the SR-Can safety assessment to estimate buffer erosion rates is described in Appendix B of SKB (2006a). The rate, R_{buffer} (kg yr^{-1}), is given by:

$$R_{buffer} = C_{Max} Q_{eq}, \qquad (2\text{-}1)$$

Where C_{Max} refers to the maximum concentration of bentonite in a water suspension (50 kg m^{-3}) and Q_{eq} denotes the equivalent flow rate (m^3 yr^{-1}). The equivalent flow rate is used to quantify the exchange of solutes between flowing groundwater in the host rock and bentonite in the deposition hole (see SKB 2006a, Section 9.3.6). The model assumes that bentonite consists only of a pure Na-montmorillonite. The value chosen for C_{max} appears to be based on empirical observations.

Equation (2-1) is used in SR-Can to estimate buffer erosion rates due to colloid release. Representative results are shown in Figure 2_1 for a stylized case in which it is assumed that flow conditions at repository depth are similar to those observed at the Forsmark site today (SKB 2006a). It is also assumed that these conditions persist for a period of 25,000 years, and

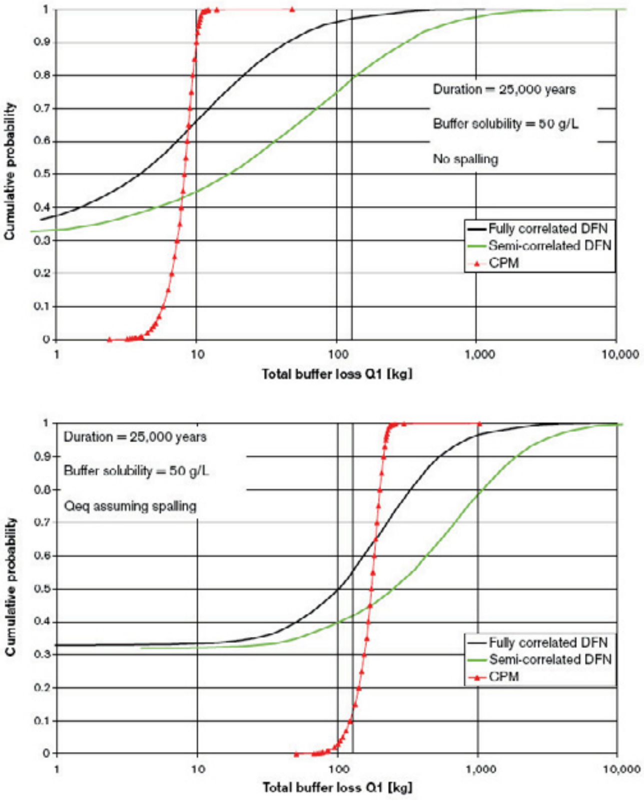


Figure 2-1. Estimated buffer mass losses from deposition holes after 25,000 years (SKB 2006a). Equivalent flow rates are estimated based on hydrogeologic modeling of the Forsmark site for temperate conditions similar to those observed at repository depth today (see text). Results are shown for the case of no spalling (upper figure) and spalling (lower figure) of the bedrock near deposition holes.

that spalling of the host rock near the deposition hole may occur. The estimated total amounts of buffer lost after 25,000 years can be compared to the benchmark value of 1,200 kg marking the threshold value above which advective conditions could be generated in the buffer (Börgesson and Hernelind, 2006). Results are shown for three alternative hydrogeologic models: 1) a fully correlated discrete fracture network (DFN) model; 2) a semi-correlated DFN model, and 3) a continuous porous medium (CPM) model (SKB 2006a, Section 9.3.6). The DFN models are generally conservative in the sense that they tend to result in more severe consequences with respect to solute release and transport to and from the geosphere.

The results in Figure 2-1 for the semi-correlated DFN model without spalling indicate that 1200 kg of the buffer would be lost from about 3% of the deposition holes. The alternative flow models predict that buffer losses would be less than 1200 kg in all deposition holes. With spalling, more than 1200 kg of the buffer is predicted to be lost after 25,000 years from 15% of the deposition holes using the fully correlated DFN model, from 35% of the holes using the semi-correlated DFN model and from none of the holes using the CPM model. Similar estimates using the semi-correlated DFN model for the Laxemar site indicate that at least 1200 kg of bentonite would be lost from 40% of the deposition holes after 25,000 years (SKB 2006a).

These illustrative results suggest that advective conditions in the buffer could be generated in a substantial number of deposition holes over a reasonable range of hydrogeological conditions at the Forsmark and Laxemar sites. SKB notes, however, that there is considerable uncertainty in the accuracy of erosion rates estimated using Equation 2-1 (SKB 2006a). This is because the calculation model represented by this equation is not built upon a mechanistic understanding of processes controlling colloid release from compacted buffer materials. Repulsive forces acting to separate, and thus stabilize, colloidal suspensions are not considered in the model, for example, and these forces should act to increase the erosion rate. On the other hand, SKB notes that "early" (albeit unreferenced) experimental and theoretical evidence suggests that colloid release from commercial bentonites, especially those in which Ca is an important exchangeable cation in montmorillonite, are much less susceptible to colloid formation than are montmorillonites in the pure Na form (SKB 2006a). For these reasons, SKB concludes that it is possible that actual erosion rates for the buffer in a KBS-3 repository could be lower, or higher, than those presently estimated using Equation 2-1.

3. SKB's mass-balance models

This section considers mass-balance models of buffer erosion that have been developed and evaluated by SKB. The original model is described in the SR-Can interim report (SKB, 2004), and a revised version is described by Liu and Neretnieks (2006). Neretnieks (2007a) refers to the latter model as the "0-th order model". Estimated erosion rates using these models were not considered in the final SR-Can safety assessment, however (SKB, 2006a). As noted in Section 2, erosion rates in SR-Can were instead estimated using Equation 2-1.

3.1. Background

SKB's mass-balance approach for estimating buffer erosion rates is based on the DLVO theory of colloid stability (Verwey and Overbeek, 1948; Overbeek, 1952a; Adamson, 1967; van Olphen, 1977; Stumm and Morgan, 1996). DLVO theory assumes that the stability of an aqueous colloidal system is controlled by a balance between electrostatic double-layer forces, which tend to repel particles of like charge, and attractive forces arising from van der Waals interactions (Figure 3.1_1). The repulsion energy depends on the electrical potential at a particle's surface and its decay with increasing distance into the diffuse double layer. The van der Waals attractive energy varies inversely with the square of the distance between two particles. Attraction outweighs repulsion when the inter-particle separation distance is small. Repulsion dominates when this distance is above a threshold value. Exact solutions to equations representing the attractive and repulsive forces in colloidal systems are available for idealized cases in which the particles are represented by parallel flat plates or spheres. Approximate solutions must be sought for more realistic systems.

Separation distances among the particles in an aqueous colloidal suspension depend on the ionic strength of the medium because this parameter determines how the electrical potential decays with increasing distance outward from the surface into the double layer[3]. The thickness of the double layer is generally taken as being equal to the reciprocal of the Debye parameter, κ; given by:

$$\kappa = \left(\frac{2F^2 I \mathrm{x} 10^3}{\varepsilon \varepsilon_0 RT} \right)^{1/2}, \qquad (3.1\text{-}1)$$

where F refers to the Faraday constant, I represents ionic strength, ε stands for the dielectric constant of water, ε_0 denotes the permittivity of free space, R represents the gas constant and T stands for temperature. The thickness of the double layer thus decreases as ionic strength increases, and this allows the individual particles in a colloidal suspension to move closer together. The particles will eventually flocculate to form a gel if the double-layer thickness falls below a value corresponding to the threshold separation distance noted above. Conversely, stable colloids may form from a gel if the ionic strength were to decrease sufficiently. Erosion is thus more likely in situations where the buffer comes into contact with groundwaters that are relatively dilute.

---

[3] Van der Waals interactions are not affected by ionic strength.

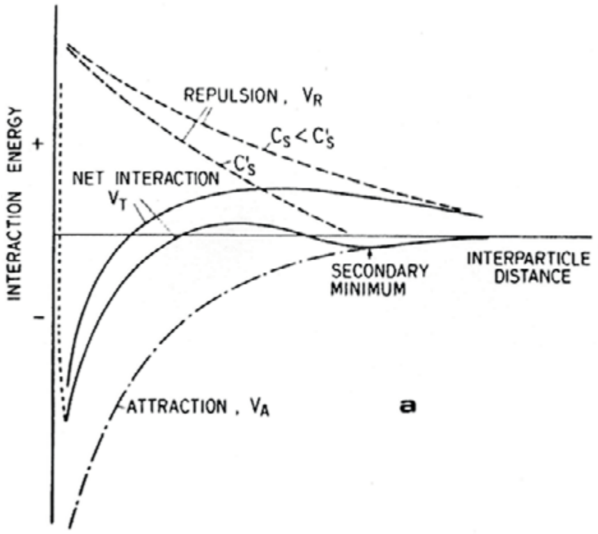


Figure 3.1_1. Schematic diagram of the physical (DLVO) model of colloid stability (Stumm and Morgan, 1996). The net interaction energy, V_T*, represents the sum of electrostatic double-layer repulsion (*V_R*) and van der Waals attraction (*V_A*) energies. At very small interparticle distances an additional repulsive force arises due to the interaction of atomic electronic clouds (Born repulsion). Colloids are stable when* $V_T > 0$ *and unstable when* $V_T < 0$*. The effects of electrolyte concentration on colloid stability are illustrated by the two lines showing variations in* V_R *as a function of interparticle distance, and associated curves for* V_T*. Because electrolyte concentration* C_s *is smaller than* C^*_s*, the diagram illustrates that colloidal suspensions are stable over a broader range of interparticle distances in relatively dilute solutions. The secondary minimum in* V_T *when the electrolyte concentration equals* C^*_s *results in the formation of a weak gel, which may re-dispersed as a colloidal suspension by stirring.*

Experience has shown that predictions using the DLVO model are reasonably accurate when applied to simple colloidal systems, such as monodisperse suspensions in dilute solutions of monovalent ions (Stumm and Morgan, 1996). Agreement is generally poorer for systems involving divalent ions (*e.g.*, Sposito, 1984; Jönsson *et al.*, 2007). Other forces not considered in DLVO theory, such as solvation, hydration and capillary effects, may be important when separation distances between colloidal particles are less than about 5 nm (Stumm and Morgan, 1996).

There are additional limitations in DLVO theory when it is applied to colloidal systems involving the clay minerals in bentonite (Stumm and Morgan, 1996; Liu and Neretnieks, 2006). One limitation stems from the fact that these minerals carry a net negative charge on faces oriented parallel to the dominant tetrahedral-octahedral-tetrahedral layering, and net positive charges on edges that are oriented normal to this layering (*e.g.*, Grim, 1968). This means that a given clay particle will have different double-layer structures associated with its faces and edges. Particle-particle interactions in clay colloidal systems must consequently involve face-to-face (FF), edge-to-face (EF) and edge-to-edge (EE) interactions. Because the EF interactions involve particle surfaces of unlike charge, particle agglomeration may occur even in dilute electrolyte solutions. The DLVO model does not account for such interactions, and may thus overestimate the stability of clay colloids.

The DLVO model also does not account for the effects of specific adsorption on colloid stability. As noted above, the model assumes only that the electrolytes in a colloidal suspension are inert, and that their effect on colloid stability is through the control on double-layer thickness expressed by Equation 3.1-1. Other electrolytes may form covalent complexes with functional groups at a particle's surface, however (*e.g.*, Langmuir, 1997). Such complexes alter the surface charge and surface potential, and thereby affect colloid stability. The concentration of a specifically adsorbable species that is needed to destabilize a colloidal suspension tends to decrease with increasing affinity of the ion for the colloid's surface. A specifically adsorbable species that coagulates a colloid at low concentration may re-stabilize the colloid at higher concentrations. Hydrogen and OH^- ions are known to be specifically adsorbed on surfaces of the clay minerals in bentonite (*e.g.*, Wieland *et al.*, 1994). This suggests that the colloidal stability of these minerals must be pH-dependent. This dependency is not accounted for in the DLVO model (Missana and Adell, 2000).

3.2. Model description

Figure 3.2_1 provides a schematic overview of SKB's conceptual model of buffer erosion (SKB 2004). Bentonite is assumed to penetrate a fracture that intersects the deposition hole. The penetration distance is controlled at steady state by the swelling pressure and by frictional forces acting at the interface between the gel and fracture surface.

SKB adopts the concept of a critical coagulation concentration (CCC) for "free" (*i.e.*, uncomplexed) Ca^{2+} to account for ionic-strength effects on colloid stability. This cation is selected because it is relatively abundant in Swedish groundwaters[4], and because its divalent character strongly influences colloid stability in accordance with the Schulze-Hardy rule[5] (Overbeek, 1952b). SKB assumes that the CCC for Ca^{2+} is 1 mmol l^{-1}. The bentonite gel within the fracture (Figure 3.2_1) is thus assumed to be stable if the concentration of Ca^{2+} in the gel's porewater is greater than this value. Conversely, colloidal suspensions of the smectite clays form if Ca^{2+} concentrations are below this value. A stable gel can persist at the boundary between bentonite and groundwater as long as the concentration of Ca^{2+} in the groundwater is at or above the CCC. It is important to emphasize that the CCC concept only approximates the effects of porewater chemistry on colloid stability. It does not fully account for the ionic-strength effects on double-layer properties noted above, nor does it account for the effects of specifically adsorbed ions on electrical potentials near particle surfaces (see Section 3.1).

SKB assumes that at some point in time the extruded bentonite gel (Figure 3.2_1) comes into contact with groundwater having a Ca^{2+} concentration below the CCC. A mass balance is used to estimate the extent to which the buffer would be transformed into a stable colloidal suspension and carried away with the flowing groundwater. This results in the following equation:

---

[4] Total dissolved Ca concentrations in Swedish groundwaters are generally greater than 1 mmol l^{-1} (SKB, 2004). Certain groundwaters (*e.g.*, glacial meltwaters) could, however, have Ca concentrations that are below this value.

[5] According to this rule, the CCC decreases with the charge (z) of mono-, di- and trivalent ions that are present in the diffuse double layer in the ratio $(1/z)^6$.

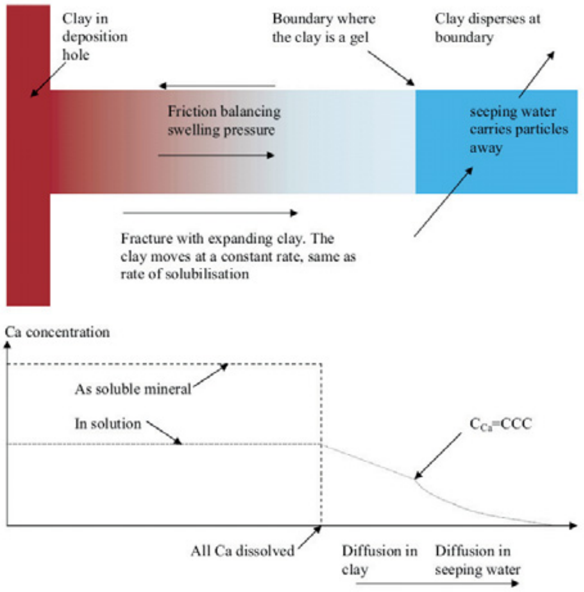


Figure 3.2_1. Schematic diagram illustrating SKB's conceptual model of buffer erosion (SKB 2004). The buffer extrudes a certain distance into the fracture under the control of swelling-pressure and frictional forces. The concentration of Ca^{2+} *in the seeping groundwater is assumed to be less than the CCC. The* Ca^{2+} *concentration at the interface between the groundwater and buffer is equal to the CCC (i.e., because the gel is stable at that point). Calcium in the buffer's porewater diffuses toward the groundwater, and this is accompanied by dissolution of Ca-bearing minerals.*

$$N_{clay} = \left(\frac{Q_{eq}(c_i - c_w)}{\varepsilon_{clay}(c_0 - c_i)} \right) \rho_{dryclay} \,, \qquad (3.2\text{-}1)$$

where,

N_{clay} = mass of buffer lost per unit time (kg yr^{-1})
Q_{eq} = equivalent flow rate (m^3 yr^{-1})
c_i = Ca^{2+} concentration in groundwater that has reacted with bentonite in the fracture ("leaving groundwater"; mol m^{-3})
c_w = Ca^{2+} concentration in groundwater prior to reaction with bentonite in the fracture ("entering groundwater"; mol m^{-3})
c_0 = concentration of Ca^{2+} that could be added to bentonite porewater by dissolution of soluble minerals (mol m^{-3}).
ε_{clay} = buffer porosity
$\rho_{dry,clay}$ = dry density of the buffer.

The equivalent flow rate, Q_{eq}, in this case represents the flow rate of groundwater that will carry away the Ca^{2+} that diffuses into the groundwater from the buffer's porewater with an average concentration equal to the difference between c_i and c_w.

3.3. Preliminary results

Equation (3.2-1) was evaluated by SKB under two limiting conditions regarding the amount of soluble calcite that is assumed to be initially present in bentonite: either 0 or 1 wt%. Any calcite in the buffer is assumed to dissolve completely and instantaneously. Other initial and boundary conditions are:

Q_{eq} = 0.001 $m^3\ yr^{-1}$,
c_0 = 10 mol m^{-3} (0 wt% calcite) or 1250 mol m^{-3} (1 wt% calcite),
c_i = CCC = 1 mol m^{-3},
c_w = 0 mol m^{-3},
$\rho_{\mathrm{dry,clay}}$ = 1600 kg m^{-3}, and
$\varepsilon_{\mathrm{clay}}$ = 0.4.

The results of the calculations indicate that N_{clay} = 0.4 kg yr^{-1} for the first case (0 wt% calcite), and N_{clay} = 0.0032 kg yr^{-1} for the second case (1 wt% calcite). If it is assumed that buffer performance could be adversely affected if 1200 kg of bentonite erodes from the fracture/deposition hole (Börgesson and Hernelind, 2006; SKB 2006a), then these estimated erosion rates suggest that this could happen within about 3000 to 375,000 years depending on the amount of calcite initially present in the buffer.

Liu and Neretnieks (2006) use a revised version of the conceptual model discussed above to obtain alternative estimates of buffer erosion rates. The revised model differs from the original in two important respects. First, groundwater flow rates are modeled explicitly in the alternative model instead of using the equivalent flow rate (values for Q_{eq} are also calculated using groundwater flow parameters, however). Second, Liu and Neretnieks (2006) assume that Ca concentrations in the buffer's porewaters are controlled by the solubility of trace amounts of gypsum (0.7 wt.%, which is assumed to be a representative value for MX-80 bentonite). In comparison, Ca concentrations in the original model were assumed to be controlled by the calcite inventory (*i.e.*, either 0 or 1 wt.%). Gypsum rather than calcite is considered in the alternative model because the solubility of calcite is considered to be too low to sustain Ca concentrations above the CCC. Gypsum solubility in the alternative model is fixed at 9.8 mM.

Liu and Neretnieks (2006) use the FEMLAB program (Comsol, 2004) to solve for the integrated total flux of Ca along the extruded bentonite-groundwater boundary. The flux is then used to estimate the corresponding buffer erosion rate by assuming that the buffer is dispersed as a colloid and lost from the fracture/deposition hole when the concentration of Ca in the buffer's porewater falls below the CCC (10^{-3} M). Results using "central values" for groundwater flow parameters [hydraulic gradient (0.01), transmissivity ($10^{-8}\ m^2\ s^{-1}$) and fracture aperture 10^{-4} m)] suggest that the erosion rate would be 0.11 kg yr^{-1}. This suggests that advective conditions corresponding to a loss of 1200 kg of bentonite (Börgesson and Hernelind, 2006; SKB 2006a) would be established within 11,000 years.

3.4. Status of SKB's mass-balance modeling

SKB notes that its preliminary mass-balance model (SKB 2004) may be overly simplistic in a number of respects. Specifically, the model neglects several potentially important constraints on reactive-transport processes that could significantly affect the buffer-dispersion rate. These constraints include:

1. explicit coupling of flow and transport at the bentonite-groundwater interface,
2. equilibrium/kinetic constraints on the extent of calcite dissolution,
3. diffusive transport in the fracture and deposition hole,
4. changes in the composition of the double layer (*e.g.*, by ion-exchange), and
5. effects of aqueous-speciation on Ca^{2+} concentrations.

These constraints are addressed to some extent by Liu and Neretnieks (2006), and are also considered further in a preliminary reactive-transport model of buffer erosion that was developed in the present study (see appendix). SKB's ongoing research activities targeting these constraints and other aspects of buffer erosion are discussed in the following section.

4. Status of SKB's current R&D program on buffer erosion

SKB convened the "Workshop on Buffer Erosion (IV)" in Stockholm on June 13, 2007. The purpose of the workshop was to bring together researchers from various organizations to discuss ongoing research projects sponsored by SKB on various aspects of buffer erosion, with an emphasis on chemical erosion. Presentations given at the workshop provide a timely overview of SKB's current R&D program. To help document the status of this program a synopsis of several of the presentations is provided below.

Neretnieks (2007b). Neretnieks (2007b) presents an overview of SKB's R&D program on buffer erosion. The program includes experimental studies, theoretical development/modeling work and investigations of potential natural analogs. The experimental work includes a number of projects addressing: 1) buffer expansion into slits representing fractures (including NMR studies of bentonite swelling behavior), 2) factors affecting the vapor pressure and swelling pressure of compacted bentonite, 3) rheology of bentonite gels/sols, and 4) filtering of smectite colloids by non-colloidal accessory minerals in a partially eroded buffer. The theoretical studies consider: 1) total force balances affecting colloid stability and transport, and 2) coupled effects of chemical concentration gradients on colloid stability. Preliminary studies of a number of potential natural analogs of buffer erosion are also underway.

SKB is also collaborating on a number of domestic and international research projects that have some relevance to buffer erosion. These projects include: 1) an examination of the CCC concept, 2) colloid transport in fractures, 3) visualization of colloid formation in fractures, 4) flow and colloid transport in fractured rocks at the Äspö HRL, and 4) modeling of chemical reactions and colloid transport. These studies were not discussed at the workshop.

Neretnieks (2007b) also identifies several R&D topics related to buffer erosion that could be addressed in future studies. These include 1) maximum groundwater flow rates during the period when dilute glacial meltwaters penetrate to repository depths (tentatively assumed to be 100 times the rate presently observed at Forsmark and Laxemar), 2) duration of enhanced groundwater flow conditions (tentatively assumed to be 10,000 years), and 3) effects of water-rock interaction on Ca^{2+} concentrations in infiltrating glacial meltwaters (tentatively assumed to be always less than the CCC).

Birgersson (2007). Birgersson (2007) discusses recent swelling pressure experiments involving a Wyoming bentonite in which Ca is the dominant exchangeable cation in smectite. He notes that the charge density (*i.e.*, the charge per unit surface area of smectite) is proportional to the layer charge resulting from isomorphous substitutions, and that this charge strongly affects variations in the repulsive double-layer energy as a function of separation distance. This suggests that there may be a critical layer charge below which clay colloids are stable regardless of separation distance. A corollary to this observation is that relatively small changes in the mineral chemistry of a smectite particle could strongly affect its colloid behavior. Birgesson (2007) makes the interesting observation that there may be considerable variability in layer charge among different bentonite samples from a given deposit.

Jansson (2007). Jansson (2007) describes an experimental program aimed at investigating the release of clay colloids into fresh water. Test-tube studies were set up to evaluate the CCC concept. For a pure Na-montmorillonite, Ca concentrations greater than about 1 mM appear to prevent colloid formation, which is consistent with the CCC value used for Ca in SKB's 0-th order mass-balance model (Section 3). No details are given regarding the chemistry of the aqueous solutions used in these experiments (*i.e.*, pH, carbonate content, etc.). Similar studies using a pure Ca-montmorillonite and Deponit CA-N smectite, are planned.

Jansson (2007) also describes an ongoing experiment in which MX-80 bentonite (excluding most accessory minerals) extrudes into an artificial fracture (aperture = 1 mm) and comes into contact with flowing groundwater (simulated using deionized water). Results over a period of 45 weeks clearly show the progressive movement of the buffer outward into the fracture and the development of distinct bands. The banding may be caused by variations in the bentonite's physical properties or mineralogy. A "post-mortem" investigation of the experimental system is planned.

Jönsson et al. (2007). The effects of salt on bentonite swelling are described in this presentation. The effects are illustrated in plots showing calculated variations in osmotic pressure as a function of the separation distance between two parallel flat plates representing a colloidal system. Results suggest that colloid stability will depend strongly on the valence of the counterion. An interesting observation is that increasing concentrations of a divalent counterion (Ca^{2+}) to a system containing a fixed concentration of a monovalent counterion (Na^{+}) can cause a stable colloidal suspension to become unstable. Jönsson *et al.* (2007) suggest that even low concentrations of trivalent cations could also act to destabilize colloids.

Karnland (2007). Karnland (2007) describes SKB's research program on thermodynamic and DLVO models of bentonite swelling pressure, and recent experimental results from swelling-pressure and colloid-formation tests. The modeling studies and earlier experimental work are described by Karnland (1997), Karnland *et al.* (2002), Muurinen *et al.* (2004) and SKB (2006b).

SKB's DLVO model relates the swelling pressure to a summation of terms representing the effects of electrical double-layer repulsion (evaluated using the van't Hoff and Poisson-Boltzmann equations for the case of parallel flat plates representing smectite interlayers), van der Waals attraction and interlayer ion hydration accounting for ion-dipole interactions. Each term is evaluated as a function of the dry density of compacted bentonite. Corresponding interlayer separation distances are estimated by dividing the total volume of water in the system at saturation by the surface area of smectite. Model predictions for the case of a Na-montmorillonite in pure water agree well with measured swelling pressures over a range of dry densities up to about 1900 kg m^{-3} (Karnland 2007). Swelling pressures at dry densities less than about 1500 kg m^{-3} are controlled by double-layer repulsion, whereas at higher dry densities the swelling pressure is dominated by the effects of ion hydration.

DLVO model predictions for the case of Ca- and Mg-montmorillonites do not agree well with recent experimental data presented by Karnland (2007). It is unclear why these discrepancies occur, but they may be related to the effects of divalent versus monovalent counterions on double-layer repulsive/attractive forces and osmotic pressures noted by Jönsson (2007). The experimental swelling pressures are close to predicted values if it is assumed that only ion-hydration effects contribute to the swelling pressure across the range of dry densities considered. Karnland (2007) concludes that the DLVO model is useful for Na-dominated systems but not for Ca-dominated systems. This is important because SKB is currently considering several different bentonite types for the buffer.

SKB's thermodynamic models of bentonite swelling behavior are described by Karnland *et al.* (2002) and SKB (2006b). Such models are potentially useful for studies of buffer erosion because they relate the ionic composition of bentonite porewaters (including regions of the double layer adjacent to smectite surfaces) to the compositions of groundwaters at the bentonite-groundwater interface (similar models have been developed for argillaceous rocks, see Leroy *et al.*, 2007). The models also deal with easily measurable quantities (*i.e.*, the swelling pressure), and do not require reliable measurements of the chemistry of bentonite porewaters for model development and testing. Difficulties associated with such measurements are discussed by Muurinen and Lehikoinen (1999), Pearson *et al.* (2003) and Muurinen *et al.* (2004).

SKB's thermodynamic models are based in part on the concept of Donnan equilibrium. This concept is relevant to systems in which two aqueous solutions are separated by a membrane that is impermeable to a colloidal constituent of one of the solutions. Equilibrium constraints result in an unequal distribution of ionic species (to which the membrane is permeable) in the two solutions. For the case of clay colloids having a fixed negative layer charge, the porewater near the clay surface (Solution 1) will have a higher concentration of cations and lower concentration of anions than the "external" water (Solution 2). These differences in solution composition affect the osmotic pressure, and hence the swelling pressure, of the system.

This view has been questioned by Bradbury and Baeyens (2002), who suggest that at high dry densities bentonite behaves like an efficient semi-permeable membrane, *i.e.*, one that is permeable to water but not to ionic solutes. Support for this view comes from the review by Dixon (2000) of the role of salinity on the development of swelling pressures in compacted bentonite. Dixon (2000) concludes that as long as dry densities are greater than about 900 kg m^{-3} the swelling pressure is unaffected by groundwater salinities up to 75 g l^{-1}.

Muurinen *et al.* (2004) have shown that the Donnan model fails to accurately predict solute concentrations in bentonite porewaters when these concentrations are relatively low (*i.e.*, for Cl^- concentrations less than about 1 M; the model works well for Cl^- concentrations up to 3 M). This is attributed to the effects of ion exclusion, which are believed to become more pronounced as solute concentrations decrease. Muurinen *et al.* (2004) attempt to couple equilibrium constraints in the model with the microstructure of bentonite. They assume that the microstructure can be represented in terms of two types of pores in bentonite: 1) interlamellar pores in montmorillonite, and 2) large pores in the gel between stacks of montmorillonite. Agreement between calculated and measured solute concentrations in waters squeezed from bentonite at dry densities up to 1700 kg m^{-3} is greatly improved using the coupled model and SAXS[6] and BET measurements of the microstructure's dimensions.

---

[6] Small angle X-ray spectroscopy

Neretnieks (2007a). Neretnieks (2007a) provides: 1) an overview of processes that are thought to control the physical and chemical stability of the bentonite buffer, 2) a description of the 0-th order mass-balance model of buffer erosion (see Section 3), 3) a comprehensive description of forces acting on colloidal particles, and 4) a summary of progress in the development of a swelling and release model for the buffer. The discussion of the first two topics closely follows that of Liu and Neretnieks (2006) and is not considered further here.

Neretnieks (2007a) points out that the ability of clay colloids to be transported away from the deposition holes in flowing groundwater depends on a number of forces that have yet to be considered in the 0-th order model. Together with the double-layer repulsive force and van der Waals attractive force considered in DLVO theory, these additional forces include the force of gravity, forces acting on particle-water collisions (diffusion), shear forces due to a particle's velocity relative to that of water, and friction forces at the walls of a fracture. In principle all these forces can be quantified and incorporated into a "force-balance" model of buffer swelling and erosion that accounts for variations in water chemistry, fracture properties and groundwater flow behavior. Neretnieks (2007a) describes preliminary calculations that have been carried out to assess the relative importance of these forces.

An important aspect of the force-balance approach is that it permits consideration of a number of processes that might tend to trap any colloidal clay particles released from the buffer. These processes include filtering of the particles in fractures due to gravitational and friction forces, and filtering of the particles by non-colloidal accessory minerals left behind as a "filter cake" in a partially eroded buffer.

It may be worthwhile noting here that indirect evidence for the efficacy of the first kind of filtering comes from reservoir-engineering studies of producing oil/gas fields. It is observed in such systems that significant reservoir damage (*i.e.*, permeability reduction) can occur when fresh or low-salinity groundwater is allowed to enter the reservoir (*e.g.*, Kia *et al.*, 1987). The damage is believed to occur when clay minerals in the reservoir are dispersed as colloids as a result of contact with the dilute groundwaters. The colloids are transported in the groundwater until they encounter local pore constrictions along the flow path. They are then deposited in these constrictions (presumably by gravitational and friction forces), and this results in an overall reduction in reservoir permeability. These processes are analogous to those that could occur during buffer erosion, which suggests that any clay lost from the buffer might tend to clog nearby fractures, thereby reducing groundwater flow rates in the vicinity of the deposition holes.

Neretnieks (2007a) describes an experimental project investigating the filtration of colloidal particles by a filter cake. The idea is that erosion of clay colloids from regions of the buffer that has extruded into a fracture will leave behind non-colloidal accessory minerals, which will tend to build up over time to form a filter cake. The filter cake could then prevent or mitigate the release of additional clay colloids from the buffer. Neretnieks (2007a) describes an experimental system that has been set up to test this idea. The experiment is apparently still in progress.

An additional model concept mentioned by Neretnieks (2007a) is that of Donnan equilibrium (*e.g.*, Overbeek, 1952c; Adamson, 1967; Karnland 2007). It is unclear, however, how Donnan effects would be incorporated into the force-balance modeling approach.

Pusch (2007). Pusch (2007) examines geological evidence for clay erosion from natural argillaceous rocks in Sweden that have been exposed to glacial cycles. The Kinnekulle bentonite deposit and clay minerals in fractures associated with the Singö fault zone are considered. It is concluded that there is no evidence for clay erosion from either of these deposits as a result of contact with glacial meltwaters. Studies have not been carried out, however, on deposits having the high smectite content of buffer materials.

Pusch (2007) also describes an experimental study on colloid release and transport from a mixture of MX-80 pellets and mud (consisting of 50% palygorskite and 50% quartz). The relevance of these experiments to the issue of buffer erosion is unclear.

Stilbs et al. (2007). Stilbs *et al.* (2007) describe the use of Nuclear Magnetic Resonance (NMR) spectroscopic techniques to obtain: 1) 2D and 3D images of swollen bentonite samples, 2) density distributions in bentonite samples undergoing swelling, and 3) releases of ions and organics from bentonite. Initial results appear to be promising. Future studies will focus on: 1) the effects of bentonite composition, compaction and ionic strength on swelling behavior, 2) investigation of T2 contrast effects, 3) expansion of bentonite into a horizontal slit representing a fracture, and 4) ^{27}Al imaging.

5. Concluding remarks

Chemical erosion rates for the buffer are approximated in SR-Can by assuming that the maximum possible colloidal concentration of bentonite in groundwater is 50 g l^{-1} (Section 2). An important question from a safety-assessment perspective is whether this value represents a credible upper bound. SKB (2006a) believes this question cannot be answered satisfactorily at the present time due to significant uncertainties in mechanistic models of buffer erosion. Based on the discussions in Sections 3 and 4 of the present report, we believe these uncertainties can be categorized in general as follows.

1. Formation and stability of clay colloids. Buffer erosion involves the formation and release of smectite colloids to groundwater. In general, colloid stability can be interpreted in terms of a balance between repulsive double-layer forces and attractive van der Waals forces considered in the DLVO model. For smectite colloids, however, additional factors might come into play. These include the existence of different double-layer structures associated with the edges and faces of smectite particles, and the effects of specifically adsorbed ions on the surface charge and surface potential. There is some evidence to suggest that these additional factors are important (Missana and Adell, 2000; Jönsson *et al.*, 2007). If so, simplifying assumptions that are compatible with DLVO theory, such as the CCC concept, may not be valid.

2. Buffer-groundwater interactions. Buffer erosion entails the interaction of glacial meltwaters with the buffer. A conceptual model for the formation of clay colloids resulting from these interactions must therefore account for the manner in which changes in groundwater chemistry affect the types and concentrations of counterions in the double layer (assuming DLVO models of clay colloid stability are approximately correct). Such changes are accounted for in SKB's thermodynamic models relating the buffer's swelling pressure to groundwater chemistry (see Section 4), and it thus seems probable that these models could be extended to the problem of buffer erosion. Unfortunately, the models appear to fail in some cases (*e.g.*, Ca-dominated systems) for reasons that are not readily apparent. The conceptual basis of the models has moreover been questioned on the grounds of 1) whether the buffer behaves like an efficient semi-permeable membrane at high dry densities, and 2) whether the microstructure of the buffer needs to be taken into account.

3. Colloid transport. The treatment of buffer erosion in SR-Can does not account for factors controlling the transport of clay colloids, should they form. These factors are being considered in SKB's current research program, however (Section 4). Filtering of colloids in fractures and in filter cakes composed of non-colloidal accessory minerals in a partially eroded buffer could potentially retain the colloidal particles in the buffer, or reduce groundwater flow rates in the vicinity of deposition holes. SKB is developing a force-balance modeling approach to help evaluate these phenomena.

4. *Hydrogeology and hydrochemistry of glacial meltwaters*. As pointed out by Neretnieks (2007b), there is uncertainty regarding the time during which glacial meltwaters might circulate to repository depths. Associated flow rates and chemical compositions are also uncertain. It seems reasonable to expect, however, that credible bounding estimates of these parameters can be obtained using observations from analogous natural systems and hydrogeological and geochemical reasoning.

A question of some concern given the complex nature of the uncertainties noted above is whether they can be satisfactorily resolved given realistic time constraints on SKB's R&D program (*e.g.*, can key uncertainties be adequately resolved by the time a license application is submitted with SR-Site for repository construction). It is therefore recommended that SKI should continue to closely monitor SKB's progress toward resolving this potential issue over the coming months and, possibly, years.

6. References

Adamson, A. W. 1967. *Physical chemistry of surfaces, 2nd ed.* Interscience Publ., John Wiley & Sons, New York.

Arthur, R. and Zhou, W. 2005. Reactive-transport model of buffer cementation. SKI Report 2005:59, Swedish Nuclear Power Inspectorate, Stockholm, Sweden.

Arthur, R., Zhou, W., Xu, T., Pruess, K. and Strömberg, B. 2006. Experimental calibration of a reactive-transport model of buffer cementation. *Chinese Journal of Rock Mechanics and Engineering*, 25 (4), 741-749.

Birgersson, M. 2007. Untitled presentation. Presented at the Workshop on Buffer Erosion (IV), June 13, 2007, Stockholm, Sweden.

Börgesson, L. and Hernelind, J. 2006. Consequences of loss or missing bentonite in a deposition hole: A theoretical study. SKB TR-06-13, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Börgesson, L. and Sandén, T. 2006. Piping and erosion in buffer and backfill materials: Current knowledge. SKB R-06-80, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Bradbury, M. H. and Baeyens, B. 2002. Porewater chemistry in compacted re-saturated MX-80 bentonite: Physico-chemical characterization and geochemical modelling. PSI Bericht Nr. 02-10, Paul Scherrer Institut, Villigen, Switzerland.

Bruno, J., Arcos, D. and Duro, L. 1999. Processes and features affecting the near field hydrochemistry. SKB TR-99-29, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Comsol. 2004. Femlab user's guide, version 3.1. The Comsol Co., Stockholm, Sweden.

Dixon, D. A. 2000. Porewater salinity and the development of swelling pressure in bentonite-based buffer and backfill materials. Posiva Report 2000-04, Posiva Oy, Helsinki, Finland

Grim, R. E. 1968. *Clay mineralogy*. McGraw-Hill, New York.

Jansson, M. 2007. Experimental evidence of colloid release into fresh water. Presented at the Workshop on Buffer Erosion (IV), June 13, 2007, Stockholm, Sweden.

Jönsson, B., Jönsson, B. and Åkesson, T. 2007. Salt effect on bentonite swelling. Presented at the Workshop on Buffer Erosion (IV), June 13, 2007, Stockholm, Sweden.

Karnland, O. 1997. Bentonite swelling pressure in strong NaCl solutions. Correlation between model calculation and experimentally determined data. SKB TR 97-31, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Karnland, O., Muurinen, A. and Karlsson, F. 2002. Bentonite swelling pressure in NaCl solutions - experimentally determined data and model calculations. In: *Symposium on large-scale field tests in granite*, Sitges, Spain.

Karnland, O. 2007. Colloid workshop IV. Presented at the Workshop on Buffer Erosion (IV), June 13, 2007, Stockholm, Sweden.

Kia, S. F., Fogler, H. S. and Reed, M. G. 1987. Effect of pH on colloidally induced fines migration. *J. Colloid Interface Sci.*, 118 (1), 158-168.

Langmuir, D. 1997. *Aqueous environmental geochemistry*. Prentice-Hall, Upper Saddle River, New Jersey.

Leroy, P., Revil, A., Altmann, S. and Tournassat, C. 2007. Modeling the composition of the pore water in a clay-rock geological formation (Callovo-Oxfordian, France). *Geochim., Cosmochim. Acta*, 71, 1087-1097.

Liu, J and Neretnieks, I. 2006. Physical and chemical stability of the bentonite buffer. SKB R-06-103, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Muurinen, A. and Lehikoinen, J. 1999. Porewater chemistry in compacted bentonite. Posiva 99-20, Posiva Oy, Helsinki, Finland.

Missana, T. and Adell, A. 2000. On the applicability of DLVO theory to the prediction of clay colloids stability. *J. Colloid Interface Sci.*, 230 (1), 150-156.

Muurinen, A., Karnland, O. and Lehikoinen, J. 2004. Ion concentration caused by an external solution into the porewater of compacted bentonite. *Physics and Chemistry of the Earth*, 29, 119-127.

Neretnieks, I. 2007a. Release of bentonite colloids into freshwater: Present ideas. Presented at the Workshop on Buffer Erosion (IV), June 13, 2007, Stockholm, Sweden.

Neretnieks, I. 2007b. Overview of experiments, modeling and other work underway and planned within the erosion project. Presented at the Workshop on Buffer Erosion (IV), June 13, 2007, Stockholm, Sweden.

Overbeek, J. T. G. 1952a. The interaction between colloidal particles. In. *Colloid science* (H. R. Kruyt, ed.), Elsevier, Amsterdam, the Netherlands, 245-277.

Overbeek, J. T. G. 1952b. Phenomenology of lyophobic systems. In. *Colloid science* (H. R. Kruyt, ed.), Elsevier, Amsterdam, the Netherlands, 58-89.

Overbeek, J. T. G. 1952c. Electrochemistry of the double layer. In. *Colloid science* (H. R. Kruyt, ed.), Elsevier, Amsterdam, the Netherlands, 115-193.

Pearson, F. J., Arcos, D., Bath, A., Boisson, J. Y., Fernández, A. M., Gäbler, H. E., Gaucher, E., Gautschi, A., Griffault, L., Hernán, P. and Waber, H. N. 2003. Mont

Terri Project - geochemistry of water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory. Reports of the Federal Office for Water and Geology (FOWG), Geology Series No. 5.

Pusch, R. 2007. Colloid release and migration. Presented at the Workshop on Buffer Erosion (IV), June 13, 2007, Stockholm, Sweden.

Stilbs, P., Dvinskikh, S. and Furó, I. 2007. Magnetic resonance imaging and localized spectroscopy of natural bentonite swelling in water. Presented at the Workshop on Buffer Erosion (IV), June 13, 2007, Stockholm, Sweden.

SKB 2004. Interim process report for the safety assessment SR-Can. SKB R-04-033, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

SKB 2006a. Long-term safety for KBS-3 repositories at Forsmark and Laxemar - a first evaluation: Main report of the SR-Can project. SKB TR-06-09, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

SKB 2006b. Buffer and backfill process report for the safety assessment SR-Can. SKB TR-06-18, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Sposito, G. 1984. *The surface chemistry of soils*. Oxford University Press, New York, NY.

Stumm, W. and Morgan, J. J. 1996. *Aquatic chemistry, 3rd ed.* Wiley Interscience, John Wiley & Sons, New York.

van Olphen, J. H. 1977. An introduction to clay colloid chemistry, 2nd ed., Wiley-Interscience, New York.

Verwey, E. J. W. and Overbeek, J. T. G. 1948. *Theory of the stability of lyophobic colloids*. Elsevier, Amsterdam, the Netherlands.

Wanner, H., Wersin, P. and Sierro, N. 1992. Thermodynamic modeling of bentonite-groundwater interaction and implications for near field chemistry in a repository for spent fuel. SKB TR 92-37, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Wieland, E., Wanner, H., Albinsson, Y, Wersin, P. and Karnland, O. 1994. A surface chemical model of the bentonite-water interface and its implications for modeling the near field chemistry in a repository for spent fuel. SKB TR 94-26, Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Xu, T. and Pruess, K. 2001. Modeling multiphase non-isothermal fluid flow and reactive geochemical transport in variably saturated fractured rocks: 1. Methodology. *Am. J. Sci.*, 301, 16-33.

Xu, T., Sonnenthal, E., Spycher, N. and Pruess, K. 2004. TOUGHREACT user's guide: A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media. LBNL-55460. Lawrence Berkeley National Laboratory, Berkeley, CA.

Appendix: Reactive-transport model of buffer erosion

A1 Introduction

This appendix describes a preliminary modeling study that was carried out using the TOUGHREACT reactive-transport simulator (Xu and Pruess, 2001; Xu *et al.,* 2004) to estimate the erosion rate of the buffer in a KBS-3 repository for spent nuclear fuel. The objective of the study is to determine whether reactive-transport models of buffer erosion can be used to help build confidence in the accuracy of estimated erosion rates, and to gain insights into key factors and processes controlling these rates.

A2 Model description

TOUGHREACT was used to simulate reactive-transport processes that are compatible with SKB's mass-balance conceptual model described in Section 3. TOUGHREACT is a simulation program for non-isothermal, multiphase reactive transport in variably saturated porous media. It is applicable to one-, two- or three-dimensional problems, and can accommodate temperatures from 0 to 300°C, pressures from 0.1 MPa to several tens of MPa, liquid saturations between 0 and 1, and ionic strengths to 2 molal. The program uses a sequential iteration approach and implicit time-weighting scheme to solve the governing mass-transport equations independently for each chemical component, followed by Newton-Raphson iteration to solve the reaction equations. Arthur and Zhou (2005) (see also Arthur *et al.*, 2006) describe a similar modeling study in which TOUGHREACT was used to simulate reactive-transport processes in the KBS-3 buffer during the early thermal period of repository evolution.

Figure A2_1 illustrates how the conceptual model of buffer erosion (Figure 3.2_1) is implemented in TOUGHREACT. The simulation considers three model domains: 1) bentonite in the deposition hole, 2) bentonite in the fracture, and 3) groundwater in the fracture. The fracture bentonite is partitioned into 50 grid blocks. Each block is 0.02 m long (*i.e.*, along the *x* axis), 2.75m wide (equivalent to one-half the circumference of the deposition hole) and 0.001 m high. The deposition-hole domain consists of a single grid block containing 12.25 m^3 of bentonite, which is the volume of bentonite called for in the KBS-3V design (*e.g.*, SKB 2006a). The groundwater domain also consists of a single grid block, and contains an essentially infinite volume of groundwater. This volumetric constraint imposes a constant-concentration boundary condition at the buffer-groundwater interface, and is used to approximate the effects of rapid groundwater flow relative to diffusional mass transport across this boundary. The dimensions of the grid blocks shown in Figure A2_1 are adjustable parameters in TOUGHREACT and can be described in terms of radial as well as cartesian coordinates.

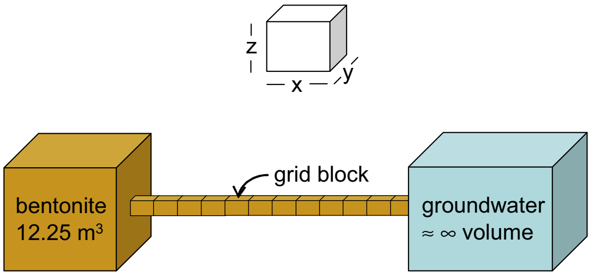


Figure A2_1. Representation of the buffer-erosion model in TOUGHREACT.

Table A2_1 lists initial and boundary conditions considered in the simulations. As a first approximation the properties of bentonite are assumed to be the same in the deposition hole and fracture. This simplifying assumption is probably unrealistic because density and related properties, such as swelling pressure, porosity and permeability, are likely to vary with distance along the fracture (SKB 2004). This possibility could be addressed in future revisions of the modeling approach.

The selected bentonite properties in Table A2._1 are consistent with values recommended by SKB (*e.g.*, SKB 2004; Bruno *et al.*, 1999). Tortuosity is an adjustable parameter in the model, and is assumed to have unit value as a first approximation. A fracture porosity of 99% is used to represent an essentially open fracture containing few fracture-filling minerals.

Bentonite is assumed to consist mainly of smectite clays having a cation exchange capacity of 85 meq $100g^{-1}$ (Bruno *et al.*, 1999). Ion-exchange constants based on the Vanselow convention at 25°C from Wanner *et al.* (1992) and Wieland *et al.* (1994) are adopted in the model. Calcite is also assumed to be present with a concentration of 1 vol.% (of solids). The porewater in bentonite (Table A2_1) is represented by a 0.1 M NaCl solution that is initially equilibrated with calcite. The near-neutral pH of this solution is constrained by charge balance. The total analytical concentration of Ca^{2+} in the equilibrated porewater is well above the CCC value of 1 mmol l^{-1}. Fracture groundwater is represented by a pH-neutral, 0.01 M NaCl solution containing 10^{-7} M Ca^{2+}. A thermodynamic database (therm208.dat) supporting

Table A2_1. Initial/boundary conditions.

Property	Value	
	Bentonite[1]	Open fracture
Temperature (°C)	15	15
Hydrostatic pressure (MPa)	5.0	5.0
Density (kg m^{-3})	2000	1000
Porosity (%)	41	99
Permeability (m^2)	1.0e-22	1.0e-16
Diffusion coeff. (m^2 sec^{-1})	1.0e-9	1.0e-9
Tortuosity	1	1
Water chemistry[2]		
pH	6.7	7
Na^+	1.0e-1	1.0e-2
Ca^{2+}	1.055e-2	1.0e-7
Mg^{2+}	1.0e-7	1.0e-7
HCO_3^-	1.055e-2	1.0e-7
Cl^-	1.0e-1	1.0e-2

[1] - in both the deposition hole and fracture.
[2] - total analytical concentration (M) for dissolved solutes other than H^+.

the TOUGHREACT simulator was used for all geochemical calculations in the present study (see Xu *et al.*, 2004 for a description of therm208.dat).

The initial differences in water chemistry on either side of the bentonite-groundwater boundary (Table A2_1 and Figure 3.2_1) set up the following transport and reaction processes:

1. Ca^{2+} diffuses across the boundary from bentonite to groundwater;

2. The resultant decrease in Ca^{2+} concentration stimulates calcite dissolution,

   $CaCO_3(s) + H^+ = Ca^{2+} + HCO_3^-$; and

3. The increase in Ca^{2+} concentration caused by calcite dissolution stimulates diffusion and ion-exchange of Ca^{2+} for Na^+, Mg^{2+} and H^+;

   $Ca^{2+} + 2NaX = CaX_2 + 2Na^+$
   $Ca^{2+} + MgX_2 = CaX_2 + Mg^{2+}$
   $Ca^{2+} + 2HX = CaX_2 + 2H^+$

These reactions, plus the effects on aqueous speciation of variations in pH and M_{HCO3-}, all affect the concentration of Ca^{2+}. The objective of the TOUGHREACT simulations is to track these temporal and spatial changes in Ca^{2+} concentration relative to the CCC for this ion. It is assumed in cases where M_{Ca2+} falls below the CCC after a given period of time, that the bentonite gel disperses as a colloidal suspension and is transported away from the fracture in flowing groundwater.

It is worthwhile emphasizing that the reactive-transport model considered here addresses several of the limitations in SKB's mass-balance approach discussed in Section 3.2. The model accounts for diffusion resistance in both the deposition hole and fracture, equilibrium (or kinetic) constraints on calcite dissolution, changes in the composition of the diffuse double layer resulting from ion exchange and the effects of aqueous speciation on Ca^{2+} concentrations. At this preliminary stage of model development we have assumed that the flow rate of groundwater in fractures is fast enough to maintain a constant concentration boundary condition at the gel-groundwater interface. Explicit coupling between the rate of groundwater flow and mass-transport across this interface could be implemented in future revisions of the model.

It should also be noted, however, that the model presently does not account for the likely dynamic nature of the bentonite-groundwater interface. Loss of bentonite at this interface by dispersion of the bentonite gel into a colloidal suspension and transport in groundwater will perturb the steady-state balance between swelling-pressure and frictional forces that control the extent to which bentonite extrudes into the fracture. Thus, as bentonite is lost by dispersion, more bentonite should enter the fracture from the deposition hole in an effort to restore the steady state. The resultant mass loss will cause the density of bentonite in the fracture and deposition hole to decrease continuously with time. It may be possible to model the dynamic nature of this interface in future revisions of the present model by treating bentonite as a viscous fluid.

A3 Discussion of results

A3.1 Diffusive transport

We first consider the effects of diffusion on Ca^{2+} molarity in the absence of any heterogeneous reactions. This is accomplished by setting both the initial concentration of calcite and ion-exchange capacity to zero. Results are shown in Figure A3.1_1, where the molarity of free Ca^{2+} is plotted as a function of distance along the fracture's *x* axis from the buffer-rock boundary. Recall that bentonite is assumed to initially extrude 1 m into the fracture (Figure 3.2_1). The molarity of Ca^{2+} at the point labeled "0" on the *x* axis in Figure A3.1_1 thus refers to the entire volume of bentonite in the deposition hole. As can be seen, Ca^{2+} concentrations fall below the CCC within a few centimeters of the bentonite-groundwater boundary during the first 10^5 years. At 10^6 years these concentrations are below the CCC throughout the fracture and deposition hole.

These preliminary results can be considered from a safety-relevance perspective. First we note that advective conditions in the buffer could be generated if as little as 1200 kg of bentonite is lost from the deposition hole (SKB, 2006a). Such conditions are potentially deleterious to repository safety because the transport of corrodants to the copper canister would then not be limited by diffusion. We also note that relatively rapid flow of dilute glacial meltwaters to repository depth may occur over a period of about 10,000 years in one glacial cycle (Neretnieks, 2007b). Now, if it is assumed that bentonite is dispersed as a sol and transported away in groundwater as soon as M_{Ca2+} drops below the CCC, then the results in Figure A3.1_1 can be used to calculate an average erosion rate. For example, these results indicate that M_{Ca2+} falls below the CCC within about 0.02m of the bentonite-groundwater interface after 1 year. Taking into account the width and height of the model grid blocks (Section A2), this translates into a volumetric erosion rate of 5.5×10^{-5} m^3 yr^{-1}, or an equivalent mass erosion rate of 0.11 kg yr^{-1} (assuming a bentonite density of 2000 kg m^{-3}; Table A2_1)[7]. This suggests that 1200 kg of bentonite could be lost from the deposition hole within about 11,000 years, which is comparable to the period of time that the buffer will be exposed to dilute glacial meltwaters during the first glacial cycle after repository closure.

The results in Figure A3.1_1 may be pessimistic in the sense that unit tortuosity is assumed in the transport model. Figure A3.1_2 illustrates the extent to which buffer erosion would change if tortuosity were increased by a factor of 10 compared to this nominal case. As can be seen, the results suggest that the buffer would remain essentially intact for at least 10^6 years. More generally, this indicates that model results may be quite sensitive to certain parameters governing solute transport, and that a more thorough sensitivity analysis is needed to identify these parameters and associated effects of uncertainties in parameter values on transport behavior.

---

[7] This mass erosion rate is comparable to that predicted by SKB using the mass-balance approach for the case, as assumed here, of no calcite initially present in bentonite (0.4 kg yr^{-1}; see Section 3.3).

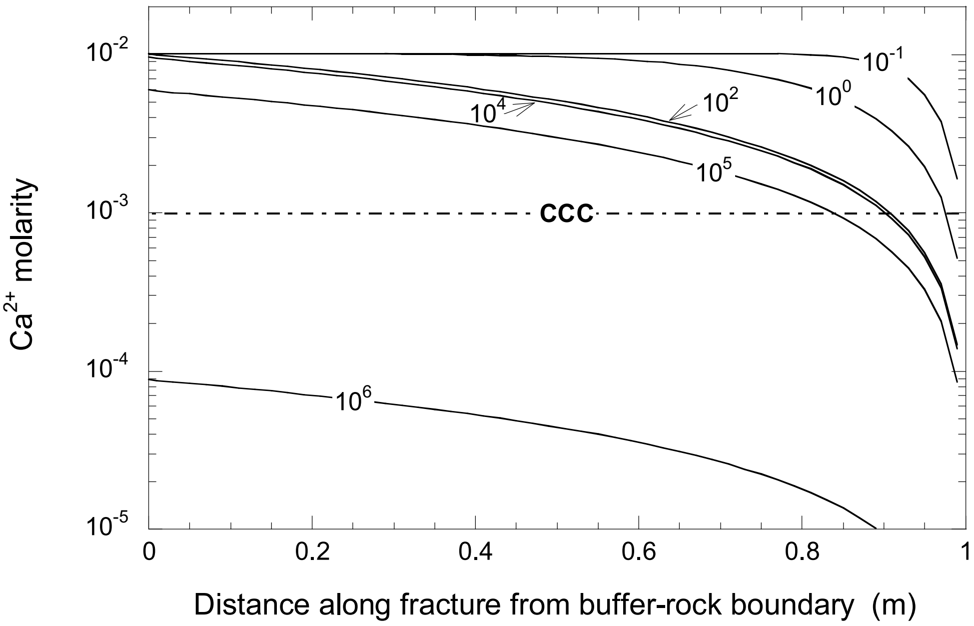


Figure A3.1_1. TOUGHREACT simulation results showing spatial variations in M_{Ca2+} as a function of time. The bentonite-groundwater interface in the fracture (see Figure 3.2_1) is located 1 m from the buffer-rock boundary. Calcite dissolution and ion-exchange reactions are not considered in the simulation. Labels on curves refer to time in years. CCC stands for the critical coagulation concentration.

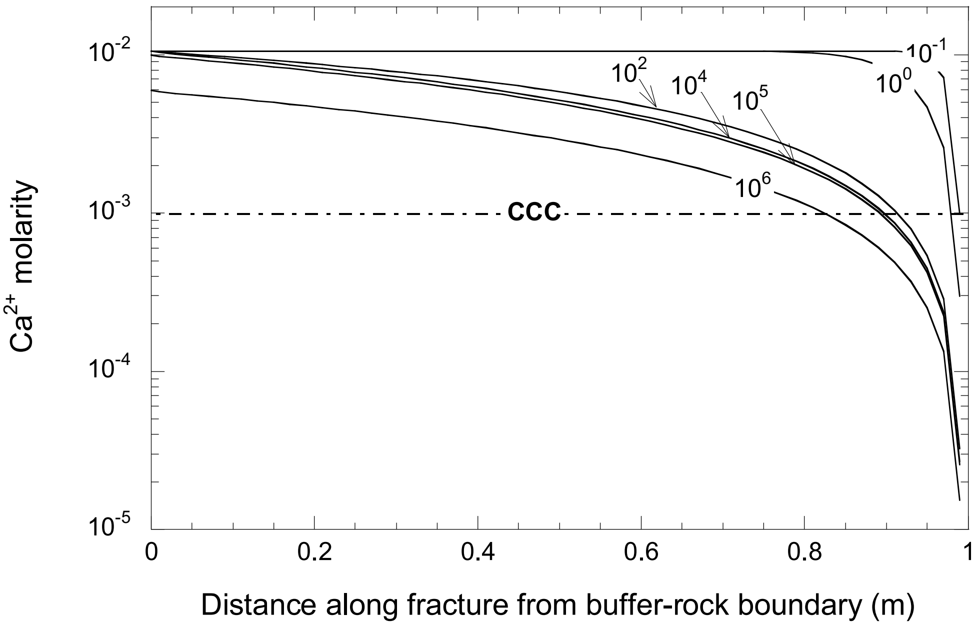


Figure A3.1_2. TOUGHREACT simulation results assuming a 10-fold increase in tortuosity compared to the nominal case (Figure A.3.1_1).

A3.2 Reactive transport

Figure A3.2_1 is the reactive-transport counterpart of Figure A3.1_1, and includes the effects of heterogeneous reactions involving calcite dissolution and ion exchange. Associated variations in calcite abundance and pH are shown in Figures A3.2_2 and A3.2_3, respectively. An example of how the concentrations of exchangeable Ca^{2+} and Na^{+} vary with distance in the fracture is shown in Figure A3.2_4 for an elapsed time of 10^{5} years.

A comparison of Figures A3.2_1 and A3.1_1 indicates that calcite dissolution and ion-exchange produce relatively minor changes in the spatial and temporal distribution of Ca^{2+} in the fracture and deposition hole compared to the case involving only simple diffusion. Calcite dissolution (see Figure A3.2_2) releases Ca^{2+} to solution, but this is partially compensated by ion-exchange of Ca^{2+} for Na^{+}, Mg^{2+} and H^{+} (*e.g.*, Figure A3.2_4), and by formation of $CaHCO_3^{+}$ and $CaCO_3$(*aq*) at the expense of Ca^{2+} as a result of the associated increases in pH (Figure A3.2_3) and dissolved carbonate concentrations. The cumulative effects of these heterogeneous and homogeneous reactions is generally to decrease M_{Ca2+} at a given time compared to the diffusion-only case (*e.g.*, Figure A3.2_5), but these changes are relatively small.

Like its diffusion-only counterpart, the reactive-transport model predicts that Ca^{2+} concentrations in bentonite porewaters in both the fracture and deposition hole would drop below the CCC between 10^{5} and 10^{6} years. Following the safety-relevance argument discussed in Section A3.1, the estimated erosion rate determined for the reactive-transport results shown in Figure A3.2_1 is about 0.05 m yr^{-1}, which suggests that advective conditions could be generated in the buffer within about 4300 years.

SKB's prediction that the presence of small amounts of calcite in the buffer would significantly lower the erosion rate (Section 3.3) is incompatible with the results discussed above. SKB assumes that all of the calcite initially present dissolves completely, and this strongly increases the amount of dissolved Ca^{2+} initially present in bentonite porewaters. In comparison, the TOUGHREACT model is based on the more realistic assumption that calcite equilibrates with these porewaters, and will only dissolve (or precipitate) to an extent determined by the evolving porewater composition and temperature. As can be seen in Figure A3.2_2, the amount of calcite that dissolves in the TOUGHREACT simulations is actually quite limited. For example, about half the calcite initially present remains in the most extensively altered region near the bentonite-groundwater interface after 10^{6} years. This suggests that the minimum erosion rate predicted by SKB using the mass-balance approach is overly optimistic.

A4 Conclusions and recommendations

TOUGHREACT can be used to model reactive-transport processes that may play a role in controlling buffer erosion. The modeling approach developed to date addresses many of the conceptual deficiencies in SKB's mass-balance model of buffer erosion. Preliminary results suggest that erosion rates would lie within the range estimated by SKB, but nearer the high end. If the simple criterion is adopted that bentonite gel would be dispersed and carried away in colloidal suspension by flowing groundwater when $M_{Ca2+} <$ CCC, then model results

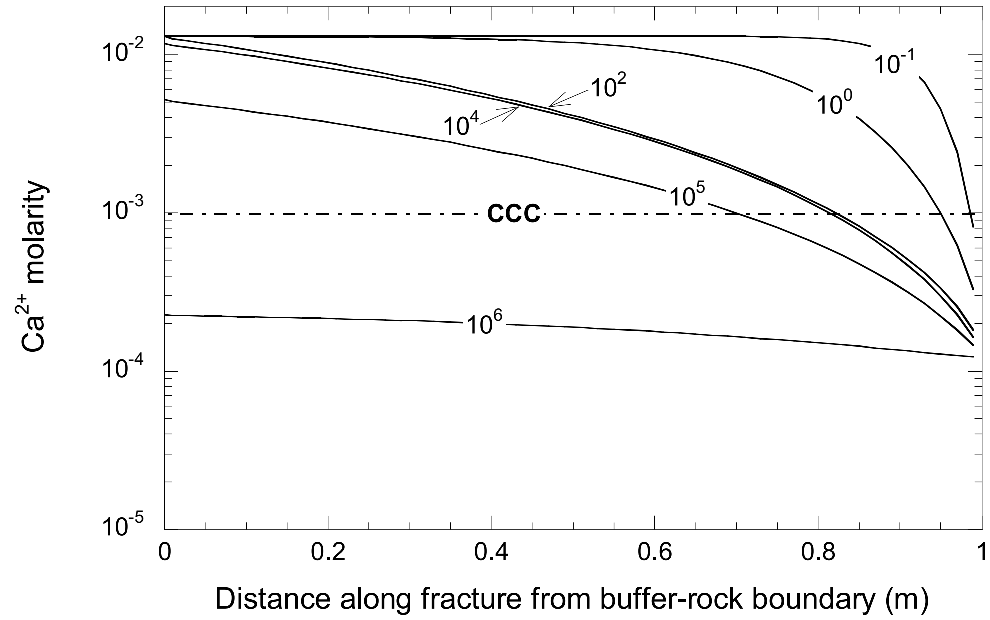


Figure A3.2_1 TOUGHREACT simulation results for the reactive-transport model including calcite dissolution and ion-exchange. Labels on curves refer to time in years.

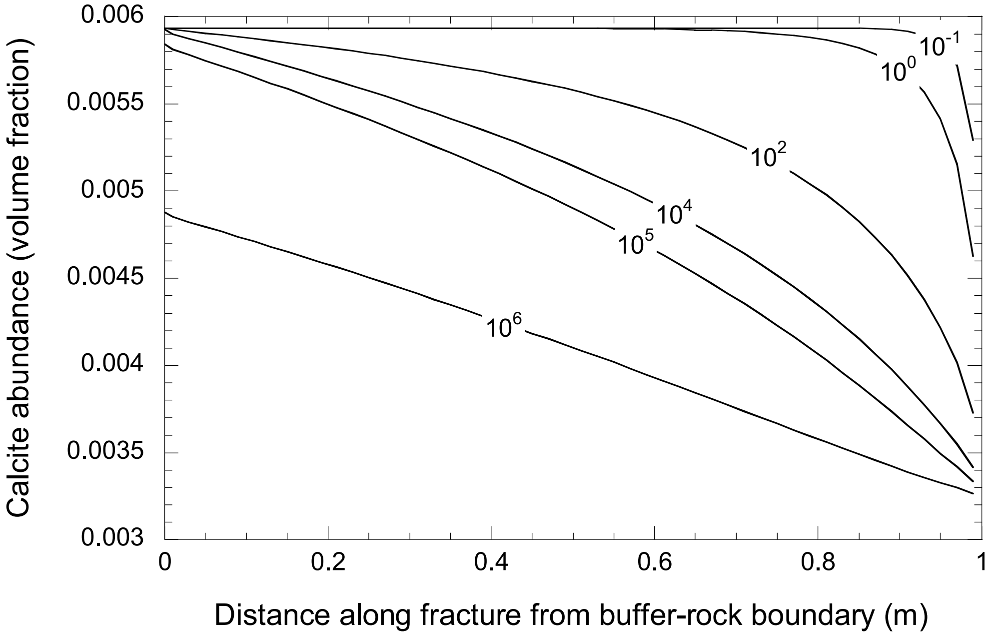


Figure A3.2_2 Spatial and temporal variations in calcite abundance. Labels on curves refer to time in years.

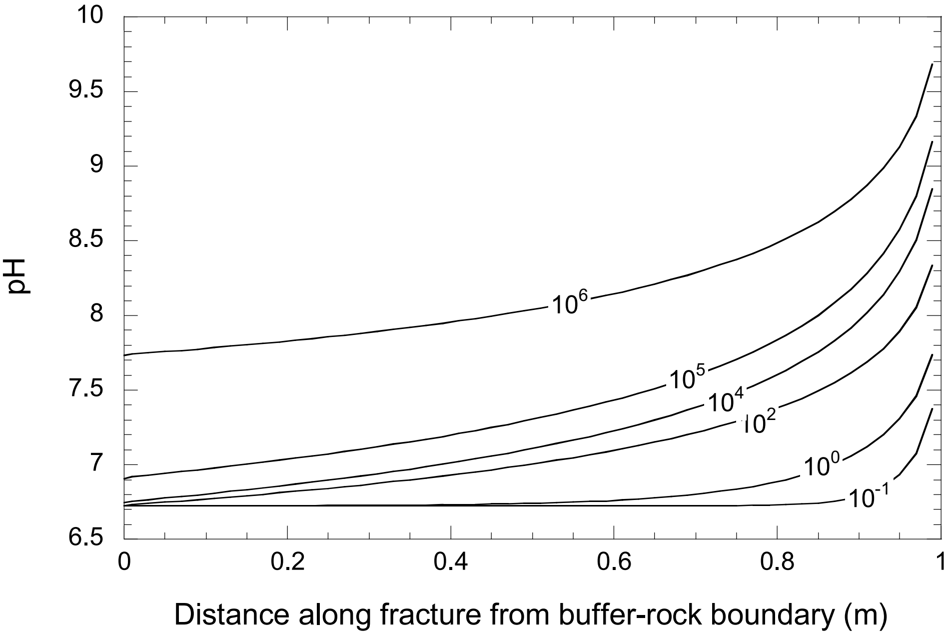


Figure A3.2_3 Spatial and temporal variations in pH. Labels on curves refer to time in years.

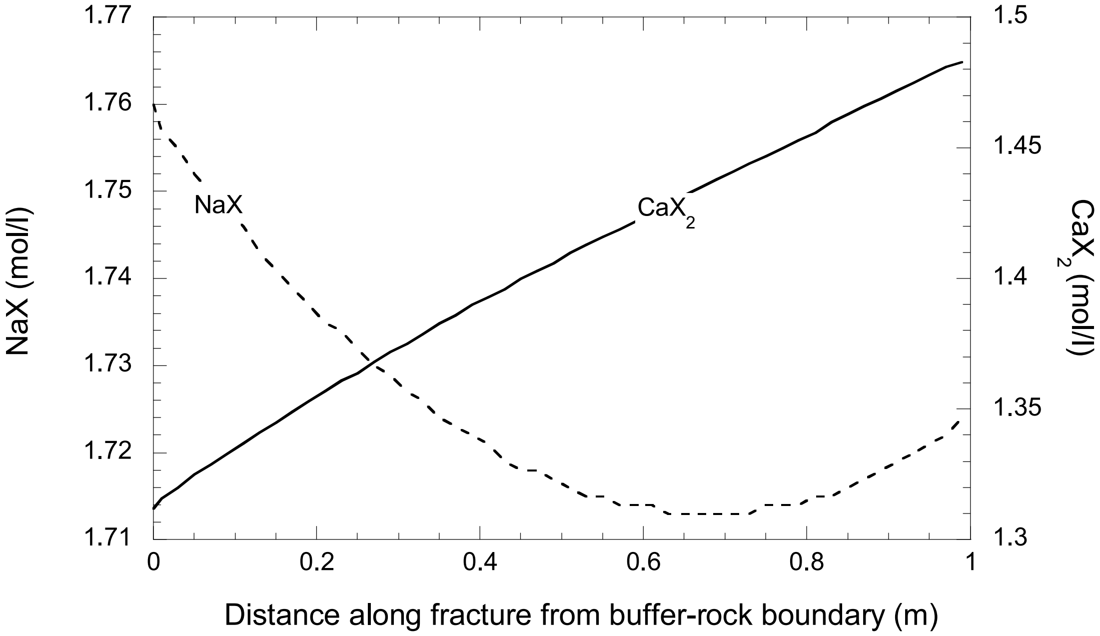


Figure A3.2_4. Spatial variations in the concentrations of exchangeable NaX and CaX_2 after 100,000 years.

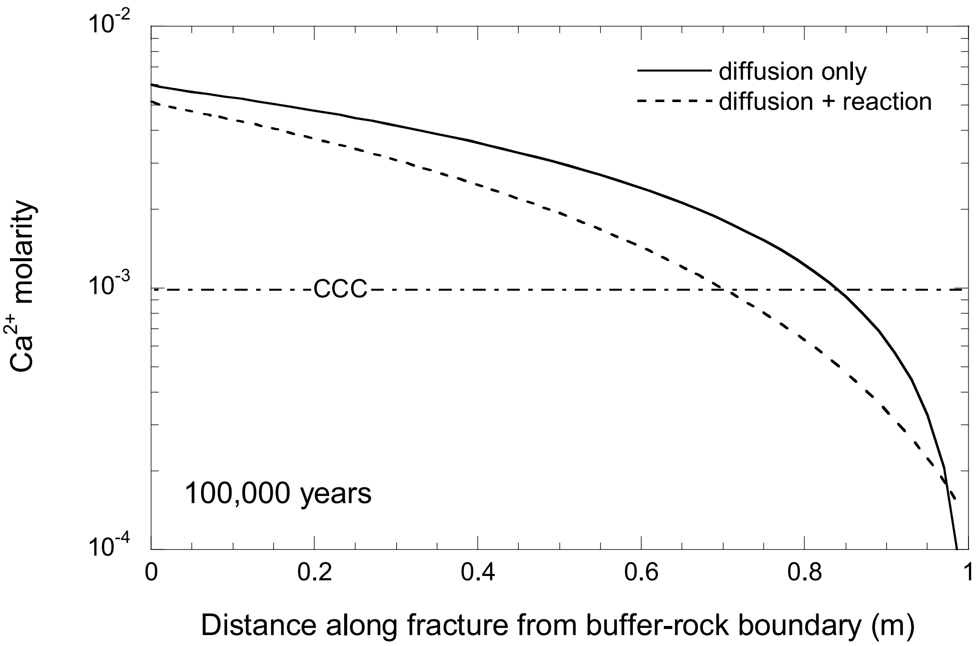


Figure A3.2_5. Comparison of the effects of diffusive versus reactive transport on M_{Ca2+} *at 100,000 years.*

suggest that advective conditions could be generated in the buffer when dilute meltwaters are expected to flow relatively quickly to repository depth during a glacial cycle. The implications of this result for repository safety are generally negative because the canister would no longer be protected by the buffer when this occurs.

A number of improvements to the current version of the reactive-transport model of buffer erosion are recommended:

1. A better conceptual understanding is needed in general of environmental factors that control the stability of clay solids/gels in compacted buffer materials. The CCC concept is a useful first approximation, but it does not fully account for ionic-strength and specific-adsorption effects on double-layer properties. A better understanding of these properties could potentially be used to relate threshold inter-particle separation distances for colloid stability to environmental factors such as groundwater composition and temperature.
2. Our preliminary results suggest that the large mass of bentonite porewater in the deposition hole constitutes a robust barrier against changes in solute concentrations induced by diffusive mass transport across the buffer-groundwater interface. Representing the deposition hole as a single grid block in the model may be overly simplistic, however, and additional work is therefore recommended to better represent diffusive mass transport both within the deposition hole and across the deposition-hole - fracture interface. This work should consider how multiple fractures can be represented in the model, and should also develop a more realistic representation of fracture geometry.
3. Two modeling improvements related to the bentonite-groundwater interface are recommended.
    a. A constant-concentration boundary condition is presently assumed at the buffer-groundwater interface to approximate the effects of rapid

groundwater flow (as a limiting condition) relative to diffusive mass transport across this boundary. It is recommended that the rate of groundwater flow and diffusive mass transport be explicitly coupled in future versions of the model.

   b. The position of the bentonite-groundwater interface is fixed in the current model, but this position will in reality be controlled by a steady-state balance between swelling pressure (and thus density) and frictional forces. It is recommended that the dynamic nature of this interface be considered in future revisions of the model, possibly by modeling the flow behavior of bentonite as an extremely viscous fluid.

4. The reactive-transport model at present is based on the assumption that the CCC for Ca^{2+} controls colloid stability. For this reason the heterogeneous reactions considered to date have been limited to ion-exchange and calcite dissolution. A more realistic model of colloid stability (item 1 above) may, however, indicate that other chemical parameters (*e.g.*, pH, presence of trace amounts of gypsum/anhydrite) are important contributors to colloid behavior, and, if so, the model should be extended to consider other heterogeneous and homogeneous reactions involving associated aqueous components.
5. Preliminary results suggest that small changes in certain transport parameters, notably tortuosity, can strongly affect estimated erosion rates. It is recommended that all such parameters be more thoroughly reviewed to better constrain estimates of nominal values and associated uncertainties. This work should be backed up with sensitivity analyses to quantitatively estimate impacts on predicted erosion rates.

4

Audit of data and code use in the SR-Can safety assessment

T.W. Hicks
T.D. Baldwin

Galson Sciences Ltd
5 Grosvenor House
Melton Road, Oakham
Rutland LE15 6AX
UK

Executive Summary

SKB produced the SR-Can safety assessment in preparation for the development of the SR-Site assessment that will be part of SKB's application for a final repository. SR-Can provides an opportunity for review and comment on SKB's safety assessment approach prior to the compilation of SR-Site. Building on the findings of previous studies on data and code quality assurance (QA) in safety assessments, this report provides a review of data and code QA in the SR-Can safety assessment.

The data quality audit aimed to check that the selection and use of data in the SR-Can safety assessment was appropriate, focusing on the data that underpin representations of and assumptions about canister, insert, buffer, and backfill behaviour. The SR-Can Data Report provided the initial focus for examining the traceability and reliability of data used in the safety assessment; the Data Report is one of the series of SR-Can safety assessment reports and, in this review, it was anticipated that it would provide the primary source of data on the canister, insert, buffer, and backfill. However, other safety assessment reports (the SR-Can Main Report, the Initial State Report, the Fuel and Canister Process Report, and the Buffer and Backfill Process Report) were found to provide key information on data used in the safety assessment.

The quality audit of codes aimed to check that code use in the SR-Can safety assessment has been justified through a transparent and traceable process of code development and selection. The Model Summary Report provided the focus for reviewing the QA status of the codes used in the safety assessment.

As well as highlighting a number of concerns regarding QA aspects of specific data sets, parameter values, and codes used in the SR-Can safety assessment (which are presented in the report), the review has led to several general observations on data and code QA that should be considered by SKB in the development and implementation of a QA system for the SR-Site safety assessment:

- The SR-Site safety assessment and associated QA records should include information that demonstrates that a full QA system has been implemented in order to build confidence in the validity of the assessment.

- The data and parameter values used directly in the safety assessment should be obtained from controlled sources or suitable external references such as textbooks or peer-reviewed journals. Information should be provided on how data are managed and controlled such that the data are selected and used appropriately in safety assessment calculations. Procedures for ensuring that controlled and quality assured data and parameter values are obtained for use in the safety assessment should be explained.

- Comprehensive references to controlled data sources and documentation on data abstraction to derive parameter values for all data sets should be included in the Data Report. The Data Report should become the primary reference for data and parameter values used in the safety assessment to build confidence that data and

parameter values are used consistently and traceably throughout the safety assessment.

- Information on the review criteria or procedures used by SKB to determine whether a particular data set is acceptable for use in the safety assessment should be provided. Procedures for accepting data for use in the safety assessment should include a check that the data qualification process has been documented, and confirmation that data were acquired under appropriate quality assurance procedures or that suitable data qualification methods have been applied (such as confirmation testing, peer review, or independent technical assessment).

- To build confidence in SKB's process of review and approval of safety assessment reports, information should be provided on the method of selection of reviewers, the review criteria, the process of comment resolution, and the availability of review records.

- The role of each code used in the safety assessment should be explained in the Model Summary Report, with cross-references to where associated features, events, and processes, input data, and code applications are presented, and to where results are used in the safety assessment documentation, possibly through greater use of the Assessment Model Flowcharts (AMFs). Traceability of information on code usage in the safety assessment could be improved by including information on the original requirement for each code in SKB's repository research programme and the rationale for the approach to developing or selecting the code (in-house or commercial).

- Confidence in code reliability could be improved by providing information on procedures for checking and reviewing code applications in the safety assessment and review records.

- The demonstration that software QA procedures have been applied appropriately in the safety assessment project should be comprehensive, covering all codes used in supporting analyses that have important impacts on decision-making for the safety assessment. Such analyses could be identified through entries in the AMFs, such as derivation of input data or intermediate assessments of data and results.

Table of contents

1. Introduction

SKB produced the SR-Can safety assessment in preparation for the development of the SR-Site assessment that will be part of SKB's application for a final repository. SR-Can provides an opportunity for review and comment on SKB's safety assessment approach prior to the compilation of SR-Site. SKI is in the process of reviewing the SR-Can safety report.

SR-Can is based on a safety assessment for the underground disposal of spent fuel in Sweden according to the KBS-3 repository concept. The assessment involves quantitative analyses aimed at presenting an understanding of how the repository system will evolve and an evaluation of the potential risks of spent fuel disposal. Such a safety assessment must be underpinned by assurances that the development and application of models and work to estimate parameter values and uncertainties have been undertaken under appropriate quality management systems.

SKI previously commissioned Galson Sciences Ltd (GSL) to undertake a series of review tasks in order to understand SKB's approach to quality assurance (QA) and the application of QA procedures in SKB's work. Initially, a review of the documentation and testing of a selection of the computer codes used by SKB in its repository research programme was undertaken (Hicks, 2005). Subsequently studies were undertaken to compare SKB's approach to QA with QA programmes used in similar radioactive waste management projects, and to perform a quality review of a selection of experiments on engineered barrier performance undertaken as part of SKB's repository research programme (Hicks, 2007).

Building on the findings of the previous studies, this report provides a review of how data and code quality assurance have been addressed and reported in the SR-Can safety assessment.

1.1. Approach

The review of the application of quality assurance in the SR-Can safety report involves quality audits of the data and codes used in the safety assessment. The data quality audit has aimed to check that the selection and use of data in the SR-Can safety assessment is reasonable. The audit has focused on review of the data that underpin representations of and assumptions about canister, insert, buffer, and backfill behaviour as described in the SR-Can Main Report (SKB 2006a), the Initial State Report (SKB, 2006b), the Data Report (SKB, 2006c), the Fuel and Canister Process Report (SKB, 2006d), and the Buffer and Backfill Process Report (SKB, 2006e); these reports form part of the series of SR-Can safety assessment reports.

The second part of the study has involved a quality audit of a selection of codes used in the SR-Can safety assessment and has focused on review of the Model Summary Report (SKB, 2006f) (also a report in the SR-Can safety assessment series). The objective of the codes quality audit has been to check that code use in the SR-Can safety assessment is justified through a transparent and traceable process of code development and selection. The codes audit has included checks that appropriate user guides and verification and validation studies have been produced, and that software configuration has been suitably managed (i.e., through version control and documentation of code changes).

1.2. Report Structure

Section 2 briefly discusses the QA framework for the SR-Can safety assessment as presented in the SR-Can documentation. Section 3 discusses the findings of the quality audit of data and Section 4 discusses the quality audit of codes. Conclusions are presented in Section 5.

2. Quality Assurance for the SR-Can Project

Safety assessments conducted as part of SKB's repository research programme are subject to SKB's project management process (as reviewed by Hicks, 2007). The SR-Can Main Report (SKB 2006a, Section 2.8) briefly outlines the QA system in place for the SR-Can safety assessment project.

SKB has applied a management system that fulfils the requirements of ISO 9001:2000 and that has been certified by DNV Certification AB, Sweden. A QA plan for the SR-Can project has been developed as part of SKB's procedures for project management. No document reference for the QA plan has been provided but the description of the plan suggests that it is similar to the draft document reviewed by Hicks (2007). SKB (2006a, Section 2.8) acknowledges that only parts of the QA plan for SR-Can have been implemented, although the extent to which the QA plan has been followed is not clear; SKB intends to implement a full QA plan for the SR-Site assessment.

Section 2.8.2 of SKB (2006a) sets out the objectives of the QA plan and Section 2.8.3 lists a series of steering documents that relate to QA issues in the SR-Can project. Of particular interest for this review of data and codes used in the SR-Can safety assessment are the QA objectives to demonstrate:

- How appropriate data for quantitative aspects of the assessment have been derived and used in the assessment in a quality-assured manner.
- How quantitative aspects of the assessment are handled by mathematical models and how the models (computer codes) have been quality assured.
- How the safety assessment reports have been properly reviewed and approved for correct and complete content.

The following steering documents are also of particular relevance:

- Procedures for quality assurance of input data.
- Template for model documentation.
- Review plan for SR-Can reports.

The steering documents have not been provided as part of the SR-Can safety assessment documentation. SKB (2006a, Section 2.8.3) notes that the documents are available in the SR-Can project archive. The approaches to meeting the QA objectives relating to data and codes appear to be described in the Data Report (SKB, 2006c, Section 2) and the Model Summary Report (SKB, 2006f, Section 2).

3. Quality Audit of Data

The Data Report (SKB, 2006c) aims to compile input data, with uncertainty estimates, for the SR-Can safety assessment calculations. SKB (2006c, Section 2.1) acknowledges that data for all the several hundred input parameters must be quality assured. However, the Data Report does not aim to confirm that data were acquired under particular QA procedures, but relies on experts to provide data reports that present QA-related information. The data reports are based on a standard structure covering (2006c, Section 2.3):

- how the data are to be used in SR-Can modelling;
- conditions under which the data are applicable;
- the potential sensitivity of the assessment to parameters;
- conceptual uncertainties related to parameters;
- data uncertainty, including uncertainties associated with analyses of field and laboratory data (such as measurement errors, bias, representativeness of the data) and spatial and temporal variability;
- correlations; and
- quantification of uncertainty.

For each subject-area considered in the Data Report, information on relevant data is presented in terms of the above-listed issues. In addition, in some cases, a section on 'source of information' is included that cites supporting analysis and experiments. If such information were to be provided for all data then traceability would be improved. Also, the experts who provide data reports should confirm that the data were acquired under appropriate quality assurance procedures or that suitable data qualification processes have been applied (such as peer review or independent technical assessment) in order to build confidence in the validity of the data.

A final level of review is undertaken by an SR-Can team that makes judgments on whether the expert input can be accepted for use in the SR-Can safety assessment calculations. The SR-Can team review should serve to build further confidence in the data qualification process for the safety assessment. However, it is not clear what review criteria or procedures are used by the SR-Can team in order to determine whether a particular data set is acceptable. It is noted that the SR-Can team (Data Report, SKB, 2006c, Section 1.6) includes experts who provided the data and therefore cannot make entirely independent judgments.

The following sub-sections examine the traceability and reliability of data on canister properties (SKB, 2006c, Section 4) and buffer and backfill properties (SKB, 2006c, Section 5).

3.1. Canister Data

3.1.1. Canister Geometry

The geometry of spent fuel canisters is presented in the Fuel and Canister Process Report (SKB, 2006d, Section 1.7.1) rather than the Data Report. Dimensions of the copper canister and cast iron insert are provided, but manufacturing tolerances and their potential significance to the safety case are not discussed.

3.1.2. Copper Physical Data

The Data Report (SKB 2006c, Section 4.1) discusses data for the canister thermal analysis and notes that properties such as conductivity and heat capacity are relatively well defined for canister materials and are available in handbooks, but does not list the values or cite any handbooks.

The Data Report does discuss the emissivity of the copper outer shell, which is required in order to perform calculations to determine the temperature at the canister-buffer interface when a gap exists between the canister and the buffer before the buffer material is fully saturated. Heat transfer by radiation is linearly dependent on the emissivity. The Data Report (SKB 2006c, Section 4.1) indicated that an emissivity of 0.1 should be assumed based on laboratory measurements on two canister lids used in welding experiments, with reference to a letter report in Swedish (Roos and Gelin, 2003), which is not available via the SKB website and does not have a document reference number in the reference list (SKB 2006c, Section 7).

The Data Report does not provide direct cross-references to where the emissivity and other thermal data are used in SR-Can, although SKB (2006c, Section 2.1.1) indicates that the emissivity is used in the thermal model presented in the Main Report (SKB (2006a, Section 9.3.4). Both the Main Report and the Fuel and Canister Process Report (SKB, 2006d, Section 3.2.1) note that the thermal evolution of the repository near field is based on the modelling analysis presented by Hedin (2004). Thermal sub-model data are presented in SKB (2006a, Table 9-4) and Hedin (2004, Section A5), but neither of these reports provide references to all of the data. For example, emissivity values for buffer, copper, iron and zircalloy surfaces and the gaps between the different interfaces are listed without reference to their derivation. The basis for the parameter values presented in SKB (2006a, Table 9-4) should be provided.

3.1.3. Initial Minimum Copper Coverage

The canister's copper shell provides a corrosion barrier to the insert. The Data Report (SKB 2006c, Section 4.2) states that the design thickness of the copper shell is 50 mm, although there is no reference to the derivation of this design thickness. Discontinuities in the copper could reduce the thicknesses of the corrosion barrier and SKB judged that such discontinuities are most likely to occur in the canister lid weld. However, there is no discussion of the potential for discontinuities occurring elsewhere in the copper shell.

SKB has opted to use Friction Stir Welding (FSW) for the canister lid welds (SKB 2006c, Section 4.2.2; 2006a, Section 4.2.4), based on a decision discussed in SKB (2006g). SKB (2006g) also derived a defect size distribution based on the analysis of a demonstration series of 20 canister lids welded under production-like conditions at SKB's Canister Laboratory. The analysis led to the conclusion that, taking into account measurement errors, all canisters sealed under normal operations would have a minimum copper thickness of 40 mm at the seal. SKB (2006g) is written in Swedish and has not been reviewed under this project. Further, SKB (2006g) appears to have the incorrect title in the Data Report reference list.

SKB (2006a, Section 4.2.4) noted that the likelihood of 'disturbed' operations leading to copper thickness of less than 40 mm was low. On the basis of the non-destructive testing requirement that there should be no defects greater than 15 mm, SKB (2006c, Section 4.2.8; 2006a, Section 4.2.4) assumed that 99% of canisters have a thickness of 40 to 50 mm at the weld and 1% of canisters have a thickness of 35 to 40 mm at the weld. Note that SKB (2006c, Section 4.2.8) states that "1% of all canisters have no defect larger than 15 mm" but probably should state that 1% of all canisters have defects greater than 10 mm but no larger than 15 mm. SKB (2006a, Section 4.2.4) acknowledges that there is no firm basis for this distribution, but claims that it is pessimistic. SKB (2006c, Section 4.2.7) states that there are no data uncertainties regarding copper coverage, whereas, in contrast, the Initial State Report (SKB, 2006b, Section 4.2.2) states that the evaluation of the occurrence of discontinuities in the canister components remains to be performed. Further support for the assumed distribution of discontinuities is required. Finally, SKB (2006a, b, and c) do not provide cross-reference to where this distribution is used in the safety assessment or its significance to the safety assessment results.

3.1.4. Cast Iron Physical and Mechanical Data

The canister must be designed to bear the maximum likely loads expected under repository conditions. The maximum pressure that a canister would experience would be provided by the combined load of hydrostatic pressure, bentonite swelling, and ice sheet loading during the glacial period. A maximum design load of 44 MPa was assumed by Andersson *et al*. (2005), Dillström (2005), and Nilsson *et al*. (2005) in analyses of canister strength as discussed in the Data Report (SKB 2006c, Section 4.3), representing a combined hydrostatic pressure and swelling pressure of 14 MPa and a pressure of 30 MPa from a 3-km-thick ice sheet. However, the bases for these maximum loads were not cited. The Data Report could make reference to the Main Report (SKB, 2006a) which provides the derivation of the bounding loads, although minor inconsistencies are apparent:

- SKB (2006a, Section 4.2.8) identified a maximum bentonite swelling pressure of 13 MPa.

- SKB (2006a, Section 9.4.6) identified hydrostatic pressures of 4 MPa for a repository at a depth of 400 m at Forsmark and 5 MPa for a repository at a depth of 500 m at Laxemar.

- SKB (2006a, Section 12.8) identified reference case glacial loads of 26 MPa for the Forsmark site and 22 MPa for the Laxemar site, and maximum glacial loads of 28 MPa for Forsmark and 23 MPa for Laxemar with appropriate references to underpinning research.

Therefore, the maximum loads would be 45 MPa at Forsmark and 41 MPa at Laxemar. The Fuel and Canister Process Report (SKB 2006d, Section 3.4.2) quoted a total load of 45 MPa based on a groundwater pressure of 5 MPa, a bentonite swelling pressure of 13 MPa, and a maximum glacial load of 28 MPa without reference to a particular site or to the source of data. The maximum design load of 44 MPa appears reasonable, but greater consistency and appropriate cross-referencing is needed when discussing such parameters in the SR-Can reports.

Andersson *et al*. (2005), Dillström (2005), and Nilsson *et al*. (2005) explained the basis for the conclusion that canister failure under the design load of 44 MPa is unlikely, as summarised in the Data Report (SKB 2006c, Section 4.3). Dillström (2005) demonstrated that the probability of initiation of crack growth in a canister insert under such conditions is negligible provided that the offset of the steel cassette relative to the centre of the insert (described as the eccentricity) is no more than 5 mm. Nilsson *et al*. (2005) demonstrated that the KBS-3 canister meets the design load of 44 MPa with a large safety margin based on tests on 'mock-ups' of the canister and insert, and finite element analyses of canister loading. Andersson *et al*. (2005) provided test plans for tensile strength tests on canister inserts and detailed discussion of other supporting tests and numerical analyses. The analyses and data to support the conclusion that canister failure under the design load is unlikely are reasonably traceable from supporting documentation to the SR-Can assessment and have been cited appropriately.

The Main Report (SKB, 2006a, Section 10.8) evaluates the consequences of canister failure under the design load at 10,000 years and 100,000 years after deposition for a single canister and for all canisters (even though such events have been estimated to be unlikely). Failure is assumed to resemble the pinhole failure case when the large hole has developed (discussed in Section 2.1.4) although it is not clear why such a configuration is appropriate. Section 12.8 of the Main Report considers canister failure due to glacial loading to be a residual scenario and reasonably excludes its consequences from the risk assessment.

The Fuel and Canister Process Report (SKB 2006d, Section 3.4.2) also considers the potential for large rock displacements across deposition holes to lead to canister failure, with reference to a report by Börgesson and Hernelind (2006a) that calculated the effects of shearing on stress and plastic strain in a canister. The parameter values used in the rock displacement analysis to describe the canister properties are unclear. Börgesson and Hernelind (2006a) referred to an earlier report by Börgesson *et al*. (2004) on the effects of rock shear for information on canister properties. In turn, Börgesson *et al*. (2004) referred to a report by Andersson (2002) on canister fabrication for information on canister properties, but it is not clear what canister properties presented by Andersson (2002) were used in the recent Börgesson and Hernelind (2006a) analyses.

Also, Börgesson and Hernelind (2006a) and Börgesson *et al*. (2004) did not explain the basis for the assumed rate and extent of shear displacement across a deposition hole. The effects of shear displacements on canister properties were calculated for an assumed shear rate of 1.0 m/s with up to 20 cm of shear displacement. These values are intended to represent the most severe forms of displacement that could be induced during an earthquake, but Börgesson and Hernelind (2006a) and Börgesson *et al*. (2004) did not provide information on, or references to, why these values are bounding. However, the Main Report (SKB 2006a, Section 9.4.5) presents a more comprehensive description of the potential for canister failure due to shear movement; the report includes a brief discussion of literature on shear velocities associated with earthquakes that supports the assumption that 1.0 m/s represents a realistic (rather than severe) estimate of shear rate. The assessment assumptions presented in the Main Report (SKB 2006a, Section 9.4.5) that a rock shear movement that exceeds 10 cm causes canister failure and that all canisters estimated to be affected by an earthquake suffer maximum possible damage are pessimistic based on the results of the supporting analyses on shear displacements. It is not clear how canister failure due to shear movement is modelled in SR-Can, although Neretnieks (2006) includes a model of radionuclide diffusion from a sheared canister that may be the model used in SR-Can.

3.1.5 Delay Time and Evolving Geometry of Canister Defects

Sections 4.2.1 and 4.4 of the Data Report (SKB, 2006c) discuss three points in time that are important to radionuclide migration:

- t_{fail} - the time at which a canister is assumed to fail. Failure may occur as a result of corrosion of the copper shell.

- t_{delay} - the time between canister failure and the establishment of a continuous groundwater pathway between the spent fuel and the canister exterior, marking the onset of radionuclide transport out of the canister.

- t_{large} - the time between the onset of radionuclide transport from the canister and complete loss of transport resistance.

SKB (2006c, Section 4.4.3) and the Main Report (SKB, 2006a, Section 10.5.2) state that no canister failures will occur in 1,000 years (t_{fail}) but provide no basis for this assumption. SKB (2006c, Section 4.4.7) states that t_{delay} is the time required for the canister to fill with water after failure, which is expected to be at least 1,000 years, although no quantitative basis for this value is presented. The stylised configuration of water entering a canister through a hole is discussed in detail in the Fuel and Canister Process Report (SKB, 2006d, Section 2.3.1), where the key reference is Bond *et al.* (1997). Bond *et al.* (1997) analysed the evolution of a breached canister based on consideration of factors including hole size, water inflow rate, iron corrosion rate, and corrosion product build-up and this analysis may be intended to support the selection of t_{delay} of 1,000 years although the referencing is unclear.

The time t_{large} is described as the time in which an initial small hole that penetrates the container becomes sufficiently large that there is no resistance to radionuclide transport out of the canister. The initial radius of the penetrating defect is assumed to be 2 mm and the ‘no resistance’ state is assumed to be reached between 1,000 and 100,000 years after failure to account for the associated large uncertainty. There is no technical basis for assuming that a 2 mm radius hole can penetrate a canister at any time and there is no basis for assuming that substantial growth of such a hole can occur between 1,000 and 100,000 years after failure. The defect distribution analysis suggests that such holes will not occur and the corrosion analysis (as discussed in Section 2.1.5) suggests that copper corrosion is likely to be negligible in this timeframe. The Data Report provides no cross-references to where or how these parameters are used in the assessment.

The growing pinhole model is one of the failure modes considered in the Main Report (SKB, 2006a, Section 10.5). Despite stating that no canister failures will occur in 1,000 years, the Main Report (SKB, 2006a, Section 10.5) assumes that a 2 mm radius hole penetrates one canister on deposition and that a large defect in this canister has evolved 10,000 years after deposition, although the results presented in Section 10.5.4 suggest that the small defect is assumed to change to a large defect instantaneously at 10,000 years. No credit is given to the integrity of the cast iron insert and it would appear that t_{fail} and t_{delay} are both zero. There appears to be no traceable rationale for this growing pinhole failure model, but this failure mode is not included in the analysis of the main scenario or as a residual scenario (SKB, 2006a, Section 12).

3.1.6 Corrosion Parameters

Copper Corrosion

King *et al*. (2001) is the main source of information regarding copper corrosion and is discussed in the Data Report (SKB, 2006c, Section 4.5). The sulphide concentration in the groundwater is regarded as the key parameter affecting copper corrosion in the long term and a pessimistic sulphide concentration limit has been specified in SKB (2006c, Section 4.5.7). It is not clear from the Data Report how the sulphide concentration limit is used in the assessment. The Data Report also discusses corrosion by reaction with oxygen but no parameters relating to copper oxidisation are specified.

The Fuel and Canister Process Report (SKB, 2006d, Section 3.5.4) and the Main Report (SKB, 2006a, Section 9.2.5, Section 9.3.12, and Appendix B) repeat the discussion of canister corrosion and include consideration of corrosion by reaction with nitric acid. It is not clear why corrosion by nitric acid is not considered in the Data Report.

The Fuel and Canister Process Report also discusses stress corrosion cracking (SKB, 2006d, Section 3.5.5) and stray current corrosion (SKB, 2006d, Section 3.5.6); these processes are noted in the canister processes table of the Main Report (Section 6.4.2) but there are no cross references to the arguments presented in the Fuel and Canister Process Report and the processes are not discussed further in the Main Report.

Based on the analysis by King *et al*. (2001), the Fuel and Canister Process Report (SKB, 2006d, Section 3.5.4) and the Main Report (SKB, 2006a, Section 9.2.5 and Section 9.3.12) conclude that copper corrosion will be negligible during the repository operational phase and for the temperate climate (which is assumed to last several thousands of years after closure). Further, the Main Report concluded that copper corrosion would be negligible if such conditions were to persist for the overall 1 million year assessment period.

Enhanced Copper Corrosion Following Buffer Erosion

The Main Report (SKB, 2006a, Section 9.4.9 and Section 9.5) discusses the possibility of enhanced copper corrosion owing to advection of corroding agents following buffer erosion and concludes that canister failure by corrosion could occur in the period after about 100,000 years (after the first glacial cycle). Table 9-22 of the Main Report presents calculations of the number of failed canisters for different deposition hole rejection criteria; results for the full perimeter intersection criterion (FPC) and various transmissivity criteria are shown. Discussion of, and cross-references to, the derivation of the different deposition hole rejection criteria are not provided, although the discussions in Sections 4.4.1 and 12.2.1 of the Main Report indicate that the FPC criterion rather than the transmissivity criteria would be implemented.

The method to determine the number of failed canisters and the timing of canister failure for each deposition hole rejection criterion has not been explained clearly and there are no references to relevant supporting documentation. Sections 12.7.2 and 12.7.3 of the Main Report describe the estimate of 10 failures to be cautious and 37 failures to be pessimistic for Forsmark, and 150 failures to be pessimistic for Laxemar (although Figure 12-13 indicates 120 failures for Laxemar). The derivation of these values is not presented.

Some discussion of the model to determine the canister corrosion rate and therefore the time of canister failure is presented in Appendix B. Here, an eroded buffer half-cylinder of height 0.35 m is assumed, but the selected height and, therefore, the exposed area of the canister appears arbitrary; should a narrower channel develop the corrosion rate would be greater. Neretnieks (2006) is the key reference for this corrosion model.

The buffer erosion and enhanced copper corrosion failure mode is considered in Section 10.6 of the Main Report and in the analysis of the main scenario in Section 12.2.1 of the Main Report. This is the only failure mode considered in the main scenario. Failure of the first copper canister is assumed to occur after 100,000 years and, consistent with the use of the FPC criterion, 10 canisters are assumed to fail in the Forsmark analysis while 50 canisters are assumed to fail in the Laxemar analysis. However, a pessimistic canister corrosion scenario in which 37 canisters are assumed to fail in the Forsmark analysis and 150 canisters are assumed to fail in the Laxemar analysis is also included in the risk summation (SKB, 2006a, Section 12.7.3).

In contrast to the growing pinhole failure analysis, credit is taken for the integrity of the cast iron insert in the buffer erosion and enhanced copper corrosion failure analysis, although it is unclear why these different assumptions have been made. The Data Report (SKB, 2006c, Section 4.5.7) lists a pessimistic iron corrosion rate parameter, but no cross-references are provided to discussions of the use of this parameter in the assessment. A more detailed discussion of corrosion of the cast iron insert is provided in the Fuel and Canister Process Report (SKB, 2006d, Section 3.5.1). Conference papers by Smart *et al.* (2002a; b) are the key references for corrosion rates; a similarly titled SKB report by the same authors (Smart *et al.*, 2001) is available but has not been cited. The time for the cast iron insert to be penetrated is assumed to be triangularly distributed between 1,000 and 100,000 years (SKB, 2006a, Section 10.6). Reference is made to the discussion of defect evolution in the Data Report (SKB, 2006c, Section 4.4), but no rationale for this distribution is presented.

3.2. Buffer and Backfill Data

3.2.1. Thermal Properties of Buffer

Section 5.1 of the Data Report (SKB, 2006c) discusses the thermal properties of the buffer, but is limited to consideration of the thermal conductivity of bentonite. A more detailed discussion of the thermal properties of the buffer is presented in the Buffer and Backfill Process Report (SKB, 2006e, Section 2.2). The Data Report refers to Hökmark and Fälth (2003) in specifying a bentonite thermal conductivity of 1.1 W/mK. However, the key experimental work to determine the thermal conductivity of bentonite that underpins all of the cited thermal analyses has been presented by Börgesson *et al.* (1994). For Mx-80 bentonite with a void ratio e of 0.8 and a saturation S_r of 0.8, the experiments indicated that the thermal conductivity of bentonite is about 1.2 W/mK, while theoretical analyses indicated that the thermal conductivity lies between about 1.0 W/mK and 1.1 W/mK. Therefore, the selected thermal conductivity of 1.1 W/mK would seem to be reasonable for initial conditions in which $e = 0.8$ and $S_r = 0.8$. The Buffer and Backfill Process Report (SKB, 2006e, Section 2.2) discusses a broader range of experiments to determine the thermal conductivity of the buffer, including experiments undertaken at the Äspö Hard Rock Laboratory, but does not refer to the value selected in the Data Report.

3.2.2. Hydraulic and Mechanical Properties of Buffer and Backfill

Section 5.2.7 of the Data Report (SKB, 2006c) presents parameter values for THM modelling. More specific referencing of data sources would improve the traceability of information on buffer parameters. Parameter values for the buffer model presented in Tables 5.3 of the Data Report appear to have been extracted from the material model presented by Börgesson and Hernelind (1999). Börgesson and Hernelind (1999) rely on the experimental results presented by Börgesson *et al.* (1994), Börgesson *et al.* (1995), and Börgesson and Johannesson (1995) to derive what is described as a preliminary material model. However, the process by which the model parameters have been abstracted from the supporting experimental results is not clear. For example, following have not been explained:

- The basis for the selection of the bentonite dry density, water ratio, and solid density, and the resultant void ratio and saturation.

- The formula used to determine the thermal conductivity as a function of saturation (especially at saturations below 0.4) based on the experimental results presented by Börgesson *et al.* (1994) (which covered saturations above 0.4).

- The basis for halving the hydraulic conductivity values presented by Börgesson and Johannesson (1995).

- The basis for changing the thermal vapour flow diffusivity, D_{Tvb}, from the value of $3x10^{-11}$ m^2/sK presented by Börgesson and Johannesson (1995) to $7x10^{-12}$ m^2/sK.

- The basis and units of the equation for specific heat, c.

Section 5.2.1 of the Data Report provides some examples of where the buffer and backfill material models have been used in supporting analyses, but there are no cross-references to where or how these parameters or the results of the supporting analyses are used in the Main Report of the safety assessment (SKB, 2006a).

3.2.3. Density and Porosity of Buffer and Backfill

The hydraulic conductivity of the buffer and backfill material is expected to increase and the swelling pressure is expected to decrease with decreasing density. Figure 5.3 of the Data Report (SKB, 2006c) shows graphs of bentonite hydraulic conductivity and swelling pressure as a function of dry density. However, an incorrect reference to a report by Johannesson and Nilsson (2006) on backfill properties has been provided. Graphs similar to those shown in Figure 5.3 have been presented in Sections 2.3.2 and 2.4.1 of the Buffer and Backfill Process Report (SKB, 2006e) and other versions are presented in Section 4.8 of the Main Report (SKB, 2006a). The latter reports make reference to Karnland *et al.* (2006) and Karnland *et al.* (2005); the Initial State Report (SKB, 2006b, Section 5.2) and the Buffer and Backfill Process Report (SKB, 2006e, Section 2.3.2) also make reference to Karnland *et al.* (2006), which is the main source of information on the composition and properties of the buffer. Karnland *et al.* (2006) provide a detailed discussion of the relevant experiments and results, and a reasonable demonstration that the required hydraulic conductivity of less than 10^{-12} m/s and swelling pressure of greater than 1 MPa are achievable under expected conditions. The Data Report does not refer to Karnland *et al.* (2006).

The Initial State Report (SKB, 2006b, Section 5.2), the Data Report (SKB, 2006c, Section 5.3.8), and the Buffer and Backfill Process Report (SKB, 2006e, Section 1.4) state that the target density for saturated bentonite is 2,000±50 kg/m^3, although a reference to a discussion of the rationale for the choice of target density has not been provided. Values of initial void ratio, porosity, dry density, and saturation are provided in the Initial State Report (SKB, 2006b, Section 5.2) and the Data Report (SKB, 2006c, Section 5.3.8); no explicit references to the origins of these values are provided, although, as noted in the Data Report, the potential to manufacture bentonite blocks of suitably high density by isostatic compaction has been demonstrated reasonably by Johannesson *et al*. (2000).

The Main Report (SKB, 2006a, Section 4.2.5) states that the bentonite, which will be bought in bulk form and transported by ship, will be subject to quality control both before loading in the ship and at reception. Additional quality control will be undertaken during the manufacture of the bentonite blocks and rings, including measurement of the water content before pressing. The uncertainty range assumed for bentonite properties should address potential variability in bentonite quality.

3.2.4. Radionuclide Migration Data for Bentonite

Section 5.4 of the Data Report (SKB, 2006c) and Section 2.5 of the Buffer and Backfill Process Report (SKB, 2006e) discuss the migration parameters for bentonite and note that these parameters are presented in the data and uncertainty expert report (Ochs and Talerico, 2004). Ochs and Talerico (2004) appear to present a reasonably comprehensive discussion of the derivation of sorption distribution coefficients, diffusivities, and porosities. However, a reference density of 1,590 kg/m^3 is noted for the diffusion studies, rather than the target density for saturated bentonite of 2,000 kg/m^3. The significance of this discrepancy is not discussed in any detail.

The sorption database draws on analyses carried out under other repository programmes (e.g. Nagra in Switzerland and JNC in Japan). A discussion of the approach to verifying the data for use in the SR-Can assessment would build confidence in the use of the data.

3.3. Discussion

The Data Report is one of the series of SR-Can safety assessment reports and, in undertaking this review of data QA, it was anticipated that the Data Report would provide the primary source of data on the canister, insert, buffer, and backfill. Further, it was expected that other reports in the safety assessment series would refer to relevant sections of the Data Report when analysing specific processes and scenarios, and that the Data Report would cross-refer to the relevant analysis in the safety assessment documentation. However, the Initial State Report (SKB, 2006b), the Fuel and Canister Process Report (SKB, 2006d), and the Buffer and Backfill Process Report (SKB, 2006e) appear to contain comprehensive discussions of data relating to relevant processes and these reports do not always make use of the material presented in the Data Report.

Also, in many cases, the SR-Can Main Report (SKB 2006a) provides the most detailed information on a particular parameter or process. For example, the Main Report presents more comprehensive information on data and parameters relating to the potential for canister failure due to shear movement and the potential for canister failure due to buffer erosion and enhanced copper corrosion than is found in other reports. In general, the approach to documenting data and parameters relating to specific processes appears not to be consistent throughout SR-Can and, as a result, some of the discussion in the Data Report appears superfluous.

The Data Report does aim to address issues related to data qualification, although the QA procedures under which data were derived are not discussed directly. Final judgments on the use of data are made by the SR-Can team. However, the team includes some of the experts who provided the data and, therefore, such judgments cannot be considered to be entirely independent.

The main findings from the review of canister, buffer, and backfill data are as follows:

- Some material properties are described as well defined and available in handbooks. Even so, values should be provided and handbooks cited.

- The Data Report does not always provide clear information on how and where data are used in the SR-Can assessment, which makes the task of checking the traceability of information through the assessment difficult. The Data Report (SKB, 2006c, Section 2.1) does mention briefly the Assessment Model Flowcharts (AMFs) which show the models used in the SR-Can safety assessment. The importance of data to the safety assessment could be clarified with reference to relevant data entries in the AMFs, the purpose of the modelling that uses the data, and its discussion in the relevant process reports and the Main Report. Tables 6-7 and 6-8 of the Main Report (SKB, 2006a) provide links to where modelling activities are discussed in the Main Report; such links could be used as the basis for providing indications of where related input data are used.

- A key decision on the use of FSW for the canister lid welds and an important discussion of defect size distribution are presented in a report that is written in Swedish and, therefore, can not be reviewed as widely as other parts of the assessment.

- There is no discussion of, or cross-references to, the derivation of deposition hole rejection criteria in the safety assessment reports, although the Main Report indicates that the FPC criterion rather than the transmissivity criteria would be implemented.

- The calculation of the number of failed canisters and the timing of canister failure for each deposition hole rejection criterion has not been explained and there are no references to relevant supporting documentation.

- The process by which the buffer model parameters have been abstracted from supporting experimental results is not clear and selection of many of these values is not traceable.

4. Quality Audit of Codes

Hicks (2005) included a brief review of software QA requirements in radioactive waste disposal programmes in the US and the UK, which provided insights into the type of code documentation that might be expected to accompany the submission of a repository safety assessment. The review highlighted the importance of demonstrating that software is managed under a rigorous but graded approach based on a software life-cycle methodology, with documentation requirements that include user's manuals and verification and validation reports, and procedures for the use of external codes. Under the graded approach, the extent of application of the software life-cycle methodology adopted for a particular code depends on the nature and importance of the application. Hicks (2005) concluded that SKB should provide details of its approach to software QA for different software categories (e.g., internal, commercial, academic, and simple codes) and applications. This section reviews the approach to software QA adopted by SKB for the SR-Can safety assessment and considers the adequacy of available code QA documentation.

As part of the SR-Can safety assessment documentation, SKB has introduced a Model Summary Report (SKB, 2006f) dedicated to providing an overview of the codes used in the safety assessment, including information on the quality assurance of these codes and their suitability for particular applications within the safety assessment. The Model Summary Report SKB (2006f, Section 2) presents a "differentiated" approach to software QA. Under this approach, in order to determine the QA procedure to be applied to a particular code, SKB (2006f) has classified each code according to categories summarised as follows:

1. Commercial system software such as operating systems, compilers and data bases.

2. Software used to solve problems that can be verified by simple hand calculations.

3. Wide-spread commercial or open source codes.

4a. Modified commercial codes.

4b. Calculations performed with codes developed in-house.

These different categories of code are subject to the following requirements concerning quality assurance and suitably for application in the SR-Can safety assessment:

1. Demonstrate that the code is suitable for its purpose. This requirement applies to all of the code categories.

2. Demonstrate that the code has been used properly. This requirement applies to all of the code categories.

3. Demonstrate that the code development process has followed appropriate procedures and that the code produces accurate results. This requirement applies to codes in category 4a and 4b. The developer's procedures are accepted for codes in categories 1, 2, and 3.

SKB's differentiated approach to software QA is is consistent with the graded approach noted by Hicks (2005), and the requirements for code application, if met, would ensure that a code is fit for its intended purpose. SKB (2006f, Section 2) includes a "template for code presentation" which sets out the information required to accompany the application of each code in the SR-Can safety assessment in order to demonstrate that the QA requirements for code application have been met. The template sets out the requirements for:

- An introduction which requires a description of the code, the version used in the safety assessment, its categorisation, information on code development, and information on previous uses in performance assessments.
- A discussion of the suitability of the code for application in the safety assessment, including model description and solution methods, and evidence that the application of the code involves parameter values for which the code has been verified.
- A discussion of the documentation available to support code usage, including input and output handling.
- A discussion of the code development process and code verification (for category 4 codes).
- The rationale for using the code in the SR-Can safety assessment.

These information requirements broadly cover the issues that need to be considered in judging the suitability of a code for use in a safety assessment. However, with regard to the fourth bullet point, a statement on how the developer's software QA procedures have been assessed and accepted for codes in category 3 should be required.

In addition, statements on the use or uses of the code in the safety assessment could be included to provide more comprehensive bases on which to present conclusions on whether a code was fit-for-purpose. Such statements could be accompanied by references to where the code application and results are discussed in the Main Report (SKB, 2006a), such as through the discussion of the AMFs as noted below. References could also be made to appropriate sections of the Data Report (SKB, 2006c), or other safety assessment reports that deal with model inputs, to improve traceability of data selection for the code application. Further, statements on how code applications and results have been checked and reviewed prior to presentation in the SR-Can documents could be included in order to engender high levels of confidence in the reliability of the modelling results. Such checks and reviews should apply to the application of category 2 as well as category 3 and 4 codes.

Section 3 of SKB (2006f) focuses on demonstrating that the appropriate QA requirements for code use have been met for codes in categories 3, 4a, and 4b. However, SKB (2006f) does not provide any QA information on codes used in supporting analyses, such as those used in the derivation of input parameter values for the SR-Can safety assessment. The demonstration that software QA procedures have been applied appropriately in the SR-Can project should be comprehensive such that reasonable levels of confidence can be achieved in all modelling results pertinent to the safety assessment.

Appendix A of SKB (2006f) comprises the two AMFs that illustrate the assessment modelling activities in the safety assessment and how they are related to each other. Each of the category 3, 4a, and 4b codes used in the SR-Can safety assessment fulfils one or more of the functions indicated on the AMFs. As discussed in more detail in the Main Report (SKB, 2006a, Section 6.5), the AMFs illustrate the relationships between the assessment modelling activities in the safety assessment; model input data and modelling results; and intermediate assessments based on model output and other information. The first AMF covers the modelling tasks relevant to the evaluation of conditions in the repository excavation and operational phases and the assessment of the initial temperate period after repository closure. The second AMF covers modelling tasks relevant to the assessment of repository safety under future permafrost and glacial conditions.

Appendix B of SKB (2006f) provides tables that indicate which codes have been used for each modelling activity shown on the AMFs. More helpful are Tables 6-7 and 6-8 of the Main Report (SKB, 2006a) of the safety assessment because they provide links to where the modelling activities are discussed in the Main Report. In order to improve the traceability of information throughout the safety assessment, greater use could be made of the information in the AMFs and in Tables 6-7 and 6-8 of the Main Report. The Model Summary Report could refer to or include these tables. Links to features, events, and processes (FEPs) addressed by the model applications should be provided.

It is not clear if the intermediate assessments indicated on the AMFs involve modelling activities and, if they do, the models used are not listed. Further, for some entries in the AMFs, modelling outputs (e.g. "peak buffer temperature") or intermediate assessments (e.g. "hydraulic conductivity and swelling pressure") do not appear to lead to further steps in the safety assessment so that the purpose of the model output or the role of the intermediate assessment is unclear. It would be helpful if any modelling activities associated with intermediate assessments shown on the AMFs were listed and links to where the intermediate assessments are discussed and results used in the Main Report, such as to evaluate safety functions, were provided.

SKB (2006f, Section 3) describes the codes used in the SR-Can safety assessment based on the template for presentation set out in SKB (2006f, Section 2). The following sections review the QA-related entries provided for a selection of these codes:

- 3DEC (category 4a)
- ABAQUS (category 3)
- Analytic radionuclide transport model (category 4b)
- Analytic Transport Model for Advective Conditions (category 4b)
- COMP23/Compulink (category 4b)
- CONNECTFLOW (category 3)

4.1. 3DEC

SKB (2006f, Section 3.1) discusses the use of 3DEC, a three-dimensional geotechnical modelling code. 3DEC is a commercial code, but for SR-Can, the functionality of 3DEC was extended by implementing algorithms using the FISH programming language embedded in 3DEC. Therefore, SKB (2006f) appropriately regards 3DEC as a category 4a code.

FISH was used to develop a technique for defining circular-shaped fractures that was applied in analyses of seismically-induced fracture shear movements, and to reduce computer run time when analysing thermo-mechanical near-field models. Although SKB (2006f) stated the specific FISH routines developed for the safety assessment calculations were rigorously tested and verified in small test models, no details were provided and no references cited.

No references to the application of 3DEC in the SR-Can safety assessment are provided in SKB (2006f), but Tables 6-7 and 6-8 of the Main Report (SKB, 2006a) indicate that Hökmark *et al.* (2006) represents the full 3DEC modelling report. Hökmark *et al.* (2006) discusses the use of 3DEC for near-field thermo-mechanical analyses and large-scale thermal stress analyses. The main features of the models were presented and the input data and assumptions were discussed. The report makes no reference to model verification or the inclusion of any FISH routines.

Hökmark *et al.* (2006) cites a report by Fälth and Hökmark (2007) for further code details. Fälth and Hökmark (2007) used 3DEC to study fracture shear displacements and fracture stresses, rock stresses close to openings, and thermal stresses between the repository and the ground surface. Fälth and Hökmark (2007) reported that the 3DEC calculations of thermal stresses agreed well with results obtained from analytical solutions, although the analytical solutions were not discussed in detail. Fälth and Hökmark (2007) noted that the FISH language was used for the development of a technique for storage and repeated use of temperature calculation results to increase the speed of thermal calculations. No details or references were provided on the documentation and testing of this FISH algorithm.

In summary, 3DEC is a widely used, tried and tested code, as previously noted in the review by Hicks (2005), and can be regarded as suitable for application in the SR-Can safety assessment. However, cross-referencing between the discussion of the code in the Model Summary Report and its application in the safety assessment would improve traceability. The main 3DEC modelling reports (Hökmark *et al.*, 2006; and Fälth and Hökmark, 2007) provide details of input data and assumptions, but insufficient information on the development, implementation, and testing of the 3DEC FISH routines has been provided.

4.2. ABAQUS

Section 3.2 of SKB (2006f) discusses ABAQUS, another commercial code used by SKB in THM analyses of the repository near field. SKB (2006f) regards ABAQUS as a category 3 code. However, SKB (2006f) includes negligible discussion of QA issues relating to the application of ABAQUS in the SR-Can safety assessment. Instead, reference is made to the code producer’s internet site for information on code QA.

SKB (2006f) does not provide references to relevant SR-Can modelling reports. However, inspection of Tables 6.7 and 6.8 of the Main Report (SKB 2006a) reveals relevant reports by Börgesson and Hernelind (2006b) and Börgesson *et al.* (2006). Börgesson *et al.* (2006) included ABAQUS calculations to investigate: the influence of the backfill properties and wetting conditions on the water saturation phase of the buffer; the influence of the rock conditions on the wetting phase of the backfill; and the hydraulic interaction between rock, buffer and backfill. The model includes a water vapour flow algorithm that is described as a user supplied routine, but no information on the development and testing of this routine has been provided. If this routine has been developed by SKB then it would suggest that ABAQUS should be classified as a category 4a code and appropriate QA procedures should be applied

Börgesson and Hernelind (2006b) used ABAQUS to investigate the swelling properties of the bentonite buffer material, but did not specify which version of ABAQUS was used. Börgesson and Hernelind (2006b) cited Börgesson *et al*. (1995), Börgesson and Hernelind (1999), and Börgesson *et al*. (2006) for an overview of how thermo-hydro-mechanical processes and buffer and backfill materials are represented in ABAQUS. As previously noted by Hicks (2005), Börgesson *et al*. (1995) defined a buffer material model for ABAQUS that they considered required further testing and Börgesson and Hernelind (1999) considered that the mechanical and vapour flux modules need to be improved. Börgesson and Hernelind (2006b) re-iterated that there were uncertainties about the validity of the material model at high bentonite swelling pressures and that the results should be checked by performing laboratory swelling tests.

In summary, inspection of the ABAQUS developer's internet site confirms that ABAQUS is a widely used and well tested code that is suitable for use in SKB's repository research programme, as concluded previously by Hicks (2005). However, the Model Summary Report should include more information on the pedigree of the code, including its QA credentials, rather than leaving readers to search for the information themselves via the developer's internet site. Also, some user supplied ABAQUS modules appear to require verification and the buffer material model appears to require further validation. It may be more appropriate to classify ABAQUS as a category 4a code if SKB has developed modules and used them in the SR-Can safety assessment.

4.3. Analytic Radionuclide Transport Model

The analytic radionuclide transport model, discussed in Section 3.3 of SKB (2006f), provides analytical solutions to radionuclide transport in the near-field and far-field and includes options for performing probabilistic calculations. The model was developed by SKB and, thus, is a category 4b code. No version control has been implemented by SKB.

The mathematical model and solution scheme has been described by Hedin (2002). SKB (2006f) states that additional details are available in a note on the SR-Can project archive (but a full reference has not been provided). No documentation relating to software QA appears to have been produced since the code was reviewed by Hicks (2005). SKB (2006f) acknowledges that no user manual has been produced and that code usage is not self-explanatory, but states that SKB intends to develop a user manual for future assessments and write the code so that it can be transferred to other users. Tables 6.7 and 6.8 of the Main Report (SKB 2006a) show that there are no modelling reports on the use of the code in the SR-Can safety assessment, but code results are presented in Sections 10.5 to 10.8 of the Main Report (SKB, 2006a).

The analytical model has been tested successfully for deterministic and probabilistic calculations by comparing results with those of COMP23 and FARF31 (Hedin, 2002; SKB, 2004; SKB, 2006a). However, inspection of Figure 10-14 in SKB (2006a) does suggest that the analytical solution may slightly underestimate peak doses (when compared to the numerical solution) for several radionuclides (e.g. ^{59}Ni). There are also small differences in the structure of the breakthrough curves generated by the numerical solution and the analytical solution (e.g. ^{135}Cs). These differences merit explanation.

SKB (2006f) does not explain the original motivation for developing the analytical radionuclide transport model or its intended role in the SR-Can safety assessment. It is not clear if the analytical model has been produced in order to verify the numerical solution scheme, to produce probabilistic solutions in place of the numerical solution scheme because the latter code's run times are too long, or for some other reason. Also, it is not explained why the analytical model was developed in favour of using commercially available and quality assured software which may be able to fulfil a similar function (e.g. GoldSim). Hedin (2002) suggested that the analytical model could facilitate regulatory review of complicated calculations. However, such use would require the above-noted code documentation to be available.

4.4. Analytic Transport Model for Advective Conditions

SKB has developed a simple model for calculating radionuclide release rates from the near-field assuming advective conditions in the deposition hole (SKB, 2006f). Geosphere transfer is calculated using the analytical model presented by Hedin (2002) for the analytical radionuclide transport model. SKB (2006f, Section 3.4) notes that the code is category 4b.

The model and its testing are described briefly in Appendix B of the SR-Can Main Report (SKB, 2006a). The model appears to be a simplified version of the analytical radionuclide transport model described in Section 3.1.3. It is unclear why the model is not included as part of the analytical radionuclide transport model. As for the analytical radionuclide transport model, SKB (2006f) acknowledges that no user manual has been produced and that code usage is not self-explanatory, but states that SKB intends to develop a user manual for future assessments and write the code so that it can be transferred to other users.

SKB (2006f, Section 3.4.2) states that the purpose of the code is to mimic COMP23 and FARF31, presumably as a verification exercise for the latter codes. However, SKB (2006f, Section 3.4.5) suggests that the code is also intended for producing probabilistic calculations, although it is not clear if this would be in place of, or to supplement, COMP23 and FARF31 calculations.

4.5. COMP23/Compulink

Section 3.8 of SKB (2006f) discusses COMP23, which is used to evaluate radionuclide transport in the repository near-field as part of safety assessment calculations. The COMP23 model has been implemented for the SR-Can safety assessment as a code called Compulink, which is written in Matlab and Simulink rather than the Fortran used for COMP23. The code is categorised as 4b.

Vahlund and Hermansson (2006) provide a comprehensive description of Compulink, including a description of the mathematical model, verification studies, the solution scheme, a user guide, test cases, and code listing. The basis for developing the Compulink version of COMP23 is not entirely clear, although Vahlund and Hermansson (2006) suggest that the graphical interface, Matlab and Simulink tools, and platform (presumably hardware) independence are beneficial.

SKB (2006f) also discusses the COMP23 user's guide (Cliffe and Kelly, 2004) and validation report (Kelly and Cliffe, 2006), with the implication that COMP23, as well as Compulink, is used in the SR-Can safety assessment. COMP23 is a submodel of the 'Proper' safety assessment calculation framework along with codes such as FARF31 (the far-field radionuclide transport model). It is not clear how the Compulink version interacts with the Proper framework.

Kelly and Cliffe (2006) outline the COMP23 mathematical models for radionuclide transport in the barrier and treatment of the source term. Analytical solutions used where numerical solutions are problematic or time consuming (transport into flowing water, transport into a large compartment, and transport into a narrow slit) are also explained. The COMP23 analytical solution results for transport into a large compartment (that is, the use of an additional diffusional resistance) showed good agreement with those from the numerical code ENTWIFE, especially for the situation in which the hole size is small compared to the larger compartment. Kelly and Cliffe (2006) noted that a series of test cases had been undertaken and documented to build confidence in the credibility of COMP23 results. The codes review by Hicks (2005) previously noted that COMP23 produces reasonably accurate results provided the numerical solution grid is suitably discretized.

In summary, COMP23 has been developed and used extensively by SKB as a near-field radionuclide transport model for use in SKB repository safety assessments for many years. User's guides and verification studies for COMP23 and the Compulink implementation of the model are available. Although SKB (2006f) discusses both the COMP23 and the Compulink versions of the model, Compulink appears to have been used in the SR-Can safety assessment. However, it is not clear how Compulink interacts with other codes used in the safety assessment.

4.6. CONNECTFLOW

SKB (2006f, Section 3.9) discusses the CONNECTFLOW groundwater modelling code, which is commercial software and thus a category 3 code. The discussion of CONNECTFLOW represents one of the more comprehensive entries provided for codes in the report, covering the background to code development and the rationale for its selection for use by SKB, information on code usage including input checking procedures, applied QA standards, and code testing. Cross-references to documents dealing with its applications and the use of results in the SR-Can safety assessment would be beneficial.

4.7. Discussion

SKB has provided a Model Summary Report that provides a useful focus for reviewing the quality assurance status of the codes used in the SR-Can safety assessment. The categorisation of the codes and associated quality assurance requirements are consistent with the type of graded approach to software QA used in other radioactive waste management programmes.

A review of the entries for a selection of codes used in the safety assessment has revealed several concerns, many of which are acknowledged by SKB in the report. In general:

- The Model Summary Report provides greatly differing levels of detail for each code. For example, the discussion of ABAQUS is minimal, but the discussion of other commercial software such as CONNECTFLOW is reasonably comprehensive. Similar levels of information should be provided for each code.

- For some codes it is noted that training courses are available. However, it is not clear if procedures are in place to ensure that code users are suitably trained to apply the code in the SR-Can safety assessment.

- It is not clear if any particular criteria are used or standards sought in judging whether commercial software is acceptable for use in the SR-Can safety assessment.

- It is not clear if all of the codes discussed in the Model Summary Report have been used in the safety assessment. For example, FARF32 and FARF33 are discussed but are not mentioned in Appendix B, although FARF32 may be the code referred to as FVFARF in Appendix B. Also, FracMan is discussed but its role in the safety assessment appears uncertain (SKB, 2006f, Section 3.15).

Traceability of information on code usage in the safety assessment and confidence in code reliability could be improved by including the following information on each code:

- The original requirement for the code in SKB's repository research programme and the rationale for choosing to develop the code in-house or to use commercial software.

- The role of the code in the SR-Can safety assessment with cross-references to where associated FEPs, input data, and code applications are presented, and to where results are used in the safety assessment documentation, perhaps through greater use of the AMFs.

- Procedures for checking and reviewing code application in the SR-Can safety assessment.

The demonstration that software QA procedures have been applied appropriately in the SR-Can project should be comprehensive, covering codes used in supporting analyses that have important impacts on decision-making for the safety assessment as well as codes used directly in the safety assessment. Potentially, such analyses could be identified through entries in the AMFs, such as derivation of input data or intermediate assessments of data and results.

5. Summary and Conclusions

SKB produced the SR-Can safety assessment in preparation for the development of the SR-Site assessment that will be part of SKB's application for a final repository. SR-Can provides an opportunity for review and comment on SKB's safety assessment approach prior to the compilation of SR-Site. SKI is in the process of reviewing the SR-Can safety report. Building on the findings of the previous studies on data and code QA in safety assessments, this report provides a review of data and code QA aspects of the SR-Can safety assessment in support of SKI's review.

The review of the application of quality assurance procedures in the SR-Can safety report involves quality audits of the data and codes used in the safety assessment. The data quality audit has aimed to check that the selection and use of data in the SR-Can safety assessment was appropriate, focusing on the data that underpin representations of and assumptions about canister, insert, buffer, and backfill behaviour in the safety assessment. The quality audit of codes used in the SR-Can safety assessment has aimed to check that code use in the SR-Can safety assessment is justified through a transparent and traceable process of code development and selection.

The SR-Can Main Report provides a summary discussion of the QA system in place for the SR-Can project and lists the QA objectives. The Data Report and the Model Summary Report provide the focus of SKB's demonstration that data and codes are of appropriate quality for use in the safety assessment. The reviews of QA issues relating to data and codes are centred on information provided in the Data Report and the Model Summary Report, respectively. Summary findings and conclusions are presented in the following sub-sections.

5.1. Canister, Buffer, and Backfill Data QA Review

The Data Report was identified as the initial focus for examining the traceability and reliability of data used in the SR-Can safety assessment. QA procedures under which data were derived are not discussed directly in the Data Report, but the report aims to cover many issues that would be covered by such procedures as a form of data qualification. Final judgments on the use of data are made by the SR-Can team, although the team includes some of the experts who provided the data and, therefore, such judgments cannot be considered to be entirely independent.

The Data Report is one of the series of SR-Can safety assessment reports and, in undertaking this review of data QA, it was anticipated that the Data Report would provide the primary source of data on the canister, insert, buffer, and backfill. Further, it was expected that other reports in the safety assessment series would refer to relevant sections of the Data Report when analysing specific processes and scenarios, and that the Data Report would cross-refer to the relevant analysis in the safety assessment documentation. However, the Initial State Report (SKB, 2006b), the Fuel and Canister Process Report (SKB, 2006d), and the Buffer and Backfill Process Report (SKB, 2006e) appear to contain comprehensive discussions of data relating to relevant processes and these reports do not always make use of the material presented in the Data Report.

Key findings of the canister, buffer, and backfill data review are as follows:

- Material properties that are described as well-defined and available in handbooks are not listed but should be provided and handbooks should be cited.

- The Data Report is one of the series of SR-Can safety assessment reports and, in this review, it was anticipated that the Data Report would provide the primary source of data on the canister, insert, buffer, and backfill. Further, it was expected that other reports in the safety assessment series would refer to relevant sections of the Data Report when analysing specific processes and scenarios, and that the Data Report would cross-refer to the relevant analysis in the safety assessment documentation. However, the Data Report does not always provide clear information on how and where data are used in the SR-Can assessment. The importance of data to the safety assessment could be clarified with reference to relevant data entries in the AMFs, the purpose of the modelling that uses the data, and its discussion in the Main Report.

- In some cases, different discussions of particular parameters and data are provided in different reports. For example, independent discussions of buffer hydraulic properties are provided in the Main Report and the Buffer and Backfill Process Report, with secondary discussion in the Data Report. Greater traceability and less potential for inconsistency might be achieved if the Data Report served as a source of information for use in other safety assessment reports.

- A key decision on the use of FSW for the canister lid welds and an important discussion of defect size distribution are presented in a report that is written in Swedish and, therefore, can not be reviewed as widely as other parts of the assessment.

- It is not clear why canister failure under the design load is evaluated as a residual scenario because such events have been shown to be unlikely. The growing pinhole failure model is also described in detail but is shown to be unlikely and is not considered as a residual scenario. The rationale for selecting residual scenarios is not clear.

- The calculation of the number of failed canisters and the timing of canister failure for each deposition hole rejection criterion has not been explained and there are no references to supporting documentation.

- The process by which the buffer model parameters have been abstracted from supporting experimental results is not clear and selection of many of these values is not traceable.

5.2. Code QA Review

The Model Summary Report provides a focus for reviewing the quality assurance status of the codes used in the SR-Can safety assessment. The categorisation of the codes and associated quality assurance requirements are consistent with the type of graded approach to software QA used in other radioactive waste management programmes.

A review of the entries for a selection of codes used in the safety assessment has found:

- The Model Summary Report provides greatly differing levels of detail for each code. Similar levels of information should be provided for each code.

- For some codes it is noted that training courses are available. However, it is not clear if procedures are in place to ensure that code users are suitably trained to apply the code in the SR-Can safety assessment.

- It is not clear if any particular criteria are used or standards sought in judging whether commercial software is acceptable for use in the SR-Can safety assessment.

- It is not clear if all of the codes discussed in the Model Summary Report have been used in the safety assessment (e.g., FARF32, FARF33, FracMan).

5.3. Conclusions

QA validates the programme of work that is undertaken towards the development of a repository safety assessment and, through planned and systematic actions and training, provides confidence in the performance of those who develop the safety assessment. SKB has developed a QA plan for the SR-Can project but acknowledges that only parts of the QA plan have been implemented. A comprehensive QA plan should be developed and implemented in a transparent way for the SR-Site safety assessment in order to build confidence in the validity of the assessment.

The SR-Site safety assessment and associated QA records should include information that demonstrates that a full QA system has been implemented. Based on a review of data and models used in the SR-Can safety assessment, the following observations can be made regarding the approach to demonstrating QA in the SR-Site safety assessment:

- The data and parameter values used directly in the safety assessment should be obtained from controlled sources or suitable external references such as textbooks or peer-reviewed journals. Information should be provided on how data are managed and controlled such that the data are selected and used appropriately in safety assessment calculations. The Data Report (SKB, 2006c, Section 1.4) notes that field data obtained from various site investigation activities are entered into the Sicada database. It should be made clear that the Sicada database or an alternative system is used to manage all data and source documents used in the safety assessment. Procedures for ensuring that controlled and quality assured data and parameter values are obtained for use in the safety assessment should be explained.

- Comprehensive references to controlled data sources and documentation on data abstraction to derive parameter values for all data sets should be included in the Data Report. The Data Report should become the primary reference for data and parameter values used in the safety assessment to build confidence that data and parameter values are used consistently and traceably throughout the safety assessment.

- Information on the review criteria or procedures used by the SR-Site team (i.e. the equivalent to the SR-Can review team) to determine whether a particular data set is acceptable for use in the safety assessment should be provided. Also, the means by which the SR-Site review team is managed in situations where the review team members have been involved in the acquisition and interpretation of the data under review should be explained. Procedures for accepting data for use in the safety assessment should include a check that the data qualification process has been documented, and confirmation that data were acquired under appropriate quality assurance procedures or that suitable data qualification methods have been applied (such as confirmation testing, peer review, or independent technical assessment).

- The Main Report (SKB, 2006a, Section 2.8) notes an objective and a review plan relating to review and approval of safety assessment reports. The preface of each report lists document reviewers. However, to build confidence in the review process, information should be provided on the method of selection of reviewers, the review criteria (which might include consideration of whether the report meets its intended purpose and consideration of the technical adequacy and accuracy of information), the process of comment resolution, and the availability of review records.

Traceability of information on code usage in the safety assessment and confidence in code reliability could be improved by including the following information on each code in the Model Summary Report:

- The original requirement for the code in SKB's repository research programme and the rationale for the approach to developing or selecting the code (in-house or commercial).

- The role of the code in the safety assessment, with cross-references to where associated FEPs, input data, and code applications are presented, and to where results are used in the safety assessment documentation (possibly through greater use of the AMFs).

- Procedures for checking and reviewing code application in the safety assessment and availability of review records.

The demonstration that software QA procedures have been applied appropriately in the safety assessment project should be comprehensive, covering all codes used in supporting analyses that have important impacts on decision-making for the safety assessment. Such analyses could be identified through entries in the AMFs, such as derivation of input data or intermediate assessments of data and results.

6. References

Andersson, C-G., 2002. Development of Fabrication Technology for Copper Canisters with Cast Iron Inserts. Status Report in August 2001. SKB Report TR-02-07. SKB, Stockholm, Sweden.

Andersson, C-G., Andersson, M., Erixon, B., Björkegren, L-E., Dillström, P., Minnebo, P., Nilsson, K-F., and Nilsson, F., 2005. Probabilistic Analysis and Material Characterisation of Canister Insert for Spent Nuclear Fuel. SKB Report TR-05-17. SKB, Stockholm, Sweden.

Bond A.E., Hoch, A.R., Jones, G.D., Tomczyk, A., Wiggin, R.M., and Worraker, W.J., 1997. Assessment of a spent fuel disposal canister. Assessment Studies for a Copper Canister with Cast Steel Inner Component. SKB TR-97-19. SKB, Stockholm, Sweden.

Börgesson, L., Fälth, B., and Hernelind, J., 2006. Water Saturation Phase of the Buffer and Backfill in the KBS-3V Concept: Special Emphasis given to the Influence of the Backfill on the Wetting of the Buffer. SKB Report TR-06-14. SKB, Stockholm, Sweden.

Börgesson, L., Fredrikson, A., and Johannesson, L-E., 1994. Heat Conductivity of Buffer Materials. SKB Report TR-94-29. SKB, Stockholm, Sweden.

Börgesson, L. and Hernelind, J., 1999. Coupled Thermo-Hydro-Mechanical Calculations of the Water Saturation Phase of a KBS3 Deposition Hole. Influence of Hydraulic Rock Properties on the Water Saturation Phase. SKB Report TR-99-41. SKB, Stockholm, Sweden.

Börgesson, L. and Hernelind, J., 2006a. Earthquake Induced Rock Shear through a Deposition Hole. Influence of Shear Plane Inclination and Location as well as Buffer Properties on the Damage Caused to the Canister. SKB Report TR-06-43. SKB, Stockholm, Sweden.

Börgesson, L. and Hernelind, J., 2006b. Consequences of Loss or Missing Bentonite in a Deposition Hole: A Theoretical Study. SKB Report TR-06-13. SKB, Stockholm, Sweden.

Börgesson, L. and Johannesson, L-E., 1995. Thermo-hydro-mechanical Modelling of Water Unsaturated Buffer Material. Status 1995. SKB AR 95-32. SKB, Stockholm, Sweden.

Börgesson, L., Johannesson, L-E., and Hernelind, J., 2004. Earthquake Induced Rock Shear through a Deposition Hole. Effect on the Canister and Buffer. SKB Report TR-04-02. SKB, Stockholm, Sweden.

Börgesson, L., Johannesson, L-E., Sandén, T., and Hernelind, J., 1995. Modelling of the Physical Behaviour of Water Saturated Clay Barriers. Laboratory Tests, Material Models and Finite Element Application. SKB Report TR-95-20. SKB, Stockholm, Sweden.

Cliffe, K. A. and Kelly, M., 2004. COMP23 Version 1.2.2 User's Manual. SKB Report R-04-64. SKB, Stockholm, Sweden.

Dillström, P., 2005. Probabilistic Analysis of Canister Inserts for Spent Nuclear Fuel. SKB Report TR-05-19. SKB, Stockholm, Sweden.

Fälth, B., Hökmark, H., 2007. Mechanical and Thermo-Mechanical Discrete Fracture Near-Field Analyses Based on Preliminary Data from the Forsmark, Simpevarp and Laxemar Sites. SKB Report R-06-89. SKB, Stockholm, Sweden.

Hedin, A., 2002. Integrated Analytic Radionuclide Transport Model for a Spent Nuclear Fuel Repository in Saturated Fractured Rock. Nuclear Technology, 138 2 179.

Hedin, 2004. Integrated Near-field Evolution Model for a KBS-3 Repository. SKB R-04-36. SKB, Stockholm, Sweden.

Hicks, T.W., 2005. Review of SKB's Code Documentation and Testing. SKI Report 2005:05. SKI, Stockholm, Sweden.

Hicks, T.W., 2007. Review of Quality Assurance in SKB's Repository Research Experiments. SKI Report 2007:11. SKI, Stockholm, Sweden.

Hökmark, H. and Fälth, B., 2003. Thermal Dimensioning of the Deep Repository. Influence of Canister Spacing, Canister Power, Rock Thermal Properties, and Nearfield design on the Maximum Canister Surface Temperature. SKB Report R-03-09. SKB, Stockholm, Sweden.

Hökmark, H., Fälth, B., Wallroth, T., 2006. T-H-M Couplings in Rock: Overview of Results of Importance to the SR-Can Safety Assessment. SKB Report R-06-88. SKB, Stockholm, Sweden.

Johannesson, L-E., and Nilsson, U., 2006. Deep Repository – Engineered Barrier Systems. Geotechnical Properties of Candidate Backfill Materials. Laboratory Tests and Calculations for Determining Performance. SKB Report R-06-73. SKB, Stockholm, Sweden.

Johannesson, L-E., Nord, S., Pusch, R., and Sjöblom, R., 2000. Isostatic Compaction of Beaker Shaped Bentonite Blocks on the Scale 1:4. SKB Report TR-00-14. SKB, Stockholm, Sweden.

Karnland, O., Muurinen, A., and Karlsson, F., 2005. Bentonite Swelling Pressure in NaCl Solutions – Experimentally Determined Data and Model Calculations. Advances in Understanding Engineered Clay Barriers. Alonso & Ledesma (eds), 2005, Taylor & Francis Group, London.

Karnland, O., Olsson, S., and Nilsson, U., 2006. Mineralogy and Sealing Properties of Various Bentonites and Smectite-rich Clay Materials. SKB TR-06-30. SKB, Stockholm, Sweden.

Kelly, M. and Cliffe, K. A., 2006. Validity Document for COMP23. SKB Report R-06-76. SKB, Stockholm, Sweden.

King, F., Ahonen, L., Taxén, C., Vuorinen, U., and Werme, L., 2001. Copper Corrosion under Expected Conditions in a Deep Geologic Repository. SKB Report TR-01-23. SKB, Stockholm, Sweden.

Neretnieks, I., 2006. Flow and Transport through a Damaged Buffer. Exploration of the Impact of a Cemented and Eroded Buffer. SKB Report TR-06-33. SKB, Stockholm, Sweden.

Nilsson, K-F., Lofaj, F., Burström. M., and Andersson, C-G., 2005. Pressure Tests of Two KBS-3 Canister Mock-ups. SKB Report TR-05-18. SKB, Stockholm, Sweden.

Ochs, M. and Talerico, C., 2004. SR-Can. Data and Uncertainty Assessment. Migration Parameters for the Bentonite Buffer in the KBS-3 Concept. SKB Report TR-04-18. SKB, Stockholm, Sweden.

Roos and Gelin, 2003. Letter Report to Lars Werme. SKB, Stockholm, Sweden.

SKB, 2004. Interim Main Report of the Safety Assessment SR-Can. SKB Report TR-04-11. SKB, Stockholm, Sweden.

SKB, 2006a. Long-Term Safety for KBS-3 Repositories at Forsmark and Laxemar – a First Evaluation (Main Report of the SR-Can Project). SKB Report TR-06-09. SKB, Stockholm, Sweden.

SKB, 2006b. Initial State Report for the Safety Assessment SR-Can. SKB Report TR-06-21. SKB, Stockholm, Sweden.

SKB, 2006c. Data Report for the Safety Assessment SR-Can. SKB Report TR-06-25. SKB, Stockholm, Sweden.

SKB, 2006d. Fuel and Canister Processes Report for the Safety Assessment SR-Can. SKB Report TR-06-22. SKB, Stockholm, Sweden.

SKB, 2006e. Buffer and Backfill Processes Report for the Safety Assessment SR-Can. SKB Report TR-06-18. SKB, Stockholm, Sweden.

SKB, 2006f. Model Summary Report for the Safety Assessment SR-Can. SKB Report TR-06-26. SKB, Stockholm, Sweden.

SKB, 2006g. Kapsel för använt kärnbränsle. Svetsning vid tillverkning och förslutning. SKB Report R-06-04. (In Swedish). SKB, Stockholm, Sweden.

Smart, N.R., Blackwood, D.J., and Werme, L., 2001. The Anaerobic Corrosion of Carbon Steel and Cast Iron in Artificial Groundwaters. SKB Report TR-01-22. SKB, Stockholm, Sweden.

Smart, N.R., Blackwood, D.J., and Werme, L., 2002a. Anaerobic Corrosion of Carbon Steel and Cast Iron in Artificial Groundwaters: Part 1 – Electrochemical aspects. In: Corrosion 8(2002):7 pp 47– 9.

Smart, N.R., Blackwood, D.J., and Werme, L., 2002b. Anaerobic Corrosion of Carbon Steel and Cast Iron in Artificial Groundwaters: Part 2 – Gas generation. In: Corrosion 8(2002):8 pp 627–637.

Vahlund, F., and Hermansson, H., 2006. Compulink – Implementing the COMP23 Conceptulisation in Simulink. SKB Report R-06-86.

5

Review of climate and climate-related issues in the safety assessment SR-Can

Per Holmlund

Department of Physical Geography and Quaternary Geology
Stockholm University
106 91 Stockholm
Sweden

Foreword

This is a review of the SKB report; Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation. Main report of the SR-Can project. (SKB TR-06-09). In order to make this review thoroughly, one contributing technical report is included in the review: Climate and climate-related issues for the safety assessment SR-Can (SKB TR-06-23).

Table of contents

1. Introduction

The review concerns climate and ice sheet issues. It is satisfactory to note that significant improvements have been made since the last SR-Can (SKB TR-04-11) report was published. There is no doubt that past evaluations have been useful to SKB and fruitful criticism has been taken into account while carrying out this work. The task to find methods to store radioactive waste in a responsible way for many generations to come is huge and requires great efforts free from prestige. I find that SKB has made serious attempts to fill in the gaps that have previously been identified by SKI in evaluation processes.

I begin this review with a short summary of the contributing technical report as it is the basis for the main report.

2. Climate and climate-related issues for the safety assessment SR-Can (SKB TR-06-23)

The review is focussing on climate and ice sheet issues. Technical descriptions on the design of the repository and rock stability is thus outside the scope of this review unless it has a direct coupling to climate and the ice itself.

2.1. Description of the report

The report describes two extreme scenarios; an ice age and a climate warmer than the present. The ice age scenario is described by the Weichselian glacial and the warmer climate is based on the GCM computations on the effect of a human induced enhanced greenhouse warming. None of the two extremes is proposed as the most likely one but they are believed to close in the future climate.

The introduction explains the climate system, giving most basic information on climate forcing and the climate of today. One paragraph describes the climate at the specific sites Forsmark and Oskarshamn.

Under the heading *Climate-related Issues* five different approaches are described where four are dependent on the first one, ice sheet modelling. The issue of numerical ice sheet modelling is based on a model which was developed by professor James Fastook at University of Maine. The model, here named UMISM, is well known and respected in the literature. Input data to the ice sheet model is; a digital terrain model, geothermal heat flux, air temperature and sea level changes over time and information on ice properties and a climate description. Output data from the model is; ice thickness, en- and sub glacial temperatures, ice velocity, direction of movement isostatic depression of crust and amount of melting/freeze on beneath the ice. The model itself is not well described but the basic physics of glaciers and ice sheets is described in a clear and for this aim thorough way. Examples of outcome data is given in a clear and concise way.

Based on the outcome of the ice sheet model four sub chapters follows on; ice sheet hydrology, isostatic movements, permafrost, and glacially induced faulting. The hydrology section describes basic knowledge in the subject and also some good examples of relevant observations from the Greenland Ice sheet.

The chapter on isostacy includes modelling experiments carried out by Dr Pippa Whiterhouse at University of Durham. The model in itself is not described but descriptions are found in references. The model gives results based on the ice sheet modelling scenario and also a sensitivity test based on alternative ice sheet thickness and duration of ice load.

The issue of permafrost is based on modelling work by Juha Hartikainen at Helsinki University of Technology and by Tomas Wallroth at Bergab in Sweden. The model is not described in the text but is to be found in the references given. The model is based on the paleo climate record used for the ice sheet model, and on duration of ice coverage and basal temperature data from the model. The complexity of the permafrost issue is well described by the influence of taliks, surface vegetation and the repository itself. In addition to the proposed climate record they use alternative colder and warmer climates just to illustrate the sensitivity of the model results.

The last issue is rock faulting due to the load and release of ice load. This chapter is written by Björn Lund at Uppsala University. It gives background to the set up of stresses in the rock and he also shows some modelling results on the distribution of stress for different ice loads. The section also gives a background to this scientific field.

After these chapters on climate-related issues there is a concluding chapter on evolution of conditions. Its is based on the modelling outcome of the ice sheet, permafrost and isostacy. The description includes two "main scenarios" flavoured by input on hydrology and geology. The first main scenario called the *base variant* includes a glacial cycle entirely based on data from the Weichselian. The second main scenario is called *greenhouse variant* based on possible effects of a human induced enhanced greenhouse warming lasting several thousands of years into the next glacial. The general conclusion is that the greenhouse variant is much less problematic than the base variant.

Finally the authors make some comparisons between the model results and present day analogies and some model tests on extreme input data indirectly concluding that the base variant seem realistic as an ice age scenario.

2.2. Strengths

This report is well written and has a good structure, though I personally would have organised the chapters slightly different upgrading the ice sheet modelling on which all other issues depend. The scientists involved are all active scientists well updated with the front of their field. The approach using the Weichselian ice age as a base variant is excellent. We know nothing about the future besides that we most probably will face a glacial and that the near future most probably will get warmer. But we know rather well what we have had. So the resultant two main scenarios are probably as close as we can get in defining boundary conditions for external forces on a repository. So the strengths are good scientists, good models and good scenarios.

2.3. Weaknesses

There are some weaknesses that need some extra consideration and they are; the climate record, limitations/undescribed weaknesses of the ice sheet model, the hydrology, the greenhouse variant and some other issues. These fields are all basically well handled in the report, but in order not to transfer uncertainties they need more consideration. I do not see anything I find incorrect, but much more is to be said.

3. Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation. Main report of the SR-Can project

This report is a synthesis of several technical reports, among them the one reviewed above. In the introduction the SR-Can safety assessment is described. It includes investigations on the state of the system, technical issues on the repository and on external forces. The methodology includes ten steps and the final step is the conclusions. However, it is very unclear how these steps interact with each other. Is there a time transgression and will the results from any of the *lower* steps have any impact on the final step? They probably will, but it is not shown in the report how this process works.

On page 38-39 a summary of received results are described and on page 53 the structure of this report is shown which shows a clear and logic structure. The climate and ice sheet related parts are described in three different domains; the glacial-, the permafrost-, and the temperate domain. The information is basically received from report SKB TR-06-23 and to some extent from SKB TR-06-34.

3.1. The climate record

The climate record is based on the GRIP data from Summit in Greenland (Johnsen et al 1995). This is a very good data set showing how climate has varied over time and the period of the last glacial is well described in the data. The most recent data from North Grip is herein believed to be an even better source of climate data for coming modelling experiments on the Weichselian. This is probably true and the North Grip data will force an ice sheet model to act slightly different than GRIP data shows.

Ice cores provide us with climate data on precipitation and to some extent wind directions but not temperature. Temperature is to be interpreted out of empirical relations between temperature and fractionations of stable isotopes of oxygen and hydrogen (Johnsen et al 1995, Jouzel et al 1997). Such relations can successively be constructed for the present day situation. The fractionation depends on temperature, but also on how much rainfall/snowfall that have drained the air mass prior to deposition, it depends on where the source for the water is. It also depends on air flow direction, on distribution of precipitation over seasons etc (Paterson 1994). Finally, the very important fact that ice core data is sampled on top of the Greenland ice sheet and not in Scandinavia. Thus, the paleo climate record must be handled with substantial care. This issue is discussed briefly on page 51-52 in SKB TR-06-23 but the large uncertainties are not really considered in the report.

For general descriptions of the glacial these data sets, with their translations into temperature, are good enough. One can argue that this is as close as we can get. The problem arises when interest is focussed on specific sites as in this case, then the uncertainties become tremendous both in time of ice coverage and in absolute air and basal temperatures. There is no way you can tell whether or not the average temperature during a certain time period was -15 or -20 or -25 ^{o} C. The ice sheet model may not be so sensitive for these differences, but the permafrost model is.

A thorough analyses of transfer functions for temperatures between Greenland and Sweden is needed and an investigation of how the fractionation may have varied over time using different possible scenarios. Special focus should be paid to the coldest parts of the glacial. If such analyses are too complicated to perform, much larger error bars are needed in all results.

On page 482 the translated GRIP-curve is presented. Due to the significant uncertainties in such translations, the curve is seldom presented like this in scientific literature anymore. A better way is to show the gradings in $D^{18}O$ and add a suggested temperature translation. An alternative is to add large error bars as a shaded zone in which the author believes the temperature falls. The way it is presented here is not good as readers may believe that this is a real temperature record. The discussion on the same page of the proxy temperature curve indicate that there are uncertainties but it is rather described as different views than a well known problem.

3.2. Permafrost

The permafrost calculations include large uncertainties which are not shown. It is both uncertainties in the estimations themselves and uncertainties in the input data. For the last glaciation, the air temperature over central Greenland might be estimated within 10 degrees or so, but not better than that. What this means for estimations of the climate in Scandinavia is difficult to say but it is very clear that the uncertainty in the temperature record is significant (Jouzel 1997). It makes a major difference to permafrost calculations if we have a several thousands of years long period with -10 or -20 degrees. The point is that we cannot tell from our paleodata what absolute temperatures we had during the ice age. A fair estimation of error bars is thus an absolute need for the interpretation of the results.

On page 480 the temperature in a repository as interpreted from sensitivity tests is shown. According to the model the temperature at Forsmark needs to be lowered by 10,5 degrees compared to the used temperature curve. The indirect conclusion is that this is not very likely. But we know that there are large error bars on the temperature curve, and the error bars of the model results are not presented so it is really difficult to judge whether or not the presented scenario is probable. And, glacial erosion over the one million year scenario is not considered which is a weakness as it will change the potential for permafrost to reach the repository during successive glaciations.

3.3. The ice sheet model and settings

The ice sheet model is well known internationally (Fastook 1994, Fastook and Prentice 1994. This may act as a guarantee for the quality of the outcome. But a model is by necessity a severe simplification of the reality, and the outcome must always be treated as model results, not the reality. A numerical model can be tuned to show a variety of results dependent on what the author intend describe or tell. And, different ice sheet models give inevitably different results as they handle the physics differently. Thus the crucial thing in a model is how the physics is simplified to make the model possible to run. A simple model has the advantage of being transparent in its response to different parameters. In a more complex model this becomes more difficult to understand. As the outcome of the ice sheet model in this case is so fundamental for the rest of the report I think it would have been useful with some sections on how the physics is handled. Effort is paid to describe ice physics, but not how it is simplified in the model.

However, this is an internationally highly ranked ice sheet model. The present day ice sheets on Greenland and Antarctica have been used for test runs to tune the model (Fastook and Prentice 1994). At these sites climate, ice sheet extensions and thickness, ice temperatures etc are fairly well known. So there are good reasons to believe that the Weichselian ice sheet is well described. The Greenland Ice sheet is about 3500 m thick and the Antarctic ice sheet is about 4500 m and the modelled maximum ice thickness of the Weichselian ice sheet lies within these numbers. The only reflection one may make is that the suggested 3300 m may be somewhat low. Besides numerical models on isostacy and the ice sheet there is one more indication on what the maximum ice thickness may have been. When the glaciation reached its maximum we know that the center of the ice was somewhere over the Gulf of Bothnia and we know that the main ice flow was towards south, but it was also a flow to north west, towards the Atlantic ocean (Kleman et al. 1997). If we generalize and say that the ground elevation at the water divide between Norway and Sweden lies at 1000 m above sea level and we assume that the ice was at least 1000 m thick (depressing the land about 300 m) end up with a surface at about 1700 m at the water divide. In order to have a flow from the Gulf of Bothnia the ice surface must be more elevated than 1700 m. Using simple theory for a parabolic ice sheet (Denton and Hughes 1981, Hooke 1977, 2005) the centre must have been 500-1000 m higher, giving an ice surface between 2200 m and 2800 m. These are low numbers. Assuming a depression of the base based on a 3:1 ratio between ice and rock this may correspond to an ice thickness of 2900-3700 m which shows a perfect match with the 3300m suggested by SKB. Thinner values are not likely, but it may have been thicker. However, the estimations shown in the SR-Can report seems realistic.

3.4. Glacial hydrology

The hydrology chapter is somewhat loosely linked to the rest of the report SKB TR-06-23 but this is not so clear in the main report. The problem is that the chapter is very general by necessity as real measurements on glacial hydrology from ice sheets are almost non existent. Some complex matters are thus in a need for a much more thorough discussion than what is found here and thus the conclusions are incomplete and do to some extent contradict the modelling results as described below. The hydrology chapter is based on findings on temperate glaciers which for simplicity can be seen as permeable for melt water. Moulins and crevasses act like entrances for the water into the glacier and water influences the ice flow (Paterson 1994). In a polar ice sheet the situation is very different. The ice is massive and is all below the freezing point. This can be seen and measured in the deep boreholes executed on the Greenland ice sheet. The problem arises when melt water is produced at the surface; how does the surface water reach the bottom? On Greenland it has recently been observed that ice velocities respond to surface melt from the front up towards the equilibrium line where the ice is 1000-1500 m thick (p. 60-62 in SKB TR-06-23)(Zwally et al. 2002). Possible processes for how water may penetrate thick cold ice has been suggested by several authors (Alley et al 2005, Weertman 1973) since the late 1960s but this is not at all a solved problem yet. And even if suggested theories are working we may keep in mind that the ice is at a temperature below the freezing point. It is not a temperate ice, though its base may reach the pressure melting point. In a figure used in this report it is shown a longitudinal section of an ice sheet approximately 500-700 km in length (p. 139 in SKB TR-06-23). It shows a frontal zone of significant extension with basal melting and the thicker the ice gets the bottom becomes gradually colder to a frozen interior. Such a thermal distribution makes sense for the hydrology discussion as it is one prerequisite for the opening of a hydrologic connection between the ice surface and the bottom. But it has absolutely nothing in common with the ice sheet model which suggests a cold frontal part and a gradually warmer base where the glacier is thick. Such a distribution is physically plausible and it is also the one which is used in most of the report.

More effort is needed on this topic as it set the boundary conditions for example groundwater hydrology calculations. A more critical analysis of observations and theories concerning ice sheet hydrology is needed and the glacial hydrology needs to be better integrated into the other climate related issues. And the critical question is never ansvered; how does the glacial hydrology evolve during a glaciation at, and what impact will it have on, the sites where Forsmark and Oskarshamn are situated?

On page 335 the glacial hydrology is discussed. A subdivision in sub- en- and supraglacial hydrology is suggested. This is the standard way of describing glacial hydrology (Paterson 1994) but this does not mean that all these sub systems are represented on all glaciers. On a polar glacier the bottom may reach the pressure melting point if for example the ice is thick enough and there may be surface melting. But it is difficult to tell how to treat the englacial system. The ice of a polar glacier is below the freezing point and thus dry. On a cold ice sheet it is more pedagogic to say that the englacial system is absent though there may be some open links between surface and bottom. In this report the englacial system is discussed as if it was in a temperate glacier which is misleading.

In the technical report SKB TR-06-34 it is stated that research is needed on existing ice sheets in order to significantly improve our knowledge. I would like to sharpen this statement and say that it is an absolute necessity to conduct research on present day ice sheets to draw reliable conclusions on ice sheet hydrology.

3.5. Glacial erosion

The effect of glacial erosion is not held as a major problem in the process which is somewhat surprising as the time perspective covers 1 million years which may include ten large scale glaciations. There are two issues to consider; the erosion potential and the duration of the ice cover. There are several estimations on the erosion potential of temperate glaciers and they all end up at 0.5-1 mm/year on crystalline bedrock, where values around 1 mm is the most commonly used value (Schneider and Bronge 1996). It is a measure of both suspended sediments and bed transport. On looser rocks such as volcanic rocks on Iceland and New Zeeland the erosion rates are significantly higher. But 1 mm/year is the commonly used average erosion rate. It means 1 m/thousand years of and wet based ice sheet. If the temperature drops below the pressure melting point the ice freezes on to the bed and no erosion will occur.

The duration of the ice coverage is much more difficult to estimate. 15 years ago I used an earlier version of the UMISM model in a modelling experiment order by the Statens Kärnbränslenämnd and later printed by Statens Kärnkraftinspektion (Holmlund 1993). The model has been developed and improved since then but the basic handling of the physics has probably not changed. In the present report the duration of the Weichselian glaciation at Forsmark and Laxemar is estimated to 30 000 years and 19 000 years respectively. In my experiment these durations were twice as high, namely 60 000 and 40 000 years. One significant difference between these two experiments is the forcing. The GRIP data were only available for the deglaciation phase so we used the Camp Century data received in the 1960s from North West Greenland. The point given here is that two different input datasets from Greenland give very different results. However, the differences may also be explained by how the model is tuned.

In the present model SKB has differentiated between warm based and cold based ice coverage. This is excellent, though a result of a simplified temperature distribution model. Geological data on glacial erosion supports the general temperature regime as presented in the model, but data are crude.

Based on these arguments I find it fair to elaborate with 30 000 and 19 000 years of glacial erosion at the sites given. On a million year time scale this would correspond to 300 m of potential glacial erosion at Forsmark and 190 m at Laxemar. Such a scenario has a major impact on for example calculations on the effect of permafrost.

Glacial erosion is a powerful land reshaping process which is not fully understood. It covers the two processes of abrasion and plucking (Sugden and John 1976). Abrasion is an areal denudation while plucking is associated to a bed relief. It is not a simple differentiation between these two types of processes which can be exemplified by first a rouche moutonnée (rundhäll) where it is obvious that plucking occurs on the leeside and abrasion on the stoss side. In a fjord details like a roche moutonnée as a whole is rather part of a large scale abrasion and plucking occurs on large scale topographic obstacles. Using a simple model Hallet (1996) argued that glacial erosion is governed by the effective pressure at the base and the rate of basal sliding. In the ice sheet model used by SKB one of the output parameters is basal sliding length which thus may be indicative to the potential glacial erosion rate. There are several studies supporting limited effect on the ground by glaciations (e.g,.Kleman 1994 Lagerbäck 1988, Lidmar-Bergström 1996) as well as there are others describing giant glacial erosion rates. A good example of the latter is the quarrying of the Norwegian Fjords, such as Sognefjord where more than a thousand of metres have been removed by glacial erosion during the Quaternary (Nesje and Whillians 1994). The difference between the study sites is that the basal ice has been at the pressure melting point while excavating the fjords and mostly been below the freezing point at the sites where only little erosion have occurred. The basal ice temperature is thus a critical value whether or not glacial erosion will occur. Thus a significant glacial erosion must be considered as a realistic possibility during periods of a glacial cycle at the sites of concern in this report.

3.6. The greenhouse scenario

Among other critical comments I would like to highlight the way greenhouse warming is treated and how it is shown in the report. It is assumed that a warm period will last several thousands of years, which is in line with what is suggested by IPCC (IPCC 2007), and that the Greenland ice sheet is in danger.In this scenario it is suggested that the ice sheet will melt down over approximately a 1000 year period. The isostatic uplift over this period is about 6 m at Forsmark and 1 m at Oskarshamn. The Greenland ice sheet corresponds to 7 metres of sea level and a West Antarctic collapse corresponds to another 5 m (IPCC 2007). On top of these potential catastrophes we have thermal expansion of the sea. These issues are mentioned on page 143-144, but not really considered. In the scenario shown on page 144 no signs of such events are indicated which is somewhat surprising. There are perhaps good arguments for not to consider sea level rise as a threat, but it needs more than two pages to convince a reader. In addition to the effect of the transgression on the hydrology, a raised sea level will significantly enhance the salt content in the Baltic water.

On the pages 112 and 129 results and calculations on sea salt content in groundwater at depth is shown. The sea water intrusion from the Littorina stage is clearly seen at depths below 700-800 m which is below the suggested repository depths. However, on page 310-312 the future scenario is shown which show no sign of anything but a normal isostatic uplift and thus a decrease in salinity. But the greenhouse scenario is not considered. If the Greenland ice sheet melts, sea level will rise and sea salt content in the Baltic will consequently increase as it did during the Littorina stage. Thus, there is a major threat of a new salt water intrusion. This threat must be considered, if not in the figures, at least in the text.

3.7. Summary

The climate, ice sheet and cryosphere sections have been reviewed and the general judgement is that this is a thorough analysis, made in a positive wish to really solve the remaining problems. However, there are some gaps and weaknesses which can be summarized as follows:

- It is still unclear how results from different projects are implemented in the decision making process.
- More caution must be paid to error estimations and also on how errors are transferred between different steps in the analyses. Error bars should be presented also in the final results as they most often are used for further calculations introducing additional errors. The most striking example is the extensive use of oxygen isotope data from Greenland.
- Permafrost calculations are presented in a too simplified manor. There is no caution paid to errors in the climate forcing and in effects of potential glacial erosion. The threat of permafrost becomes more severe if these items are considered.
- The models used for different calculations should be better described. Much attention is paid to describe the physics of the real world, but less to how the physics is handled in the models which is crucial for the reliability of the model.
- The glacial hydrology section needs to be better linked to the ice sheet modelling results and more adopted to polar environments.

- Glacial erosion is not considered for some unexplained reason.
- The green house scenario must be considered in a better way than at present. Melting Ice Sheets can certainly influence the sea level to such an extent that sea salt intrusion and influences on the ground water aquifers will occur.

More research including field campaigns is needed on

- Glacio-hydrology. Field studies must be performed at the Greenland Ice Sheet to obtain good analogies to a Scandinavian future ice sheet. The basis for the existing report is field experience and research carried out on temperate or polythermal glaciers. Polar ice sheets are very different, basically as a result of their different thermal regime.
- The common knowledge on potential glacial erosion of ice sheets is poor. More research is needed focussing on large scale glacial erosion. Both on variability in erosion rates, and on erosion processes coupled to the thermal conditions beneath ice sheets.

4. References

Alley, R.B., Dupont, T.K., Parizek, B.R. and Anandakrishnan, S., 2005: Access of surface meltwater to beds of subfreezing glaciers: Preliminary insights. *Annals of Glaciology* 42: 8-14.

Hallet, B., 1996: Glacial quarrying: a simple theoretical model. *Annals of Glaciology* 22: 1-8

Holmlund, P., 1993: Den senaste istiden I Skandinavien. En modellering av Weichselisen. SKI Teknisk Rapport 93:44

Hooke, R. LeB., 1977: Basal temperatures in polar ice sheets: a qualitative review. *Quaternary Research* 7: 1-13.

Hooke, R.LeB., 2005: *Principles of glacier mechanics.* Second Edition. Cambridge University Press, Cambridge

IPCC 2007: *IPCC 4th assessment report*. http://www.ipcc.ch

Johnsen, S.J., Dahl-Jensen, D., Dansgaard, W., Gundestrup, N., 1995: Greenland Palaeo-temperatures derived from GRIP bore hole temperature and ice core isotope profiles. *Tellus* 47B(5): 624-629.

Johnson, J. and Fastook, J.L., 2002: Northern Hemisphere glaciation and its sensitivity to basal melt water. *Quaternary International* 95-96: 65-74.

Jouzel, J., Alley, R.B., Cuffey, K.M., Dansgaard, W., Groots, P., Hoffmann, G., Johnsen, S.J., Koster, R.D., Peel, D., Shuman, C.A., Stievenard, M., Stuvier, M. and White, J., 1997: Validity of the temperature reconstruction from water isotopes in ice cores. Journal of Geophysical Research, 102 (C12): 26,471-26,487.

Kleman, J., 1994: Preservation of landforms under ice sheets and ice caps. *Geomorphology* 9: 19-32.

Kleman, J., Hättestrand, C., Borgström, I., Stroeven, A., 1997: Fennoscandian palaeoglaciology reconstructed using a glacial geological inversion model. Journal of Glaciology, 43 (144): 283-299.

Lagerbäck, R., 1988: The Veiki moraines in Northern Sweden – widespread evidence of early Weichselian deglaciation. *Boreas* 17 (4): 469-486.

Lidmar-Bergström, K., 1996: A Long-term Perspective on Glacial Erosion. *Earth Surface Processes and Landforms*. 22:297-306.

Nesje, A. and Whillians, I.M., 1994: Erosion of Sognefjord, Norway. Geomorphology 9: 33-45.

Paterson, W.S.B., 1994: *The Physics of Glaciers.* 3rd Edition. Oxford, Pergamon Press, 480 pp.

Schneider, T., and Bronge, C., 1996: Suspended sediment transport in the Storglaciären drainage basin. *Geografiska Annaler* 78A (2-3): 155-161

Seppälä, M., 2005: Glacially Sculptured Landforms. In *The Physical Geography of Fennoscandia* (Ed. By Seppälä), Oxford University Press, 432 pp: 35-57.

SKB TR-04-11, Svensk Kärnbränslehantering AB, 2004, Interim main report of the safety assessment SR-Can, Svensk Kärnbränslehantering AB, Stockholm.

SKB TR-06-23, Svensk Kärnbränslehantering AB, 2006, Climate and climate-related issues for the safety assessment SR-Can, Svensk Kärnbränslehantering AB, Stockholm.

SKB TR-06-34, Jansson, P., Näslund, J.-O., and Rodhe, L., 2007, Ice sheet hydrology - a review, , Svensk Kärnbränslehantering AB, Stockholm.

Sugden, D.E., and John, B.S., 1976: Glaciers and Landscape. (ISBN 0713158409), Edward Arnold, London, 376 pp.

Weertman, J., 1973: Can a water-filled crevasse reach the bottom surface of a glacier? In: IUGG-IAHS Symposium on the Hydrology of Glaciers, Cambridge 7-13 September 1973, 1969. *IAHS Publication* 95: 139-145.

Zwally, H.J., Abdalati, W., Herring, T., Larsson, K., Saba, J., and Steffen, K., 2002: Surface melt-induced acceleration of Greenland ice-sheet flow. *Science* 297(5579): 218-222.

6

Future intrusion of oxygenated glacial meltwaters into the Fennoscandian shield: a possibility to consider in performance assessments for nuclear-waste disposal sites?

Pierre Glynn

U.S. Geological Survey
Reston, VA 20192
U.S.A.

Table of contents

1. Introduction

Provost et al. (1998) and Glynn and Voss (1999; also published in Glynn et al., 1999) considered the possibility that during future glaciations, oxygenated glacial meltwaters from two- to three-kilometer thick ice sheets could potentially intrude to the 500 m depth of planned nuclear-waste repositories. This possibility has been of concern because of potential negative effects on the stability of the repository engineered environment, and because of the potential mobilization of radionuclides should the oxygenated waters come into contact with the radioactive waste. The above reports argued that given the current state of knowledge, it was hard to discount the possibility that oxygenated waters could penetrate to repository level depth. The reports also suggested that oxidizing conditions might be present in the fractured rock environment for significant amounts of time, on the order of thousands to tens of thousands of years. In some earlier reports, Swedish and Finnish governmental agencies in charge of nuclear-waste disposal had considered the possibility that oxygenated meltwaters might intrude to the repository depth (SKI: 1992; Martinerie et al, 1992; Ahonen and Vieno, 1994). Subsequent to the publication of Provost et al. (1998), Glynn et al. (1999) and Glynn and Voss (1999), the Swedish Nuclear Fuel and Waste Handling Company (SKB) commissioned efforts to examine more thoroughly the possibilities that oxygenated meltwaters might occur under ice-sheet conditions and intrude to the repository depth.

The present review considers the following SKB reports that address this matter:

1) "Groundwater chemistry around a repository for spent nuclear fuel over a glacial cycle" by Auqué et al. (2006). This report summarizes and briefly discusses earlier work on the issue by Gascoyne (1999), Guimera et al. (1999; 2006), Puigdomenech et al. (2001: SKB TR-01-28 and SKB TR-01-05), and Sidborn and Neretnieks (2004). The report also refers to research conducted on the hydrogeochemistry of glacial meltwaters that has been published in the peer-reviewed literature.

2) “Changes in groundwater composition as a consequence of deglaciation: implications for performance assessment” by Guimera et al. (2006). This report follows up on the earlier O_2 transport modeling work of Guimera et al. (1999) and the recommendations of Gascoyne (1999). This report is extensively referred to and summarized by Auqué et al. (2006).

3) “Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation”. This is the main report of the SR-Can project (SKB, 2006). It does not add significant new insights regarding the possibility of penetration of oxygenated meltwaters, but does reflect the extent to which SKB has considered the possibility.

4) “Assessment of the oxygen consumption in the backfill: geochemical modeling in a saturated backfill” by Grandia et al. (2006). This report provides some mineralogical information that is of interest in the O_2 story, especially as it concerns O_2 consumption in the backfill.

5) “Mineralogy and geochemistry of rocks and fracture fillings from Forsmark and Oskarshamn: compilation of data for SR-Can” by Drake et al. (2006). This report on fracture mineralogy is of significant interest in relation to the possibility of penetration by oxygenated meltwaters, and is often referred to in Auqué et al. (2006) and Guimera et al. (2006).

The present review comments on three different issues relating to the possible penetration of oxygenated glacial meltwaters to repository depth: 1) the initial dissolved oxygen concentration in the intruding meltwaters, 2) the physical processes responsible for the intrusion of glacial meltwaters, and 3) the reactions of ferrous silicate minerals with the intruding oxygenated waters.

2. Dissolved oxygen in glacial meltwaters?

Based on their literature review, Auqué et al. (2006) comment that it is highly unlikely for glacial meltwaters beneath an ice sheet to have significant dissolved oxygen. They generally refer to meltwaters that have been sampled from the toe of alpine glaciers, and they comment that the few O_2 levels measured in these waters are generally at or below equilibrium with the atmosphere, and show significant dissolved sulfate as a product of the reaction of dissolved O_2 with pyrite made accessible from the glacial flour. As a result of their review, Auqué et al. (2006) use a dissolved O_2 value of 8 mg/L in all their subsequent calculations, although they state that levels of up to 45 mg/L might be reasonable.

Similarly, the initial dissolved oxygen concentration of 10 ppm used in the transport simulations conducted by Guimera et al. (2006) is 4 to 5 times lower than the values calculated by Glynn and Voss (1999) from actual measurements of basal ice gases in the Greenland ice sheet. Guimera et al. (2006) state that dissolved oxygen concentrations measured in meltwaters from alpine glaciers are at most 30 ppm, and are usually much lower than that.

Several concerns with the arguments presented in Auqué et al. (2006) and Guimera et al. (2006) are discussed below:

1) A small alpine glacier does not provide a relevant setting for the performance assessment. An alpine glacier is not anywhere near the dimensions of a 2- to 3-km thick ice sheet. The ice-flow and erosion dynamics, and consequently the opportunities for ice-trapped or meltwater-trapped oxygen to react or escape to the atmosphere are likely to be very different; indeed, it makes sense that meltwaters from small glaciers would have lower dissolved oxygen concentrations than would be found at the warm base of an ice sheet (i.e. the large area over which the ice sheet undergoes basal melting). Additionally, the amount of flushing of glacial rock flour, the nature of the flow (turbulent vs. laminar), the amount of available organic carbon, and the dissolved oxygen concentrations in meltwater beneath a warm-based ice sheet might be radically different from what is encountered in an alpine-glacier setting; especially in situations where dissolved oxygen analyses are performed on samples taken from meltwaters exiting the glacier, i.e. after the samples have had opportunity for significant degassing.

2) The geology and mineralogy of the rocks under the alpine glaciers considered by SKB differ from the conditions expected underneath a Fennoscandian ice sheet. For example, in the case of the Glacier d'Arolla, referred to in Auqué et al. (2006) and other SKB reports, it is expected that reaction with sulfides will consume dissolved oxygen because the glacier overrides schists (likely to contain significant pyrite) and gneisses. The granitic rocks of the Fennoscandian shield probably have a lower pyrite content, and also probably have different erosion characteristics.

In summary, the initial dissolved oxygen concentrations assumed for intruding glacial meltwaters by Auqué et al. (2006) and Guimera et al. (2006) and in prior SKB reports do not provide a "conservative approach" in approximating what the source dissolved oxygen levels might be beneath an ice sheet. Instead, measurements that have been made in basal ice from the Greenland ice sheet should be considered. Glynn et al. (1999) and Glynn and Voss (1999) cited such measurements by Souchez et al. (1995) and Stauffer et al. (1985) and came to a "conservative conclusion" that dissolved oxygen levels in glacial meltwaters beneath an ice sheet could exceed 45mg/L, which is a concentration 5 to 6 times greater than those used in Auqué et al.(2006), Guimera et al. (2006), and in other SKB reports.

3. Meltwater intrusion beneath an ice sheet?

Auqué et al. (2006) assume that glacial meltwaters will infiltrate into the ground-water environment only as the steep toe of the ice sheet passes above the repository, during glacial retreat. In their shortest scenario (case A), this passage takes only 40 years. In their longer scenario (case B), the toe of the ice sheet remains above the repository for a longer time, i.e. 1300 years.

Going beyond the situation considered in their cases A and B, Auqué et al. (2006; p. 77) state that the glacial meltwater gradient near the toe of the ice sheet is 160 times greater than the natural topographic gradient. They comment that under ice-free conditions, the shortest travel times to the repository canisters are on the order of about a year for "the worst placed canisters," based on flow simulations by Hartley et al. (2006: SKB R-06-98 and R-06-99). Consequently, Auqué et al. (2006) reason that under glacial conditions near the toe of the ice sheet, transport times might be as short as a few days. However, they do not consider this a realistic result and instead assume that the shortest realistic advective transport times are on the order of a few years.

The Guimera et al. (2006) report focuses primarily on the retardation of oxygen penetration, relative to the water, due to the reaction of the dissolved oxygen with reducing minerals. Similarly to Auqué et al. (2006), Guimera et al. (2006) assume that glacial meltwaters will only penetrate the ground-water environment during deglaciation as the toe of the ice sheet passes above the repository site. In the "worst case scenario" presented by Guimera et al (2006), the oxygen reaches a depth of 250 m after 2000 years of meltwater penetration.

In contrast to the Guimera et al. (2006) and Auqué et al. (2006) reports, the simulations made by Provost et al. (1998) show that glacial meltwaters infiltrate not only beneath the toe of the ice sheet, but rather over the entire area where the ice sheet is warm-based (a natural consequence of the geothermal gradient and of the insulation provided by the ice sheet). Furthermore, the infiltration occurs primarily as the ice sheet is advancing and increasing in size and height, rather than during glacial retreat. The regional hydraulic gradient established by a 2-km thick ice sheet, with a significant warm-based area, advancing over hundreds of kilometers, is the primary driving force responsible for the intrusion of glacial meltwaters in the ground-water flow simulations conducted by Provost et al. (1998). Although some of the glacial meltwaters may escape through channels near the base of the ice sheet, the sheer size of the ice sheet prevents this mechanism from being the dominant outlet for glacial meltwaters, as long as the basal meltwater pressures do not increase beyond the hydrostatic head represented by an up to 2-km thick water column. The results and conclusions of Provost et al. (1998) with respect to glacial-meltwater intrusion mechanisms and timing are further substantiated by the ground-water and ice-sheet simulations of Boulton et al. (1995a, 1995b). The simulations of glacial-meltwater intrusion offered by Provost et al. (1998) suggest that glacial meltwaters could be infiltrating for a minimum of 5000 years, and, conservatively, for 15000 years or more.

In light of the Provost et al (1998) and Boulton et al. (1995a, 1995b) simulations, and in a spirit of "conservatism", SKB could consider that glacial-meltwater intrusion into the ground-water system above and around a nuclear-waste repository may occur for at least 10,000 years, and probably longer. Considering these longer intrusion times, if the oxygen-penetration rates calculated by Guimera et al. (2006) are adopted (although those are still subject to question), oxygenated meltwaters would reach the repository depth (500 m) after 4000 years, and the contact with intruding oxygenated meltwaters could continue for at least another 6000 years.

The consequence of a longer period of potential infiltration is that oxygenated glacial meltwaters could potentially have 10 to 15 times longer than currently considered in SKB calculations to reach the repository before flow is reversed upward. In addition, this possibility strongly affects the possible degradation of the bentonite buffer through either: 1) the longer time of strong flushing with very dilute waters, or 2) the longer upward-flow periods during which highly saline waters might also degrade the bentonite.

4. How fast will ferrous-silicate minerals react with dissolved oxygen?

Mineral-water reactions and their rates are key in determining whether dissolved oxygen in intruding glacial meltwaters will reach repository depths, and how fast the redox front associated with the dissolved oxygen will travel through the ground-water system. This review comments first on how the Auqué et al. (2006) and then how the Guimera et al. (2006) reports have addressed this issue.

4.1. Comments on the reaction- rate analysis by Auqué et al. (2006)

Auqué et al. consider two possible cases in their discussion of the reactive transport of dissolved oxygen.

1) Transport in a single fracture

In this case, Auqué et al. (2006) assume that the oxygen does not react with minerals in the fracture, but instead diffuses into the matrix and reacts there with reducing Fe(II)-containing minerals, such as biotite. Because "matrix diffusion is slow compared to the kinetics of mineral dissolution," they consider that the entire Fe(II) content of the rock matrix is available for reaction with the oxygen as soon as it diffuses into the matrix. Auqué et al. (2006) assume that the matrix diffusion model of Sidborn and Neretnieks (2004) applies. For their "pessimistic case" (case B, with 1300 yrs of meltwater intrusion time), they estimate that the oxygen penetration depth in a single fracture would be 580 m, assuming an initial O_2 concentration of 8 mg/L. A 4x higher initial O_2 concentration would result in a doubling of this penetration depth according to the Sidborn and Neretnieks (2004) formula. A 9x longer intrusion time would result in a tripling of the O_2 penetration depth. If, in the spirit of conservatism, the higher initial dissolved oxygen concentration (45 mg/L) and longer meltwater intrusion time (15,000 yrs) suggested by Glynn and Voss (1999) had been used, an oxygen penetration depth of over 4.5 km would have been calculated using the Sidborn and Neretnieks (2004) formula.

The other consideration in the Sidborn and Neretnieks (2004) formula used by Auqué et al. (2006) is the factor Q/W (volume flux over fracture width) average, which corresponds to the product of a single-fracture transmissivity and the head gradient. This product linearly affects the estimated O_2 penetration depth. The Auqué et al. (2006) calculations assume a transmissivity of 10^{-7} m^2/s and a 1% gradient (in contrast to the 32% slope originally estimated for the toe of the glacier). It is unclear what reasonably "conservative" values of Q/W might be, but it seems that the Sidborn and Neretnieks (2004) model adopted by Auqué et al. (2006) could potentially be neglecting the effects of flow channeling in the fracture. Channeling could significantly reduce the surface area available for matrix diffusion, and could increase the advective velocity by at least a factor of 10 compared to that in a fully open fracture plane.

Auqué et al (2006) comment that investigations of matrix diffusion at the Pocos de Caldas site in Brazil provide "validation" of the Sidborn and Neretnieks matrix diffusion model: specifically, the extent of redox alteration observed along the fractures in the sandstone at this site is in line with the model calculations. Although the hydraulic, mineralogical and chemical properties, and matrix diffusion potential for granitic rocks are likely to be different than those for sandstone, these differences and their possible effects on matrix diffusion and redox reactions are not evaluated by Auqué et al. (2006).

2) O_2 transport in a deformation zone

The second case considered by Auqué et al. (2006) relates to O_2 transport in a "deformation zone" with a transmissivity of 10^{-4} m^2/s. They state that in this case, the higher transmisssivity prevents significant matrix diffusion and that, consequently, transport of the dissolved O_2 depends on its retardation through its reaction with reducing, fracture-filling Fe(II) minerals. In this case, the kinetics of the dissolution of the Fe(II)-containing minerals need to be considered at least over an initial travel distance over which the rate of release of Fe(II) from the minerals is less than what is needed to react with the infiltrating flux of dissolved O_2. Once the rate of release of Fe(II) is matched by the rate of influx of O_2, i.e. at a given "steady-state penetration distance," the further transport of oxygen and of the redox front associated with it depends entirely on the amount of available reactive Fe(II) compared to the amount of dissolved O_2 initially in the meltwater. Auqué et al. (2006) discuss and use results from Guimera et al. (1999, 2006) to calculate the steady-state distance, *ds,* and the further rate of advancement, *vr,* of the steady-state redox front.

For their kinetics calculations, Auqué et al. (2006) invoque the laboratory investigations of Malmström and Banwart (1997) and Samson et al (2005) on the dissolution of crushed powdered biotite in the absence of other dissolving silicate minerals. Auqué et al. (2006) also refer to the laboratory chlorite dissolution experiments by Brandt et al. (2003), Gustafsson and Puigdomenech (2003), Gustafsson et al. (2004), and Lowson et al. (2005) on crushed, powdered, pure chlorite. Auqué et al. (2006) comment that Guimera et al. (2006) used a much smaller specific-surface area for biotite (0.015 m^2/g) in modeling O_2 transport, compared to the specific-surface areas measured on the crushed, powdered, samples (2-5 m^2/g for the biotite and 0.5-7 m^2/g for the chlorite) used in the laboratory investigations mentioned above. Beyond the issue of the difference in specific-surface area, it is well known in the geochemical literature that mineral-dissolution rates obtained in the lab are invariably several orders of magnitude faster than rates observed under natural field conditions (cf. the discussions in Glynn et al. [1999] and in White and Petersen [1990]).

Auqué et al. (2006) comment that the laboratory dissolution results obtained for chlorite show dissolution kinetics that are 1.4 orders of magnitude slower than for laboratory biotite dissolution. In their Fe(II)-release rate calculations, however, Auqué et al. (2006) use the laboratory dissolution rate measured for biotite rather than that measured for chlorite.

Furthermore, they comment correctly that both biotite and chlorite have slower dissolution kinetics at near-neutral pH than either has under more acidic or more alkaline conditions. In fact, the minimum lab dissolution rates seem to occur around a pH of 8. It is debatable whether the minimum rates applicable under field conditions also occur near a pH of 8. In any case, based on the specific alpine glacial conditions in Grimsel Glacier meltwaters, they estimate that the rates applied to the modeling calculations should actually be those estimated for a pH of 9.4. This pH seems high given 1) a few available, generally lower pH measurements determined for glacial meltwaters; 2) the significantly lower pH values (near 8) measured at Äspö and in other ground waters from the granite-rich Fennoscandian shield; 3) the argument of partial pyrite reduction of the available dissolved glacial ice-derived O_2, which would produce protons and lower the pH; and 4) the fact that dissolved CO_2 could also be expected to be significant in the glacial meltwaters and would also lower the pH. In any case, a "reasonably conservative" assessment would consider a pH of 8 to be applicable; raising it by a unit or more essentially increases the dissolution rate by at least 0.3 orders of magnitude (i.e. at least a factor of 2, possibly more).

Using their chosen parameters, Auqué et al. (2006) estimate a steady-state penetration depth, *ds,* of 113 m for the oxygen redox front. Adjusting the initial dissolved oxygen concentration by a factor of six (to 45 mg/L), and the Fe(II) release rate by a factor of 2 means that a more conservative *ds* value would be about 1400 m; this calculation does not account for the fact that field dissolution rates are at least several orders of magnitude less than laboratory rates.

Furthermore, once the steady-state redox-front movement has been achieved, Auqué et al. (2006) estimate that the mass-balance-controlled rate of movement of the redox front will be on the order of 0.1 m/yr for a water advective rate of 316 m/yr. The Fe(II) mineral estimate used by Auqué et al. (2006) in their calculation, 0.6kg of Fe(II) mineral per liter of water, seems high given that this entire amount is expected to react with the intruding oxygenated water, without significant matrix diffusion taking place.

Similarly to the single fracture case, Auqué et al. (2006) do not evaluate the possibility that the entire deformation zone might not be available for water and O_2 transport; channeling of water flows is likely to occur, which could result in faster transport times and possibly less opportunity for matrix diffusion and for reaction with Fe(II) minerals.

4.2. Comments on the reaction rate analysis by Guimera et al. (2006)

Guimera et al. (2006) state that there is evidence of microbes in glacial ice (in cores from Antarctica) and that consequently the presence of microbes will enhance "the capacity of the system to buffer a redox front." However, it is not microbial presence but rather microbial activity that is important if indeed microbes have a role in accelerating the dissolution of Fe(II)-containing silicate minerals. This concept is somewhat questionable, although there is general agreement that microbes often serve to catalyze redox reactions. However, irrespective of whether microbes can actually enhance silicate dissolution, the catalytic/enzymatic activity of microbes in glacial meltwaters waters would be strongly impeded at lower temperatures, but would increase as the intruding meltwaters became warmer with depth.

Several other comments can be made concerning the reaction kinetics calculations (or the way they are reported) in the Guimera et al. (2006) report:

1) The calculations assign the total measured iron (both ferrous and ferric) to the ferrous iron of biotite, although the authors state that there are many other Fe fracture minerals, such as epidote and hematite. The iron in hematite is definitely ferric (i.e. already oxidized) and the iron in epidote is also usually in Fe(III) form. Therefore, this is not a conservative assumption in the Guimera et al. (2006) analysis.

2) Although the rate law used only applies far from equilibrium, the calculations do not lower the reaction rates as the waters approach saturation, or as the mineral becomes coated and passivated with Fe(III) oxyhydroxides. These assumptions result in significant overestimation of the oxygen consumption rate.

3) The calculations assume that the available Fe(II)-biotite (annite) surface area is 8.64 m^2/L. However, the calculated value is 100 times that, but as a measure of conservatism, the authors reduced it to 8.64. Two problems are identified as a result. First, the simulations assume that although the annite is reacting, the surface area available for reactions stays constant, which is not likely. There is evidence that only the edges of annite platelets commonly react, rather than the entire surface area (e.g. Samson et al., 2005). Secondly, a number of estimates are available for the exposed total mineral surface area in a fracture, and although those estimates vary widely, the calculations in Glynn and Voss (1999) using ^{222}Rn and U data from Äspö suggest that a total surface area of about 3 m^2/L is reasonable. The Guimera et al. (2006) calculations more than double this surface area and assume that it applies only to the biotite. This is not a conservative assumption in the Guimera et al. (2006) analysis.

4) It is well known that laboratory rates are many orders of magnitude faster than field rates because of higher surface areas, crushing of grains and creation of high-energy surface features, lack of passivation effects, and other conditions associated with laboratory experiments. The "safety factor" of 100 used in Guimera et al. (2006) should probably be greater, given “a spirit of conservatism”. Indeed, field rates for mineral dissolution are commonly slower than laboratory rates by 2 to 3 orders of magnitude or more. A “safety factor” should presumably exceed this relative rate difference between field and laboratory rates.

In summary, the Guimera et al. (2006) report does not appear to provide a conservative perspective in the investigation of the potential for oxygenated meltwater to penetrate to repository depths. The report might have been conservative, however, in choosing a maximum advective velocity of 500m/year for the glacial meltwaters. That velocity seems fast, although it may be reasonable when placed in the context of the SKB concept that glacial meltwaters intrude only when the steep toe of the ice sheet retreats above the repository site.

5. Conclusions

The SKB analyses conducted in the Guimera et al. (2006) and Auqué et al. (2006) reports do not provide sufficient evidence to discount the possibility that during glacial cycles over the next 120,000 to 1,000,000 years, oxygenated glacial meltwaters could intrude to repository depths (500m) and could stay in contact with the near-field environment of a nuclear-waste repository for 10,000 years or more. The performance analyses and calculations conducted by SKB seem optimistic, rather than conservative with respect to the possibility of oxygen intrusion for the following reasons.

1) The studies minimize the dissolved oxygen concentrations likely to occur in the intruding waters; they do not consider the physical differences between small alpine glaciers and continental ice sheets. Dissolved oxygen concentrations in waters exiting atmospherically equilibrated channels in these small glaciers are a fraction of those likely to occur in meltwater beneath an ice sheet.

2) The calculations do not consider the physical processes that could be responsible for significant and enduring meltwater intrusion over large warm-based areas of the advancing ice sheets (as argued by Provost et al., 1998).

3) The calculations overestimate the reaction potential and reaction rates for ferrous silicate minerals with the dissolved oxygen in the intruding glacial meltwaters.

6. References

Ahonen L, Vieno T, 1994. Effects of glacial meltwater on corrosion of copper canisters. YJT-94-13, Nuclear Waste Commission of Finnish Power Companies, Finland.

Auqué L F, Gimeno M J, Gómez J B, Puigdomenech I, Smellie J, Tullborg E-L, Wallin B, 2006. Modelling of groundwater chemistry over a glacial cycle. Background data for SR-Can. SKB TR-06-31, Svensk Kärnbränslehantering AB.

Boulton, G.S., Caban, P.E. , and Van Gijsell, K., 1995a, Groundwater flow beneath ice sheets: Part I - Large scale patterns: Quaternary Science Reviews, v. 14, p. 545-562.

Boulton, G.S., and Caban, P.E. , 1995b, Groundwater flow beneath ice sheets: Part II - Its impact on glacier tectonic structures and moraine formation: Quaternary Science Reviews, v. 14, p. 563-587.

Brandt F, Bosbach D, Krawczyk-Bärsch E, Arnold T, Bernhard G, 2003. Chlorite dissolution in the acid pH-range: A combined microscopic and macroscopic approach. Geochim. Cosmochim. Acta, 67: 1451–1461.

Drake H, Sandström B, Tullborg E-L, 2006. Mineralogy and geochemistry of rocks and fracture fillings from Forsmark and Oskarshamn: Compilation of data for SR-Can. SKB R-06-109, Svensk Kärnbränslehantering AB.

Gascoyne M, 1999. Long-term maintenance of reducing conditions in a spent nuclear fuel repository. SKB R-99-41, Svensk Kärnbränslehantering AB.

Glynn, P.D., and Voss, C.I., 1999, Geochemical characterization of Simpevarp ground waters near the Aspo Hard Rock Laboratory, Swedish Nuclear Power Inspectorate (SKI), SKI report 96:29, 210 p.

Glynn, P.D., Voss, C.I., and Provost, A.M., 1999, Deep penetration of oxygenated meltwaters from warm based sheets into the Fennoscandian Shield, in Use of Hydrological Information in testing groundwater flow models: Technical Summary and Proceedings of a Workshop organized by the NEA Coordinating Group on Site Evaluation at Design of Experiments for Radioactive Waste Disposal (SEDE) and by the Swedish Nuclear Fuel and Waste Management Company (SKB), Borgholm, Sweden, September 1-3, 1997, p. 201-241.

Grandia F, Domènech C, Arcos D, Duro L, 2006. Assessment of the oxygen consumption in the backfill. SKB R-06-106, Svensk Kärnbränslehantering AB.

Guimerà J, Duro L, Jordana S, Bruno J, 1999. Effects of ice melting and redox front migration in fractured rocks of low permeability. SKB TR-99-19, Svensk Kärnbränslehantering AB.

Guimerà J, Duro L, Delos A, 2006. Changes in groundwater composition as a consequence of deglaciation: implications for PA. SKB-R-06-105, Svensk Kärnbränslehantering AB.

Gustafsson Å B, Puigdomenech I, 2003. The effect of pH on chlorite dissolution rates at 25°C. In: R.J. Finch, D.B. Bullen (Editors), Scientific Basis for Nuclear Waste Management XXVI. Mat. Res. Soc. Symp. Proc., Vol. 757. Mater. Res. Soc., Pittsburgh, Penn., pp. 649–655.

Gustafsson Å, Molera M, Puigdomenech I, 2004. Study of Ni(II) sorption on chlorite – a fracture filling mineral in granites. In: J.M. Hanchar, S. Stroes-Gascoyne, L. Browning (Editors), Scientific Basis for Nuclear Waste Management XXVIII. Mat. Res. Soc. Symp. Proc., Vol. 824. Mater. Res. Soc., Warrendale, Penn., pp. 373–378.

Hartley L, Hoch A, Jackson P, Joyce S, McCarthy R, Rodwell W, Swift B, Marsic N, 2006. Groundwater flow and transport modelling during the temperate period for the SR-Can assessment: Forsmark area – Version 1.2. SKB R-06-98, Svensk Kärnbränslehantering AB.

Hartley L, Hoch A, Jackson P, Joyce S, McCarthy R, Swift B, Gylling B, Marsic N, 2006. Groundwater flow and transport modelling during the temperate period for the SR-Can assessment: Laxemar area – Version 1.2. SKB R-06-99, Svensk Kärnbränslehantering AB.

Lowson R T, Comarmond M-C J, Rajaratnam G, Brown P L, 2005. The kinetics of the dissolution of chlorite as a function of pH and at 25°C. Geochim. Cosmochim. Acta, 69: 1687–1699.

Malmström M, Banwart S, 1997. Biotite dissolution at 25°C: The pH dependence of dissolution rate and stoichiometry. Geochim. Cosmochim. Acta, 61: 2779–2799.

Martinerie P, Raynaud D, Etheridge D M, Barnola J-M, Mazaudier D, 1992. Physical and climatic parameters which influence the air content in polar ice. Earth Planet. Sci. Lett., 112: 1–13.

Provost, A.M., Voss, C.I., and Neuzil, C.E., 1998, Glaciation and regional ground-water flow in the Gennoscandian shield, SKI Technical Report 96:11, Swedish Nuclear Power Inspectorate, Stockholm, Sweden, 82 p.

Puigdomenech I, Ambrosi J-P, Eisenlohr L, Lartigue J-E, Banwart S A, Bateman K, Milodowski A E, West J M, Griffault L, Gustafsson E, Hama K, Yoshida H, Kotelnikova S, Pedersen K, Michaud V, Trotignon L, Rivas Perez J, Tullborg E-L, 2001a. O2 depletion in granitic media: The REX project. SKB TR-01-05, Svensk Kärnbränslehantering AB.

Puigdomenech I, Gurban I, Laaksoharju M, Luukkonen A, Löfman J, Pitkänen P, Rhén I, Routsalainen P, Smellie J, Snellman M, Svensson U, Tullborg E-L, Wallin B, Vuorinen U, Wikberg P, 2001b. Hydrochemical Stability of groundwaters surrounding a spent nuclear fuel repository in a 100,000 year perspective. SKB TR-01-28, Svensk Kärnbränslehantering AB.

Samson S D, Nagy K L, Cotton W B, III, 2005. Transient and quasi-steady-state dissolution of biotite at 22–25°C in high pH, sodium, nitrate, and aluminate solutions. Geochim. Cosmochim. Acta, 69: 399–413.

Sidborn M, Neretnieks I, 2004. Modelling biochemical processes in rocks: Analysis and exploratory simulations of competition of different processes important for ferrous mineral oxidation and oxygen depletion. In: V.M. Oversby, L.O. Werme (Editors), Scientific Basis for Nuclear Waste Management XXVII. Mat. Res. Soc. Symp. Proc., Vol. 807. Mater. Res. Soc., Pittsburgh, Penn., pp. 829–834.

SKB, 2006, Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation. Main report of the SR-Can project. SKB TR-06-09, Svensk Kärnbränslehantering AB.

SKI, 1992, SKI 1991 – Final disposal of spent nuclear fuel. Importance of the bedrock for safety. SKI Technical Report 92:20, Souchez, R., Lemmens, M., and Chappellaz, J., 1995, Flow-induced mixing in the GRIP basal ice deduced from the CO_2 and CH_4 records: Geophysical Research Letters, March 1995, p. 41-44.

Stauffer, B., Neftel, A., Oeschger, H., and Schwander, J., 1985, CO_2 concentration in air extracted from Greenland ice samples, *in* Greenland Ice Core: Geophysics, Geochemistry and the Environment: Langway, C., C., Oeschger, H., and Dansgaard, W., eds., American Geophysical Union, Geophysical Monograph 33, p. 85-89.

White, A.F. and Peterson, M.L., 1990, Role of reactive-surface-area characterization in geochemical kinetic models: *in* Chemical Modeling of Aqueous Systems II, Melchior, D.C.,and Bassett, R.L., eds., American Chemical Society Symposium Series, v. 416, p. 461-475.

7

Ekosystem och miljöpåverkan: Slutrapport för uppdrag inom SSI:s delprojekt

Karolina Stark

Systemekologiska institutionen
Stockholms universitet
106 91 Stockholm
Sweden

Innehållsförteckning

1. Inledning

Svensk kärnbränslehantering AB:s (SKB) säkerhetsanalys SR-Can är en första samlad bedömning av den långsiktiga säkerheten för ett KBS-3 slutförvar i Forsmark och Laxemar. Bedömningen i SR-Can är ett förberedande steg för en slutlig bedömning, kallad SR-site, som ska stödja en tillståndsansökan om ett slutförvar av använt kärnbränsle och kärnavfall i Sverige. SR-Can projektet avser även att skapa en dialog med tillsynsmyndigheter som SSI vad gäller exempelvis tolkning och tillämpning av föreskrifter.

SKI och SSI utför för närvarande en gemensam granskning av SKB:s SR-Can. Inom ramen för SSI:s delprojekt Ekosystem och miljöpåverkan har Karolina Stark utfört ett 5-veckors granskningsuppdrag. Nedan följer en sammanfattning av förslag och slutsatser i Karolina Starks uppdrag inom delprojektet. Syftet med uppdraget var att granska SKB:s redovisning av slutförvarets miljöpåverkan och de ekosystem modeller som SKB använder i förhållande till kraven i 6 och 7 §§ i SSI:s föreskrift 1998:1 och tillhörande allmänna råd SSI FS 2005:5.

SKB har i tidigare säkerhetsredovisningar inte redovisat slutförvarets framtida påverkan på miljön. Granskningen av SR-Can utgör en första möjlighet för SSI att ge synpunkter på SKB:s hantering av dessa frågor.

SKB har i SR-Can gjort en preliminär uppskattning av möjliga stråldoser till biota (djur och växter) från ett eventuellt framtida läckage från slutförvaret av använt kärnbränsle och kärnavfall. Hanteringen av strålskyddet av miljön är under förändring och har varit fokus för omfattande internationella satsningar det senaste decenniet. De senaste åren har nya riktlinjer och rekommendationer kommit från ICRP (ICRP, 2003) (som också ledde till nya råd i SSI:s föreskrifter) och EU-projekt som FASSET (FASSET, 2004) och ERICA (ERICA, 2007) som gör att det krävs nya ställningstaganden och rutiner för hantering och redovisning av dessa frågor.

I Karolina Starks uppdrag ingick att granska SKB:s rapporter (TR-06-09, R-06-82, R-06-83, R-06-81) utifrån ett antal granskningsfrågor. Under arbetets gång har ytterligare SKB rapporter använts (R-05-03, R-05-18, TR-06-15). I mån av tid skulle även fyra andra SKB rapporter användas (TR-04-08, R-06-46, R-06-11, R-05-61). Nedan redovisas Karolinas förslag och slutsatser efter varje granskningsfråga.

2. Granskningsfråga 1

Har SKB gjort en tydlig problembeskrivning vad gäller t ex i vilka ekosystem radionuklider kan antas ackumulera, urval av nuklider, mest exponerade typ av organism, vilka effekter på miljön som kan tolereras respektive måste undvikas?

I stora drag kan jag sammanfatta SKB:s dosuppskattning till biota (djur och växter) till att vara gjord med ett antropocentriskt perspektiv, trots deras landskaps- och ekosystemmodeller i platsbeskrivningen. En tydlig beskrivning av exponeringsvägar till organismer i relevanta ekosystem saknas i riskanalysen (se SSI FS 2005:5 Miljöskydd). Istället ligger fokus på möjliga exponeringsvägar till människa där även speciella scenarion så som exponering från en borrad brunn identifierats och undersökts med dosberäkningar. Inga sådana speciella scenarion har identifierats, beskrivits eller undersökts för exponering av biota. Att identifiera och beskriva exponeringsvägar är en mycket viktig del i riskbedömningen och utgör grunden från vilken dosuppskattningen utgår. I dosverktyget ERICA påpekas också att denna del i analysen är grundläggande och kan vara avgörande (D-ERICA, 2007).

Några exempel hämtat från SKB:s rapporter:

I SKB:s rapport TR-06-09 avsnitt 10.2.1 nämns att det finns en möjlighet att det sker en ackumulering i ’bottom sediment’. Det är oklart vad ’bottom sediment’ syftar på men om SKB menar havssediment så kan en ackumulering ge en stråldos till biota som lever där vilket SKB inte nämner. Vidare skriver SKB att de högsta doserna väntas när platsen inte är täckt av vatten, vilket säkert stämmer för människa men dock inte är helt övertygande när det gäller exponering av djur och växter i havssediment.

I SKB:s rapport R-06-82 avsnitt 8.1.4 skriver SKB att när det är tre färskvattenobjekt (två sjöar och en flod) i landskapsmodellen uppskattas aktivitets koncentrationerna till att bli tio gånger högre i floden. Det påpekas då att en flod inte kan försörja en människa med föda underförstått att exponeringen från floden blir liten. Detta gäller dock inte för exponering till flodlevande biota men detta redovisas inte vidare i dosuppskattningar.

I SKB:s rapport R-06-82 avsnitt 5.3.1 beskriver SKB att den platta topografin i Forsmark kan innebära att våtmarker intill åar kommer att översvämmas regelbundet och att det finns en möjlighet för en signifikant ackumulering av materia (radionuklider) i sådana områden. Vad detta skulle innebära för exponeringen till biota och ett möjligt scenario beskrivs inte vidare.

På sidan 7-8 beskriver jag några möjliga scenarion där dos till biota (djur och växter) kan beräknas som inte finns med i SKB:s bedömning.

När det gäller urval av radionuklider så har SKB säkert utgått från vad som finns/kommer att finnas i avfallet och varje radionuklids betydelse ökar med dess halveringstid och dess förmåga att komma upp till biosfären. Jag har inte bedömt SKB:s hantering av denna fråga närmare. Dock kan jag påpeka att SKB har valt att inte göra någon bedömning för ett antal radionuklider (se svar under fråga 2) då jag förmodar att de saknar data och egenskaper för dessa.

Vad gäller mest exponerade typ av organism så använder sig SKB av ERICA-verktygets tier 1 som automatiskt väljer ut den organism av referens organismerna som antas vara känsligast oavsett ekosystem. SKB gör ingen egen bedömning rörande detta eller kommenterar inte heller om ERICA resultaten verkar logiska. SKB diskuterar inte vidare om vilka effekter på miljön som kan tolereras respektive undvikas. Det som SKB gör är en kort jämförelse med bakgrundsvärden i Sverige och världen för ett antal radionuklider.

3. Granskningsfråga 2

Är den utvalda metodiken för analysen av miljöeffekter den rätta? (Användandet av riskkvoter utgående från koncentrationer i miljön, generella dosratgränser, fallspecifika dosberäkningar, framtagande av dos-effekt samband mm.)

I uppskattningen av stråldoser till biota i SKB:s rapport R-06-82 (p. 100) samt sammanfattning i TR-06-09 (kapitel 10) avsnitt 10.2.5, 10.5.5 och 10.6.6 har ERICA-verktyget med Environmental Media Concentration Limits (EMCL) utvecklat av det EU-finansierade ERICA-projektet (ERICA, 2007) använts för att jämföra med maximala aktivitetskoncentrationer i vatten och jord. Inga koncentrationer och beräkningar för sediment visas i SKB:s rapport. Enligt ERICA-metoden beräknas riskkvoter (RQ) i tier 1 (av totalt 3 tiers), som är det första screening steget i riskuppskattningen. Om riskkvoten är under 1 förväntas ingen hög risk för exponering och dosuppskattningen kan avslutas.

Jag bedömer ERICA-modellen till att vara ett bra verktyg för riskuppskattning av dos till biota i klass med övriga metoder som utvecklats så som USDOE:s graded approach (USDOE, 2002) med tillhörande dosmodell RESRAD-BIOTA (ISCORS, 2004). En ny screening nivå används (10 uGy/h) baserat på PNEC-metoden och inkluderar en säkerhetsfaktor på fem. Metoden ligger i linje med riskbedömningar för andra typer av föroreningar (kemikalier) vilket är mycket positivt, tycker jag. Jag tycker även att den nya screening nivån verkar rimlig att utgå ifrån i tier 1 och 2. Ett annat positivt nytt inslag i ERICA-verktyget är en effekt databas mot vilken de beräknade stråldoserna kan jämföras. Verktyget har förenklats och utformats till att kunna användas av icke-specialister i tier 1. ERICA uttrycker också en avsikt att verktyget ska förmå att screena ut merparten av fallen i tier 1 men ändå vara tillräckligt konservativt för att täcka in osäkerheter och kunskapsluckor. Denna balansgång tycker jag att de har lyckats med i stor utsträckning. Däremot är det viktigt att notera att liksom de flesta modeller så är det mycket viktigt att input data är korrekt för att man ska få ut något värdefullt i output. Se även bilaga 1 där jag gjort en sammanställning av ERICA-verktyget.

I SKB rapporten R-06-82 är det det andra utsläppsscenariot (av två testade, advection/corrosion base case) som genererar i RQ över 1 (se tabell 8-5, 8-6, och 8-7) för Po-210 och Ra-226. Begränsande organismer var: bivalve mollusc, vascular plant, zooplankton, rat, deer, worm, detrivourous invertebrate, flying insect. Det påpekas då att en utförligare uppskattning måste göras som rekommenderas i ERICA-metoden som går vidare till tier 2. Detta har ännu inte gjorts, istället jämför man med bakgrundsvärden i Sverige och i världen vilket inte är helt relevant i detta sammanhang. Något mer intressantare vore det om en jämförelse gjorts med bakgrundsvärden i det aktuella området. Betydligt mer relevant vore dock en diskussion och vidare utveckling av dosuppskattningen angående varför det är just dessa radionuklider som visar höga RQs, egenskaper hos radionukliderna, om begränsande organism är logiskt och relevant för det aktuella området och radionukliderna eller om det finns andra organismer i området som skulle vara med i undersökningen/beräkningen. Kanske måste en ny organism skapas i ERICA-tool wizard som är av en annan kroppsstorlek och har en annan uppehållstid i olika ekosystem än vad som redan finns i ERICA programmet? (se exemplet black-headed gull i ERICA D10, 2007). Behövs det göras kombinationer av ekosystem (marine, freshwater eller terrestrial) i dosberäkningen (se exemplet transition areas i ERICA, 2007). SKB gör ingen identifiering eller beskrivning av exponeringsvägar och endpoints för biota, eller vilka ekosystem som man tänker sig kan vara mest kritiska för biota (se SSI FS 2005:5). Endast en jämförelse med koncentrationer i jord och vatten görs rakt upp och ner.

SKB gör heller ingen summering av riskkvoter för samtliga organismer och radionuklider som det enligt ERICA tier 1 ska göras. Om detta görs så är det det andra utsläppsscenariot (advection/corrosion base case) som resulterar i en summa för RQs över 1. Det bör dock noteras att ERICA just nu håller på att uppdatera sitt dosverktyg och några EMCLs har ändrats. Den slutgiltiga versionen är ännu inte klar (2007-05-04).

För ett antal radionuklider (Ca-41, Zr-93, Pd-107, Ag-108m, Sn-126, Sm-151, Ho-166m, Th-229, Pa-231, U-233, U-236, Pu-242, Am-243, Cm-245, Cm-246) så har en dosberäkning inte gjorts i ERICA-verktyget då de inte finns med i databasen. Jag har inte hittat någonstans att SKB kommenterar detta. I ERICA-verktygets tier 2 kan man lägga till fler radionuklider om man känner till deras egenskaper.

En diskussion saknas om varför det blev Po-210 och Ra-226 som visar de högsta RQs. Inte heller diskuteras begränsande organismer eller om vad dosresultaten kan ha för betydelse för populationer i området.

4. Granskningsfråga 3

Är analysen av miljöeffekter enligt angiven metodik genomförd på ett godtagbart sätt? (transparens, välunderbyggt underlag, relevanta resultat, dras rätt slutsatser från resultaten?)

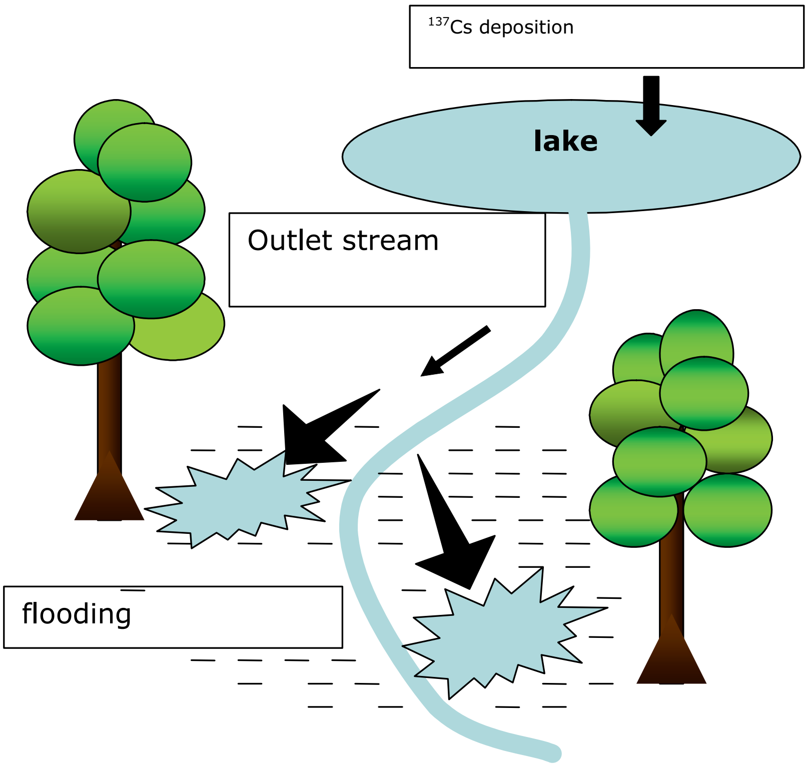
Det är mycket möjligt att SKB:s slutsats är rätt (t ex TR-06-09, kap. 10 intro) om att stråldoserna från ett slutfövar skulle resultera i ett lågt dosbidrag till biota (djur och växter), men jag tycker inte att det finns ett välunderbyggt underlag som stödjer deras slutsats. Exempelvis så saknas det en helhetssyn på allt material SKB samlat in under åren vilket i detta fall resulterar i att jag får en känsla av att allt inte framgår (eller används) i den så kallade huvudrapporten, och som sagt en del exponeringsscenarion saknas som kan vara av betydelse och värda att utvärdera när det gäller ackumulering av radionuklider i biosfären. Jag upplever också ett glapp mellan SKB:s C-budget modeller/resonemang och deras radionuklidmodeller. I övrigt så är transparensen i dosberäkningarna till biota bra (i R-06-82) och det går att replikera resultaten. Lite otydligt är det dock med de olika namnen på SKB:s läckage scenarion och dessutom byter de namn längre fram i rapporten (TR-06-09) och som sagt en beskrivning av resonemang och diskussion saknas. Observera dock att jag här inte kommenterar transparensen i radionuklidtransport och koncentrationsmodellen (som jag förstått inte finns med i någon rapport) utan endast dosberäkningarna till biota.

Övrigt:

I R-06-82 avsnitt 3.2 beskrivs biotiska egenskaper i området men beskrivningen är knapphändig. Till exempel saknas det en beskrivning av reptiler och amfibier i området. Av särskilt intresse kan vara en grodart Rana lessonae (Gölgroda) som endast finns längs Nordupplandskust och lägger sina ägg i gölar som bildas vid kusten med landhöjningen. Gölgrodan skiljer sig genetiskt från övriga grodor i Europa. I SSI FS 1998:1 samt SSI FS 2005:5 bilaga 2 ska särskild hänsyn tas till genetiskt särpräglade populationer. Kanske skulle en modell av en groda med Gölgrodans egenskaper skapas i ERICA-modellen för riskuppskattningen? En beskrivning av reptiler och amfibier i området finns däremot med i R-05-03 och R-05-18 med en citering till C. Andrén (2004). Gölgrodan finns inte med i den föreslagna artlistan vilket kan tyckas vara förvånande eftersom arten förekommer mycket nära det aktuella området. Jag noterar dock att Andrén valt att nämna Hasselsnok i artlistan för Laxemar i R-06-11. Hasselsnoken är även den sällsynt och förekommer nära Laxemar-området.

Beskrivningen av människor i Forskmarksområdet (R-06-82 avsnitt 3.3) är även den knapphändig, tycker jag. Det nämns ingenting om förekomst av fiske i området, campingplatser, närliggande naturområden (ex. Kallriga), närheten till sommarstaden Öregrund och Gräsö eller turister i bruksorten Forsmark. Beskrivningen i R-05-03 och R-05-18 tycks vara utförligare.

För övrigt i TR-06-09 avsnitt 13.3.3 noterar SKB att det inte finns någon indikation i SSI:s föreskrifter om hur länge doser till biota ska uppskattas. Föreskrifterna kan tolkas så som att närhelst det kan vara aktuellt att förhöjda stråldoser kan förekomma till biota pga en mänsklig aktivietet ska en sådan uppskattning och bedömning göras.



Figur 1: Översvämning av flod med sedimentpartiklar till strandsumpskog (våtmark) med efterföljande ackumulering av radionuklider.

Möjliga exponeringsscenarion för biota (djur och växter) som inte finns med i SKB:s modell/analys:

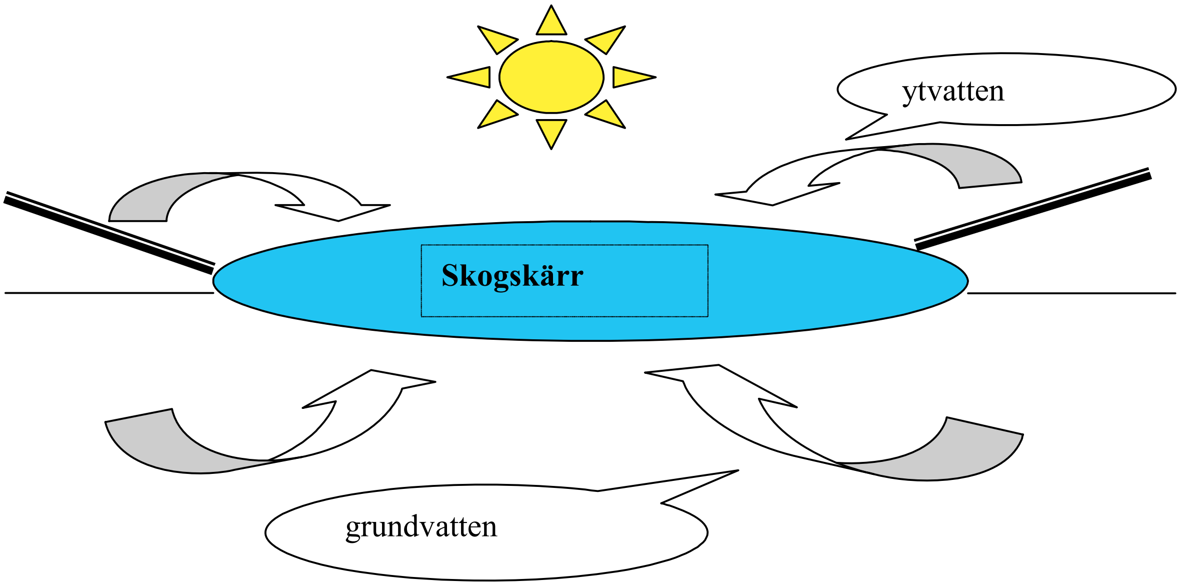
- Översvämning av flod med sedimentpartiklar till strandsumpskog (våtmark) med efterföljande ackumulering av radionuklider (så som ’hot spots’ på flygmätningskartan av Cs-137; Figur 1)

Man kan tänka sig ett scenario där ett biosfärsobjekt läcker aktivitet till ett annat objekt, t ex en sjö läcker aktivitet till en sumpskog (våtmark). Vilket resulterar i en högre koncentration i sumpskogsobjektet och lägre i sjöobjektet. Något sådant scenario finns inte med i landskapsmodellen som jag har förstått det.

- Grundvatten och ytvatten tillflöde till ett litet (100 m^2) skogskärr (’fen’; vanlig lekplats för groddjur, lokal för reptiler; Figur 2).

- En omvandling av ett sjöobjekt till alsumpskog istället för myr/mosse

- Översvämning av strandkant och vassområden runt sjö vilket resulterar i ’hot spots’ av radionuklider runt sjön.



Figur 2: Grundvatten och ytvatten tillflöde till ett litet skogskärr.

5. Kommentarer till aggregated transfer factors (TF_{agg}) till människa i R-06-81

I avsnitt 3.1 förklaras att endast fisk antas som födokälla till människa från hav, sjö och flod. SKB har alltså inte räknat på en överföringsfaktor från räka, mussla, kräfta. En intressant fråga vore om detta påverkar uppskattningen av överföringen positivt eller negativt (gör de en överskattningen eller en möjlig underskattning). För exempelvis Po-210 så har man sett att räkor (släktet *Gennadas*) innehåller högre halter än sill i marina miljöer (Cherry, 1994).

I avsnitt 3.2.1 beskriver SKB att man för jordbruksprodukter valt rötter, säd, grönsaker, komjölk, nötkött och sedan beräknat ett medelvärde på överförningsfaktor från dessa fem. Blir detta en underskattning eller en överskattning?

I avsnitt 3.2.2 beskriver SKB att överförningsfaktorn för skog och myr beräknats på kött från rådjur och älg. Överföring från bär och svamp är inte inkluderat i faktorn. Blir detta en underskattning eller överskattning av upptaget till människa. För Cs-137 exponering kan bär och (framförallt) svamp vara en viktig födoväg för människa (Persson & Preuthun, 2002).

Ytterligare en fundering som jag har kring SKB:s beräkning av TF_{agg} är om SKB:s antaganden resulterar i en underskattning av hur många människor ett objekt i deras landskapsmodell kan försörja? T ex om man bara räknar på fisk som födokälla från en flod och inte tar med alternativ som räkor, kräftor och musslor eller inte tar med bär och svamp som födokälla för skog och myr.

6. Tilläggsfrågor:

6.1. Hur ska SKB gå vidare med dosberäkningarna till biota i tier 2?

Det första steget blir att invänta den slutliga versionen av ERICA-verktyget samt se över exponeringsvägar till biota och komplettera där luckor upptäcks och se till att samtliga exponeringsscenarion täcks in i dosuppskattningarna. I de fall där RQ överstiger 1 så ska fallet gå vidare till tier 2. Om det går ska samtliga radionuklider läggas till i dosuppskattningen. Frågan är om inte SKB egentligen skulle ha börjat med en tier 2 just på grund av detta. I tier 2 kan man också välja vilka referens organismer man vill använda. För SKB kanske det bästa är att använda samtliga beskrivna samt lägga till någon extra om så bedöms nödvändigt.

6.2. Vad skulle SSI kunna kräva i en tier 3 bedömning?

Fall som hamnar i tier 3 är förmodligen unika och komplexa fall och ges därför ingen specifik vägledning i ERICA men en ram för hur man kan göra finns precis som i tier 1 och 2. En bedömning i tier 3 bygger till stor del på en realistisk dosuppskattning och en jämförelse med kunskaper om effekter på biota av strålning. I detta fall behöv en expertbedömning. Därför är det väldigt viktigt att bedömaren gör en tydlig beskrivning av exponeringen, antaganden, motiveringar, resonemang och bedömningen i och med jämförelse i effektdatabasen. Populationer och ekosystem ska skyddas så effekter på en del individer kan vara acceptabelt. I dosuppskattningen kan man i detta steg ta hänsyn till biotas mest troliga ’occupancy factor’, alltså tid som de spenderar i det kontaminerade området. Djur med stor home range kan antas spendera mindre tid i ett litet kontaminerat område. Se även bilaga 1.

6.3. Ytterligare granskningsfrågor i mån av tid:

1. **Identifiera typ av våtmark som finns i Forsmark och Laxemar, baserat på SKBs rapporter, R-05-03, R-06-11, TR-04-08.**

I SKB:s rapport R-06-82 beskrivs det att våtmarker täcker 10-20 % av området i Forsmark och att rikkärr (fens) till medelrika kärr är vanliga pga kalk i berggrunden. Mossar (bogs) är än så länge inte så vanligt i området. Det sägs också att våtmarkerna i Forsmark kan antingen ha direkt kontakt med grundvattenzonen eller vara separata hydrologiska system med täta bottnar med lite eller ingen kontakt med grundvatten. Under rubriken ’Running water’ beskriver SKB att pga den platta topografin i Forsmark så kommer våtmarker bredvid åar att bli regelbundet översvämmade. I SKB:s rapport R-06-46 med våtmarksmodellsimuleringar refereras det till TR-04-08 (Kellner, 2003) om att den mest troliga typ av våtmark som bildas i Forsmark är ’mesotrophic fen’ (kärr). Kellner har dock inte skrivit något om vilken den mest troliga våtmarkstypen i Forsmark är. SKB säger också att det är störst sannolikhet att en sjö i området ombildas till en ’mire’ (myr) som kan bestå av både kärr och mossar.

I SKB:s rapport R-06-11 beskrivs det att våtmarker i Laxemarsområdet är näringsfattiga myrar och att mossar inte är så vanligt förekommande än. Alltså borde det vara kärr de menar. I SKB:s rapport R-05-61 har Brunberg et al. 2004 gjort platsundersökningar och beskriver våtmarker i Laxemar som normal sankmark till olika typer av skog. Jag förstår inte riktigt vilken klassificeringsmodell av våtmarker hon har gått efter. Platsundersökningarna indikerar dock att våtmarkernas bottenlager har låg permeabilitet vilket skulle innebära en begränsad kontakt mellan grundvatten och ytvatten.

2. **Identifiera radionuklidtransportprocesser i våtmark och jämföra med processbeskrivningar i den våtmarksmodell som SKB använder.**

Sorption (adsorption och absorption) är en viktig process för ackumuleringen av radionuklider och metaller i våtmark för långa tidsperioder (Sobolewski, 1999; Kellner, 2003 (TR-04-08); Syrovetnik et al., 2006). Alltså kan man där använda sig av Kd-värden för de olika radionukliderna. Kellner (2003, TR-04-08) skriver också att innehållet av mineraler i torv och torvvatten reflekterar på många sätt resultatet av vattnets ursprung, vattnets rörelse och diffusion. Reid et al. 1994 citeras av Kellner och ska ha gjort en våtmarksmodell för Kanadas slutfövar. I figur 8-1 (i TR-04-08) beskrivs hur uran fördelade sig i ett kärr med uranrik berggrund. De högsta halterna uran återfanns närmast berggrunden. Viktiga processer som Kellner pekar på är också grundvattnetsflödesmönster och hydrauliska konduktiviteten i torv samt till viss del diffusion. Upptag av växter är också en viktig process i torvmarker (särskilt för K, N och P). I SKB:s våtmarksmodell finns ingen koppling mellan underliggande sediment och den partikulära fasen eller den lösta fasen i våtmarksmodellen vilket är underligt tycker jag. Tycker SKB att det blir en överskattning av stråldos då till den framtida jordbruksmarken? Men man missar ju då exponeringen från våtmarker, tycker jag. Jag tycker de borde lägga in processerna sedimentation och resuspension i sin modell och kanske en box med fast material från vilken erosion kan förekomma eller där fastläggning av sediment kan ske. Influxet borde också kunna komma från grundvatten (i ett kärr). I SKB:s rapport R-06-46 finns en annan våtmarksmodell där man simulerat utsläpp från grundvatten och vart det kan ackumuleras i våtmarken (här en mesotrophic fen/kärr). Transportprocesser som de anger att de använt är advection, dispersion och sorption.

I en artikel (Stark et al. 2006. Journal of Env. Rad. 87:175-187) så sammanfattade jag olika faktorer som påverkar Cs-137 ackumulering i översvämmade våtmarker (tabell 1).

Tabell 1. The main factors influencing an accumulation of ^{137}Cs in a flooded wetland.

Factor	Example	Mechanism of retention	Reference
Type of soil	peat or mineral soil	^{137}Cs high affinity to clay minerals	Sawhney (1972), Broberg & Andersson (1991), Avery (1996)
Duration of saturation	permanent or temporary	dry periods, in constantly saturated area ^{137}Cs is more mobile	Nylén & Grip (1991), Hilton et al. (1993), Saxén (1994)
Type of vegetation	tall or short, thick or sparse	tall and thick vegetation filter colloids & particles	Horrill (1984), Mungur et al. (1995)
Degree of salinity	marine water or freshwater	freshwater, in saline water Cs^+ is more mobile	Horrill (1984)
Level of pH	high, neutral, low	high or neutral pH, high level of H^+-ions (low pH) releases Cs^+ from soil particles	Staunton & Roubaud (1997), Munthe et al. (2001)
Level of nutrients in soil	high or low	high uptake of ^{137}Cs by plants if low K^+ and high NH_4^+ concentration	Camps et al. (2003)
Topography	elevated or low areas	hollows and depressions can enhance sediment deposition	Jeffries et al. (2002), van der Perk et al. (2002)

3. Granska parameter som används i PA modellering i samband med platsbeskrivningsmodell/platsundersökning, t ex vattens residenstid i våtmark (se rapporter R-05-03, R-06-11, TR-04-08, R-06-48 och R-05-61)

Inget svar. Vattnets residenstid kan förlängas under perioder av högt vattenstånd som resulterar i att ytterligare ytor blir översvämmade (Reddy et al., 1999).

7. Slutsats

Sammanfattningsvis kan sägas att jag tycker SSI kan efterfråga från SKB en tydlig identifiering, beskrivning och eventuell modellering av möjliga exponeringsvägar till biota i det aktuella området, dos/riskuppskattning till relevant biota i området i de identifierade ekosystemen och en förklaring och diskussion om varför resultaten blev som de blev även om doserna i fråga beräknas bli låga. SKB borde också vara tydligare överlag när de redovisar sitt resonemang för olika steg i bedömningen genom att förklara syften och motivera varför de har valt att göra på det ena eller andra sättet.

Vad gäller SKB:s beskrivning av våtmarker så verkar de helst vilja generalisera fram en typ av våtmark där kärr verkar vara den vanligaste typen. Dock tycker jag att det är lite olyckligt med deras fokusering på torvmarker i texten, kanske som en följd av Kellner (2003) indelning av våtmarker med kärr, mossar och ’marshes’ (där alla andra typer buntas ihop) och hans ingående beskrivning av torv. Jag tycker SKB skulle ha utgått ifrån vad man vet idag om var radionuklider ackumuleras och läcker ut i olika typer av våtmarker. SKB behöver förnya sin våtmarksmodell. En variant vore att göra en modell för ett kärr (TR-04-08, s.13, figur 2-1 b), en modell för en mosse (TR-04-08, s.13, figur 2-1 a) och en modell för en strandnära översvämningsvåtmark (alsumpskog) (TR-04-08, figur 2-3, s.16).

8. Referenser

Cherry, R.D., Heyraud, M., Rindfuss, R. 1994. J of Env. Rad. 24:273-291.

ERICA, 2007. D-ERICA. An integrated approach to the assessment and management of environmental risks from ionising radiation. Beresford, N., Brown, J., Copplestone, D., Garnier-Laplace, J., Howard, B., Larsson, C-M., Oughton, D., Pröhl, G., Zinger, I. (Eds). 82 pp. EC 6th Framework programme, Contract FI6R-CT-2004-508847. Swedish Radiation Protection Authority, Stockholm, Sweden.

ERICA D10, 2007. Deliverable 10. Application of ERICA integrated approach at case study sites. Beresford, N., Howard, B.J., Barnett, C.L. 126 pp. EC 6th Framework programme, Contract FI6R-CT-2004-508847. Swedish Radiation Protection Authority, Stockholm, Sweden.

FASSET, 2004. Deliverable 6. Framework for assessment of environmental impact of ionising radiation in major European ecosystems. Larsson, C-M., Jones, C., Gomez-Ros, J.M., Zinger, I. (Eds). 70 pp. EC 5th Framework programme, Contract FIGE-CT-2000-00102. Swedish Radiation Protection Authority, Stockholm, Sweden.

ICRP, 2003. A framework for assessing the impact of ionizing radiation on non-human species. Publication 91. Pergamon Press, Oxford and New York, 2003.

ISCORS, 2004. RESRAD-BIOTA: A tool for implementing a graded approach to biota dose evaluation. ISCORS Technical Report 2004-02; DOE/EH-0676. National Technical Information Service, Springfield, VA. Available from: http://homer.ornl.gov/oepa/public/bdac/.

Persson, K. & Preuthun, J. (Eds), 2002. Livsmedelsproduktionen vid nedfall av radioaktiva ämnen. Jordbruksverket. Edita Västra Aros AB.

Reddy, K.R., Kadlec, R.H., Flaig, E., Gale, P.M., 1999. Critical Reviews in Environmental Science and Technology 29(1): 83-146.

Sobolewski, A., 1999. International Journal of Phytoremediation. Vol. 1(1): 19-51.

Syrovetnik, K., Malmström, M.E., Neretnieks, I., 2006. Env. Poll. 1-10 (in press).

USDOE, 2002. DOE standard. A Graded Approach for Evaluating Doses to Aquatic and Terrestrial biota. US Department of Energy, DOE, Washington.

Bilaga 1. Sammanfattning av ERICA-verktygets upplägg

Om ERICA-verktyget används i en dosuppskattning bör utföraren:
- skapa en detaljerad beskrivning av riskanalysen
- lista exponering- och överförningsvägar och endpoints
- skapa en konceptuell modell
- välja det ekosystem som ska bedömas (i modellen finns freshwater, marine eller terrrestrial) eller en kombination av flera (se ERICA rapporten D-ERICA 4.5 Complex assessments)
- välja radionuklider till bedömningen
- förse verktyget med media aktivitets koncentrationer
- välja screening dosrat som tier 1 och 2 jämförs med

Tier 1

- Mycket konservativ screening bedömning
- Kräver minimalt med input data
- Enkel bedömning och kan användas av icke-specialister
- Maximala uppmätta/modellerade media koncentrationen föreslås som input
- Jämför input data med Environmental Media Concentration Limits (EMCL) beräknade för den ”begränsande referens organismen” för varje radionuklid
- Summerar riskkvoterna (RQs) från alla radionuklider oavsett begränsande organism
- Om modellen rekommenderar att analysen kan avslutas (RQ < 1) kan situationen bedömas vara av mycket liten radiologisk betydelse
- Det är för avsikt att många analyser ska avslutas efter tier 1 (be screened out)

Tier 2

- Det rekommenderas att man nu ser över (review) och förfinar (refine) sin analys/bedömningsunderlag och frågeställning
- Mindre konservativ screening bedömning
- Användaren kan välja organism/er samt definiera en egen organism
- Användaren kan ändra överföringsfaktorer (CR och K_d)
- Media och biota aktivitets koncentrationer kan vara input och det bästa uppskattade värdet rekommenderas (ex. medelvärde)
- Användaren kan lägga till fler radionuklider
- Uppskattade helkropp absorberade dosrater jämförs direkt med screening dosraten
- En summering av RQs från samtliga radionuklider för varje organism görs
- Resulterar i ett förväntat värde på RQ och ett konservativt värde på RQ som inkluderar en säkerhetsfaktor på 3 eller 5. Detta gör att den konservativa bedömningen behålls från tier 1 till tier 2.
- Ett ”trafikljus” system används som indikerar om situationen är:
  -av mycket liten radiologisk betydelse (med god marginal) grönt
  -av möjlig radiologisk betydelse (användaren rekommenderas att granska och förbättra analysen) gult

-av radiologisk betydelse (användaren rekommenderas att fortsätta analysen) rött

- Resultaten kan jämföras med tabeller av effekter och exponering som en följd av naturligt förekommande radionuklider
- Det är för avsikt att tier 2 ska identifiera situationer där det är väldigt liten sannolikhet att dosen till vald organism överskrider screening dosraten
- Ett värde på RQ som överstiger 1 betyder inte automatiskt att tier 3 ska göras. Istället kan en förfining (refine) av input data göras och tier 2 kan köras igen

<u>Tier 3</u>

- Situationer som leder till tier 3 är förmodligen komplexa och unika därför är det inte möjligt att ge specifik vägledning
- En mycket site-specifik bedömning bör göras
- En revidering av problemställningen kan/bör göras
- Inget screening steg –så alltså ingen jämförelse med screening dosrat. Istället kan en jämförelse med effekt data göras
- Inte föreskrivande och har inga ”ja/nej” svar
- Förser användaren med vägledning, mall och verktyg som hjälp att utföra en mer detaljerad bedömning
- Användaren kan ta hänsyn till en organisms tid spenderad utanför det kontaminerade området (kan minska dosen till organismer med stor home-range)
- Probabilistiska och känslighetsanalyser kan göras
- Osäkerheten i olika input faktorer bör bedömas
- Tillgång till up to date on-line databas med radiologiska effekter
- Kräver en erfaren och kunnig bedömmare eller konsultering med expertis

<u>Post-assessment considerations:</u>
- Socio-economic factors
- Evaluation of assessment results against criteria set up during problem formulation

Om inte ERICA-verktyget används kan en bedömning med motsvarande innehåll krävas/rekommenderas.

8

Impacts of Future Glaciations on Geochemical Conditions at Repository Depth: Review of SKB's Approach

A Bath[1]
H-P Hermansson[2]

[1]Intellisci Ltd, Loughborough, UK
[2]Studsvik Nuclear, Nyköping, Sweden

Executive Summary

This review examines SKB's approach in the SR-Can preliminary safety evaluation to the potential impacts of future glaciation on geochemical conditions at repository depth. Primarily, it considers the issues involved in assessing the possibility that dissolved oxygen might penetrate through the geosphere to repository depth under the anomalous hydraulic influence of sub-glacial conditions. The potential significance of this scenario is increased because it is coupled with the possibility that an increased flow rate of dilute groundwater around deposition holes might disperse and erode bentonite buffer, thereby exposing waste canisters to advective transport of oxygen or other corroding solutes.

There are also some other potential processes for which potential secular variability through glacial climate stages needs to be considered in this context for a long-term safety assessment: sulphate reduction to sulphide which is corrosive towards copper, the role of microbial activity in mediating reactions such as oxygen-consuming and sulphide-generating, variations of groundwater salinity both to fresher and more saline compositions, and effects of salinity variations on the stability and mobility of colloids.

Two basic environmental conditions will affect the geosphere during a glacial episode: permafrost and glaciation. The potential impacts of both are considered. It is apparent that the treatment of processes caused by both scenarios is based mostly on hypothetical considerations and theoretical physical models. It is problematic to constrain the potential scale of their hydrogeological and hydrochemical impacts. These impacts are very likely to be rather site specific and in addition will depend on the duration of these environmental conditions and especially of the periods of most severe effects on the groundwater system. For example, the period of potential rapid infiltration of melt water is considered to be limited to the relatively brief period when the ice front passes over the site. For both permafrost and glaciation, direct evidence from present-day systems and from palaeohydrogeological studies would improve confidence in the way that these models and supporting calculations have been used to constrain the impacts.

Some basic thermodynamic background is provided to provide context for the likely sensitivity of copper corrosion to the chemistry of water in contact with the canisters. This is done with respect to oxygen and sulphide with oxidising and reducing E_h conditions respectively and also with respect to other solutes, chloride, carbonate and iron that have secondary effects. This is done by means of Pourbaix equilibrium calculations and E_h-pH phase/species predominance diagrams. These show that the primary corrosion reactions for oxygen and sulphide are affected to minor degrees by variations of other aspects of water chemistry, mainly salinity. Microbial activity is a much more important factor that affects corrosion rates; microbes have a direct role in the production of sulphide from sulphate.

SR-Can concludes that there is only a very low probability of dissolved oxygen penetrating to repository depth in sub-glacial water, based on models for sub-glacial hydrodynamics, sub-glacial oxygen availability, and on the capacity of natural reductants in the geosphere (principally Fe^{2+} released from minerals) to attenuate any oxygen. However this conclusion makes various assumptions and simplifications. Consequently uncertainties may be underestimated. Although the assumed maximum infiltration rate appears to be pessimistic, the duration over which moderately high infiltration rates might prevail could be higher than has been assumed. There is a general absence of observations in real systems with which these hypothetical models might be constrained.

Evidence to generalise and quantify a model for Fe^{2+} release from minerals is not strong, though the REX experiments at Äspö do provide compelling direct evidence in a relevant rock type. A greater degree of uncertainty in the mechanism and kinetics of O_2-consuming reaction would be realistic. An uncertainty range of about two orders of magnitude in the kinetics of Fe^{2+} release from these minerals is probably reasonable. Some confidence that Fe^{II} release and reaction really has occurred over a long timescale might be obtained from direct observation of the oxidising reaction products in fractures and/or in rock matrix. Alteration patterns in such rocks would be strong supporting evidence for the oxygen consumption model.

Reactive mass transport modelling with the geochemical code PHREEQC has replicated SKB's geochemical modelling of oxygen consumption by Fe^{2+} released by the dissolution of Fe^{II} minerals. It is concluded that, given the model assumptions and parameters, it is likely that oxygen will be consumed by redox equilibration before it could reach repository depth. However there are significant uncertainties, namely in the maximum downwards sub-glacial water velocity and in the kinetics of release of Fe^{2+} from biotite or chlorite. The modelling shows that the uncertainty range of two orders of magnitude in the reaction kinetics is significant in terms of oxygen attenuation. Along with the uncertainties about the duration of anomalous sub-glacial hydraulic conditions, it can be concluded that there is a low but non-negligible probability of oxygen reaching repository depth. Whether that oxygen could then have any impact on copper canisters would depend on the performance of the near-field rock barrier and of the bentonite buffer.

SR-Can makes various assumptions and uses models to estimate the limits on variations of salinity at repository depth through the glacial cycle. These are mostly reasonable, though the uncertainties generally are not constrained by observations on present-day or palaeohydrogeological analogues. In addition to the freshening effect of glacial melt water inflow, there are also possibilities of salinization due to freeze-out by permafrost or by sea freezing, or due to upconing of deeper groundwaters during glacial advance/recovery or permafrost. Other aspects of sub-glacial and sub-permafrost geochemistry, for example, the possibility of methane hydrate accumulating and then being released, might be significant if they affected redox equilibria at depth, especially with respect to sulphate reduction and sulphide production. At present, there is no evidence that these types of processes coupled to the physicochemical impacts of glaciation or permafrost have occurred in the past. As with all of these uncertain hypothetical impacts of environmental processes at climate stages in the distant future, it would build confidence if there were more evidence of what happened in past glaciations.

Table of contents

1. Introduction

1.1. Context of review

This review and modelling report has been commissioned by SKI to examine the approach of SKB to the potential geochemical impacts of future glaciation on the integrity of a repository at either of the investigated areas at Forsmark and Laxemar. The Reference Evolution in SKB's SR-Can preliminary evaluation of long-term safety of a repository [1] has a full glacial period starting at about 50 ka in the future and has glaciation persisting for about 30 ka at Forsmark and 19 ka at Laxemar in the period to 120 ka into the future. In the same period out to 120 ka, the Reference Evolution has permafrost occurring at Forsmark for 41 ka and at Laxemar for 46 ka, with maximum depths of freezing being 160 m at Laxemar and 250 m at Forsmark.

The range of possible physical effects of these glacial processes on the groundwater system is coupled with hydrochemical effects. During glaciation (i.e. cover by ice), infiltration into underlying bedrock may be enhanced by pressurised sub-glacial water. The enhanced infiltration of oxygenated water would change redox conditions. This gives rise to a concern that there might be a scenario in which dissolved oxygen might reach repository depth and thus affect adversely the corrosion of copper waste canisters. The other potential major hydrochemical effect of sub-glacial infiltration would be the freshening of groundwater. This gives rise to a concern that a prolonged period of melt water infiltration would cause groundwater at repository depth to become very dilute and thus to change the electrostatic equilibria in the bentonite-based backfill and buffer which would then tend to disperse when coupled with the physical effect of faster water movement.

During the much longer period of permafrost in the Reference Evolution, the freezing of groundwater could have the hydrochemical effect of 'freezing out' the solutes and thus of causing a progressive fractionation of solutes and salinization of underlying liquid water. This suggests a possible scenario where groundwater at repository depth would have raised salinity and thus would reduce the swelling pressure of clays in the backfill and buffer. There could also be a general change of groundwater flow conditions, due to freezing and resultant permeability and infiltration changes, that would potentially change the hydrochemical conditions at repository depth.

1.2. SKI's requirements

The variability and uncertainty of key hydrochemical parameters within the SKB site investigations have been reviewed and assessed in a previous report for SKI from Intellisci and Studsvik: 'Variability and Uncertainties of Key Hydrochemical Parameters for SKB Sites' [2]. Phenomenological understanding and modelling approaches developed in that task are utilised in the present task to assess SKB's methods in SR-Can for estimating geochemical implications of climate change at repository depth. Both independent modelling and detailed scientific review should be used to assess significant redox parameters: dissolved oxygen (which is a corrosive agent with respect to copper and may be affected by oxygen penetration during glacial melt water intrusion) and dissolved sulphide (which is also a corrosive agent), and also possibly ionic strength and geochemical signatures that might contribute to understanding of overall system evolution and the potential impact of a glaciation scenario on long-term performance of the engineered barrier system (EBS). In view of the potential importance of dissolved sulphide as an agent for general corrosion in chemically reducing deep groundwater conditions throughout the reference evolution scenario of a repository, a review of factors controlling dissolved sulphide under different conditions is also required.

1.3. Scope of this report

The scope of this report is limited primarily to considering the issues surrounding the scenario of dissolved oxygen penetration during a glaciation. Firstly, in Chapter 2, SKB's and SKI's past and ongoing approaches to this scenario and the geochemical modelling of potential oxygen consumption are reviewed.

In Chapter 3, the basic background to theoretical redox chemistry in the Engineered Barrier System (EBS), especially oxygen and sulphur chemistry with respect to the chemistry of corrosion of copper canisters is summarised. This is the primary safety assessment issue associated with potential hydrochemical changes during a glaciation. Corrosion potential is illustrated via Pourbaix (Eh versus pH) diagrams. More comprehensive presentation and discussion of the corrosion processes and issues has been reported by SKI in research and workshop reports specifically on this issue.

In Chapter 4, an assessment of the uncertainties and robustness of SKB's approach to oxygen penetration in a future glaciation is provided. There are critical comments identifying the assumptions, simplifications, uncertainties and remaining questions in the present status of scenario development and modelling. In this report, the assessment focuses mainly on the phenomena of dissolved oxygen penetration and its consumption, i.e. on the possibility of transient oxidising and oxygenated conditions at repository depth at some time in the future. The geochemistry of dissolved sulphide and potential scenarios in which sulphide concentrations might cause concern about corrosion are covered briefly here and will be assessed more thoroughly in a subsequent report. Microbial populations and activity, and their potential roles in reactions involving dissolved oxygen and sulphide, are also considered as an important aspect of geochemical conditions at repository depth.

Chapter 5 summarises some new geochemical modelling carried out for SKI as part of this study. It comprises calculations with the PHREEQC program of the consumption of dissolved oxygen by ferrous iron (Fe^{2+}) which is assumed to be released by the dissolution of a mineral source of reduced iron – biotite in this case. The calculations aim to replicate the model calculations done for SKB in reports TR-99-19 and R-06-105 [3, 4] and to test the sensitivity of this model to the selected assumptions and parameters.

Chapter 6 identifies some other geochemical and biogeochemical processes related to glaciation or permafrost growth and its impact on groundwater flows and compositions. These are (i) fresh meltwater flushing to repository depth, (ii) formation and downflow of saline water due to freeze-out from permafrost, (iii) upconing of saline water due to post-glacial recovery, (iv) methane hydrate associated with permafrost, (v) general issues of microbial activity at repository depth including sulphate reduction. Issues arising from these could be considered in greater detail in a subsequent report.

The main conclusions from this review and modelling exercise are summarised in Chapter 7.

2. Current approach in SR-Can and past work by SKB and SKI

2.1. What are the issues?

Glaciation and permafrost periods have both been examined in the Reference Evolution of SKB's SR-Can report [1]. SKB consider that the geochemical implications of both can be discounted:

- For the case of oxygenation at repository depth due to sub-glacial infiltration, SKB has carried out geochemical modelling and concludes that, for all reasonable scenarios, dissolved oxygen would be attenuated by reaction with reducing Fe-containing minerals in the fracture and matrix.

- Another issue related to changing redox conditions at repository depth through both glacial and non-glacial periods is the rate at which microbially-mediated sulphate reduction occurs, possibly leading to increased sulphide concentrations that would accelerate canister corrosion. SKB concludes that the production rate and concentration of sulphide will not be larger than they are under present-day conditions.

- For the case of freshening due to infiltration of glacial melt water, consequent destabilisation and dispersion of clays in buffer/backfill, SKB concludes that this scenario cannot be ruled out and that current knowledge about the processes involved is deficient.

- A more general issue arising from freshening of water would be the stabilisation of colloids in general (i.e. including natural colloids) and the possibility of enhanced colloidal transport of radionuclides. SKB concludes that the upper limit for natural colloid concentrations may reasonably be assumed to be the highest concentrations measured in present-day groundwaters at repository depth.

- For the case of salinization at repository depth due to freezing out by permafrost, SKB concludes that salinity will not become so high as to lower the swelling pressure of buffer and backfill. In general, SKB concludes that the respective safety function indicators for long-term performance of canisters, buffer and backfill will not be compromised by these glacial episodes in the Reference Evolution of SR-Can.

2.2. Previous models and assumptions in SR-97 and SITE-94

The climate scenario in SR-97 [5] considered both production of saline water due to salt exclusion during ice formation from groundwater and increased groundwater flows, potentially coupled with dissolved oxygen penetration, during ice sheet regression. The transport of dissolved oxygen to repository depth was discounted on the basis of modelling that suggested that, at the expected flow rates, the rock's redox-buffering capacity would consume all such oxygen (see below; [3]).

SKI's SITE-94 exercise [6] also carried out geochemical modelling of the same scenario of oxygen penetration under the hydraulic influence of an overlying ice sheet (but, in contrast to the scenario in SR-97, the increased intrusion of melt water and of dissolved oxygen was considered to occur during glacial advance [7].

Concentrations of dissolved oxygen were inferred to be potentially as high as 3 to 5 times higher than concentrations due to atmospheric equilibrium. This inference was based on evidence from the Greenland ice sheet GISP ice core that basal ice beneath the 2000m thick ice sheet has up to 1.40 mmoles of O_2 per kilogram of ice (roughly 45 mg/L of resulting melt water).

Modelling with the PHREEQM program assumed downwards water advection through a 1000m-long fracture path length with a water travel time of 100 years, with instantaneous and irreversible reaction of available Fe-containing minerals in fractures with oxygen. The total reducing capacity of Fe-minerals in fractures was estimated to be equivalent to 1.22×10^{-2} moles of O_2. In-diffusion of oxygen to the rock matrix and reaction with Fe-minerals there was not considered.

The conclusion from the SITE-94 modelling was that abundances of the Fe^{2+}-containing minerals, pyrite, biotite and chlorite, would not be sufficient to ensure that oxygen would not penetrate to repository depth of 500m. For example, the central model suggested breakthrough of oxygen at 500m along the fracture within about 720 years.

The same report [7] examined the mineralogical evidence that oxygenated water might have penetrated to repository depth range at times in the past. Although it accepted that the evidence is not conclusive, it was suggested that at least some of the reported observations of Fe-oxyhydroxide found at depth might be indications of past transient oxidising conditions. However it was also agreed that it is problematic that these amorphous Fe oxides have not subsequently transformed to the more stable forms of goethite or hematite.

Another line of evidence suggested in support of Fe-oxyhydroxide preservation was the interpretation by Grenthe et al. [8] that redox potentials in Fennoscandian groundwaters are controlled by an amorphous ferric oxyhydroxide redox couple with Fe^{2+} (although those redox potentials are now actually reducing).

2.3. Approach to the issues in SR-Can

The approach used by SKB to handle the hydrochemical issues that arise in the glaciation and permafrost periods of the glacial cycle reference scenario of SR-Can is described below (Sections 2.3.1 to 2.3.5) in summaries of the relevant supporting reports.

2.3.1. Effects of ice melting and redox front migration in fractured rocks of low permeability [3]

This modelling study was a response to the scenario emphasised by SKI's SITE-94 of oxidising sub-glacial water infiltrating to repository depth under influence of transient high hydraulic gradients wet-based edge of ice sheet. The scenario is supported by isotopic evidence of glacial water relict at depths of ≥ 400m.

The assumption and simplifications in the modelling were:

- water infiltration occurs during deglaciation and lasts for ~ 5000y,
- next glaciation will occur in ~60-75 ka,
- ice melting rate ~50 L/m^2/y = infiltration of ~50 mm/y,
- fluctuations/variability of infiltration and duration are uncertain,
- reductive capacity (RDC) in system is due to Fe^{II} minerals in fractures and rock matrix, main minerals pyrite, biotite, chlorite,
- information on reaction kinetics is limited if velocity is less than characteristic reaction time (i.e. <3 m/y), then equilibrium is achieved; if velocity is >3 m/y, then reaction assumed to be kinetically-controlled,
- 400m depth of reducing zone above repository at 500m,
- duration of maximum infiltration is 1000-2000y,
- dissolved oxygen (DO) in melt water is 1.4mM (~45 mg/L) [9],
- redox state in deep granite groundwaters is controlled by Fe^{II}/Fe^{III} and equilibrium $Fe^{2+} \leftrightarrow Fe(OH)_3$.

Chlorite is identified as the main Fe^{II} mineral in fracture fillings at Äspö: 35% of fracture filling and average 20% FeO, i.e. 1.5 moles Fe per mole chlorite. Formulae and equilibrium constants for dissolution reactions are:

Chlorite $Fe_{1.5}Mg_{3.5}Al_2Si_3O_{10}(OH)_8$ log K = 59.9
Biotite $KMg_2AlFeSi_3O_{10}(OH)_2$ log K = 35.88

A preliminary PHREEQC model assumed equilibrium, i.e. that there is always enough Fe^{2+} available to consume O_2 instantaneously, so O_2 consumption is controlled by thermodynamics only. There were two variant models:

(i) Reactions in fractures only: O_2 reacts with Fe^{II} from chlorite and $Fe(OH)_3$ plus Mg-chlorite are precipitated.
(ii) Reactions with rock matrix: O_2 reacts with pyrite and biotite, or with pyrite only or biotite only, precipitating $Fe(OH)_3$.

The second model, using the ARASE reactive transport model, introduced reaction kinetics into the release of Fe^{II} from chlorite, biotite and pyrite. The kinetics depend on pH for chlorite and biotite and on O_2 concentration for pyrite. The rate expressions used were:

Chlorite $R_{diss} = 0.08457[H^+]^{0.51} + 6.437.10^{-11}[H^+]^{-0.65}$ mol.m^{-2}.y^{-1}
Pyrite $R_{diss} = 0.044[O_2]_{aq}$ mol.m^{-2}.y^{-1}

The reaction kinetics model for dissolution of chlorite used reactive surface area values 100 to 0.01 m^{-1}, downwards water velocity range from 10^{-7} to 10^{-5} m/s, and mineral amounts of chlorite = 91.8 mol/L, pyrite = 22.5 mol/L, and biotite = 447 mol/L. Modelled breakthrough of oxic conditions at 400m depth occurred within hundreds of years (as indicated by rising calculated pe values).

2.3.2. Changes in groundwater composition as a consequence of deglaciation: Implications for performance assessment [4]

This modelling study is an update of Guimerà et al's previous study using new data from sites. It asserts that the previous study suggested "breakthrough of oxic conditions but not oxygen" to repository depth. Gascoyne [10] had suggested that the earlier modelling was excessively conservative.

The model assumes that dissolved O_2 in water flowing in fractures is consumed by reaction with Fe^{II} released from kinetic dissolution of biotite. The kinetic rate expression for biotite dissolution is:

$$R_{diss} = 6.96.10^{-2}\,[H^+]^{0.51} + 5.28.10^{-11}\,[H^+]^{-0.65}\ \mathrm{mol.m^{-2}.y^{-1}}$$

The surface area of biotite was assigned a 'conservative' low value of 8.64 m^2/L; the value for initial concentration of biotite was 1.125 mol/L. The composition of glacial melt-water is assumed to be that of Grimsel water equilibrated with O_2 at $P_{O2} = 0.2$ atm, $[O_2] = 2.74 \times 10^{-4}$ mol/L.

There are two basic model variants: (i) reaction of O_2 with biotite in fracture only, (ii) reaction of O_2 with biotite in rock matrix. In (i), $v = 10^{-7}$ m/s, biotite = 1.125 mol/L, surface area = 8.64 m^2/L; in (ii): $v = 10^{-9}$ m/s, biotite = 15.58 mol/L, surface area = 8.64 x 10^{-2} m^2/L. The PHREEQC reaction-transport model was used, discretised into a 400m column of 400 cells, each 1m long; the 5000y simulation time was discretised into time steps of 27.4 days.

Modelling results for reaction in fracture (variant i) indicate that the O_2 'front' would penetrate about 2 metres in 1000y. Sensitivity analysis covered variation over velocity range 10^{-9} to 10^{-5} m/s, biotite up to 7.875 mol/L, surface area between 1 and 17 m^2/L. O_2 penetration in the model is most sensitive to groundwater velocity. With $v = 10^{-5}$ m/s and base case values for other parameters, O_2 penetrates to 250m depth in 2000y. With $v = 10^{-6}$ m/s, O_2 penetrates to 50m in 5000y. No sensitivity analyses with respect to surface area variation outside 1-17 m^2/L range were carried out. The base case value of 8.64 m^2/L is anyway two orders lower than experimental values for Äspö rock.

A simple calculation assuming instant dissolution of biotite and availability of Fe^{2+} (i.e. similar assumption as an equilibrium model) suggests O_2 penetration to 175m in 2000y for $v = 10^{-5}$ m/s and to 44m in 5000y for $v = 10^{-6}$ m/s. Thus ignoring reaction kinetics suggests slightly slower O_2 penetration, as expected.

Modelling results for reaction in rock matrix (variant ii) indicate that the O_2 'front' would reach about 2m depth in 5000y. Note that the dissolution rate of biotite is pH-dependent. Rate is slowest at neutral pH. Therefore higher pH as shown by model shows better attenuation of O_2.

The report concludes that "it is reasonable to assume that under these specific circumstances [i.e. high groundwater velocity and non-equilibrium kinetic reaction of biotite], oxic conditions could reach repository depths after 5000 years".

It is also suggested in the report that the Guimerà et al [3] calculations of redox were in error, predicting high Eh values of up to +180mV, whereas this new modelling indicates that Eh remains at -180 to -360 mV ahead of the O_2 front. It is stated that "the explanation for this [discrepancy between previous and present models] is the lower (*sic*) mineral abundance used in the present calculations". It is assumed that "lower" is an error and that "….higher mineral abundance…." is the correct statement.

2.3.3. Modelling of groundwater chemistry over a glacial cycle - background data for SR-Can [11]

This report describes the detailed reasoning for the position taken in SR-Can for 'groundwater chemistry around a repository over a glacial cycle". The evolution of geochemical conditions over three periods is considered: excavation/operation, post-closure temperate climate, and remaining parts of reference glacial cycle. Only the last of these is summarised here – covering the permafrost and glaciation stages of the reference glacial cycle.

Geochemical modelling of future groundwater evolution due to mixing of different components has been carried out using PHREEQC but with an 'uncoupled' thermodynamic model for the Fe^{2+}/Fe^{3+} and SO_4^{2-}/HS^- redox couples. The controlling Fe phases are assumed to be either FeS (amorphous) or $Fe(OH)_3$ (i.e. the 'Grenthe' redox couple). The redox model assuming equilibrium with $Fe(OH)_3$ is used as the 'reference method' for Eh, this being conservative in terms of giving rather higher Eh values than the SO_4^{2-}/HS^- couple. It is noted that measured Fe^{2+} and HS^- are not generally consistent with values calculated by this reference couple. Some of the variability is attributed to microbial involvement. Higher HS^- values obtained from the FeS model are more consistent with what is measured at Laxemar than at Forsmark. FeS is assumed to control the abundance of dissolved HS^-.

CH_4 and H_2 are considered to be of potential importance as nutrient sources for microbially-mediated production of HS^- from SO_4. However CH_4 and H_2 concentrations are low and therefore their role in producing HS^- is limited to ≥ 10^{-5}M HS^- (averaged over time).

In general, it suggests that redox conditions will tend to remain with low Eh values as meteoric water infiltration increases in the future. The main reason is attenuation of O_2 in the soil zone during the temperate period. Slightly higher Eh values will be promoted by concurrent calcite precipitation in deep groundwaters which lowers pH and raises equilibrium Eh (because pH and Eh are correlated via the redox equilibria).

Production of saline groundwater by freezing out of salts when permafrost forms has been modelled by Vidstrand et al. [12]. Freezing out of salts from a 300m column of groundwater which originally varied linearly from 0 to 1.5% TDS is modelled as producing a 10m thick zone of underlying groundwater at 22% TDS. Downflow and dispersion of this dense water is modelled to give a salinity at repository depth of 9% TDS within 300y and for a 'few years' duration. However, allowing for the period of dilution of existing groundwaters before onset of permafrost, it is suggested that salinity is more likely to be around 2% rather than 22%.

Changes to the hydrogeological conditions when ground freezes and thaws are also likely to change the flow system and thus also salinity distribution. Salinity changes potentially associated with flow to taliks and with thawing of permafrost are considered qualitatively and are suggested not to be significant. Nor are any consequent changes of redox conditions expected.

Modelling of groundwater impacts of a glaciation by Jaquet and Siegel [13] suggest that saline upconing is likely as the ice sheet advances or retreats over the site. Salinities up to 5% TDS are said to be possible transiently at repository depth. If the ice sheet were to be warm-based (i.e. melting), then dilute water would infiltrate and could possibly reach repository depth. The reference climate evolution in SR-Can has the future 60 ka glaciation lasting about 5000 years and the future 100 ka future glaciation lasting about 10000 years (see Figs. 1-1 and 1-2 in [11]). Therefore the duration of glacial melt water infiltration could be up to 10000 years, but it is suggested that the high hydraulic gradient and high downwards water velocity would not persist for all of this time.

Potential changes of redox conditions due to infiltration of oxygenated sub-glacial water are considered with two modelling approaches: (i) reaction with Fe^{II} minerals in the rock matrix according to a matrix diffusion model [14], and (ii) reaction with Fe^{II} minerals in fractures [4]. Sidborn and Neretnieks [14] derive an analytical expression for the consumption of oxygen in terms of flow rate in the fracture and diffusivity of oxygen in the rock matrix. This approach assumes that the rate of Fe^{2+} release from biotite in the matrix is fast relative to the rate of in-diffusion of oxygen. Two cases are considered: 40 and 1300 years duration for passage of the glacier front (i.e. assuming that infiltration occurs only under the glacier front). The maximum depths of penetration suggested by modelling are 10m and 60m respectively for the particular parameters used (1% Fe^{II} in rock, $T \sim 10^{-7} m^2/s$, hydraulic gradient 0.01, $D = 5 \times 10^{-14} m^2/s$). Guimerà et al's model is described above. It describes oxygen consumption by Fe^{2+} released from biotite in fracture fillings (an alternative set of parameters simulates reaction with matrix minerals), and this Fe^{2+} release is kinetically restricted so the ability to remove oxygen during infiltration is an interplay between water infiltration rate and Fe^{2+} release rate. Maximum depth of penetration suggested by the model is, for example, 113m for water velocity 10^{-5} m/s for a period of 1200 years after which the biotite buffering capacity is exhausted and the oxygen front restarts a downwards movement.

The possibility that there might be future parameter values that lie outside the ranges assumed for the geochemical reaction-transport models is discussed. Such possibilities could in theory suggest that O_2 would reach repository depth. For example, very high O_2 concentrations are mentioned, or absence of Fe^{II} minerals in transmissive fractures, or much higher water velocity. It states that these possibilities should be considered in terms of 'what if' scenarios. In SR-Can ([1] Section 9.4.7), this possibility is discounted on the grounds that high flow velocities would persist for only short periods of time.

2.3.4. Geosphere process report for the safety assessment SR-Can [15]

Permafrost processes

The DarcyTools code is used to simulate the movement of saline water resulting from salt exclusion during permafrost formation. Permafrost formation may be a cyclical or progressive process, and it is inferred that the result of possibly repetitive cycles of salt exclusion could be a body of saline water accumulating below the front of perennially frozen ground.

The saline water could be up to brine salinity (>100 g/L TDS). Depending on the concentration of original groundwater before freezing, the brine could be a Na-SO_4 or Na-Cl solution. Degree of concentration is likely to depend on site-specific factors;

laboratory experiments have simulated x 5 concentration of sea water to give a SO_4-rich brine.

It states that the stable isotopic fractionation during ice formation may be characteristic of the permafrost process, 'producing lighter $\delta^{18}O$ and $\delta^{2}H$ than the original groundwaters' [The water-ice fractionation is about +3‰ $\delta^{18}O$ at 0°C, i.e. ice is isotopically lighter than the water from which it forms, resulting in a Rayleigh fractionation whereby the early-formed ice would be isotopically light and late-formed ice would get heavier as the residual liquid water gets isotopically heaver.]

It is suggested that many freeze-out brines may have been flushed or diluted by subsequent groundwater flow since the last glaciation. However it is also suggested that deep groundwaters with relatively light $\delta^{18}O$ that are usually interpreted as glacial melt waters might instead by freeze-out brines. [This is unlikely – freeze-out brines would be isotopically heavy relative to original groundwater, but thawed permafrost water would be isotopically light and would also be dilute].

Methane hydrate associated with permafrost
Methane hydrate formation is considered as a possible process associated with permafrost. In theory, it could occur where the temperature is low enough and hydrostatic pressure high enough (e.g. >380m depth and T<4°C). Methane hydrate is not stable at <200m hydrostatic head, so it is most likely in association with deep permafrost.

Methane hydrate formation in bulk amounts requires a large-enough flux of methane. The structure of the hydrate means that it will form only in conductive fractures. Due to the thermodynamic 'salting out' effect the stability field of the hydrate in saline groundwater expands and therefore it will be slightly easier for hydrate to form under such conditions. Destabilisation of methane hydrate at the same time as permafrost thaws would potentially release large amounts of methane in the vicinity of a repository at the end of a future glacial period. There is no direct evidence of methane hydrate having been associated with past or present permafrost in northern Europe or Canada.

Sub-glacial groundwater and meltwater processes
CONNECTFLOW is used to simulate the sub-glacial groundwater system, i.e. under a future ice sheet. This modelling and its results are presented in separate reports. The rate of melt water production, i.e. infiltration rate, is derived from an ice sheet model. The models show that melt water infiltration and movement towards repository depth is dependent on site-specific features i.e. the distribution of transmissive HCDs.

The potential hydrochemical process of dissolved oxygen being transported to repository depth is considered in separate reports by Guimerà et al and Sidborn & Neretnieks (see above). A potentially significant factor in dissolved oxygen hydrochemistry in glacial melt waters is that there may be no soil cover which normally is the source of organic carbon and is thus the primary sink for dissolved oxygen.

Microbial processes
Microbial processes are considered to be ubiquitous, potentially catalysing the important hydrochemical redox transformations. However high pressures and low permeabilities in deep groundwaters may limit microbial transport, sizes of microbial

populations and their activity. Other hydrochemical factors such as salinity may also be significant.

Carbon sources for microbial respiration and for biomass formation are likely to be a major constraint on microbial processes at repository depth. Organic carbon is present only at low concentrations in these rocks, as also is methane, presumably from deep abiogenic sources with unknown fluxes. Inorganic carbon as HCO_3/CO_2 is only a viable C source for microbes where there is a strong electron donor e.g. hydrogen, 'the importance of hydrogen as a base for microbial communities should not be underestimated'.

In the absence (or paucity) of organic carbon, deep-sourced CH_4 and H_2 are the key factors in microbial involvement in deep redox reactions such as the consumption of dissolved oxygen by mineral-sourced Fe^{2+} or by methane itself (though the mass budget of CH_4 is probably too low for this reaction on its own to be the main cause of O_2 consumption except when O_2 is in low concentrations).

Sulphate reduction to sulphide is the other microbially-mediated reaction that is potentially significant at repository depth. The importance of microbial mediation of O_2 consumption reactions was established by microbial studies in the Redox Zone and REX experiments at Äspö. The Redox Zone experiment was at relatively shallow depth and showed the importance there of organic carbon drawn in from overlying soil in depleting dissolved oxygen [16].

The REX experiment [17, 18] showed that the rate of O_2 consumption in groundwaters towards repository depth may be accelerated by microbial mediation, having characteristic times in the order of months to years. Methane is proposed as the dominating electron donor for O_2 reduction; its concentration in deep Äspö groundwaters was reported to be 1 to 75 micromoles per litre.

In addition to the processes of naturally-occurring gases at repository depth and their interdependence on microbial activity, it is pointed out that hydrogen will be produced in the canisters in the repository. Its release into buffer and geosphere will depend on when the canisters are breached. When released, the hydrogen could stimulate microbial involvement in redox reactions.

3. General background to chemistry in the EBS and potential impacts of glaciation

The overall focus of this chapter is to assess the information needs about dissolved oxygen, redox, reduced sulphur and related geochemistry of future groundwaters at repository depth, in relation to the required inputs to EBS modelling, i.e. buffer/backfill reactions and canister corrosion.

The parts that are relevant to the present review are:

(i) The reference evolution of the repository system for the reference glacial cycle, which is described in section 9.4 of SR-Can [1].

(ii) The scenario where canister failure occurs due to corrosion for which two of the potential causes could be oxygen penetration or high sulphide concentrations coupled with buffer degradation as described in section 12.7 of [1].

In Section 13.7.6 of [1], SKB conclude that ‘More challenging is predicting the groundwater composition during a glacial cycle. As shown in section 9.4.7, upconing during glaciation will not result in excessively high salinity values, whereas intrusion of dilute glacial melt water, which may result in buffer erosion, cannot be excluded. Furthermore, for the case of an eroded buffer, the sulphide content becomes important, since excessively high values may lead to total corrosion of the copper canister’.

In discussing attenuation of dissolved oxygen by the geosphere, and the resulting risk of oxygen penetrating to repository depth and coming into contact with canisters, it needs to be remembered that the backfill and buffer in the EBS offer additional oxygen-consumption capacity and redox control. The overall risk to canister integrity by penetration of sub-glacial oxygen has to be considered against several factors causing oxygen attenuation: (i) consumption by reaction in the geosphere (as considered in this report), (ii) location of deposition holes in non-fractured, non-transmissive rock, thus reducing strongly the probability of entry of substantial amounts of oxygenated water into deposition holes, (iii) consumption by reaction with reducing minerals in the backfill and/or buffer.

The understanding in SR-Can [1] of copper corrosion under repository conditions is provided by the review report by King et al. [19]. For the temperate climate stages of the normal evolution of the repository, when near-field chemistry will be reducing, corrosion is assumed to be caused by sulphide, Corrosion by oxygen is considered in SR-Can only for the glacial stages of normal evolution in the long-term safety model. A model for the capacity of the bentonite buffer to react with any oxygen that does penetrate as far as deposition holes is provided by Bruno et al. [20].

3.1. Comments by SKI’s EBS Review Group

Some of the comments from SKI’s EBS review group during the recent SR-Can review are relevant to this review:

- Choice of clay material for the buffer will, amongst many other factors, take into account the mineral contents with respect to buffering of redox conditions adjacent to the canister; this refers mainly to the contents of pyrite and any other trace minerals containing reduced iron. SKB have yet to make their choice of buffer and backfill materials and to justify this choice in terms of overall benefit to long-term repository performance.

- In addition to redox-controlling reactions with trace reducing minerals, the mineral composition of the buffer will also influence the pH of pore water in contact with canisters. Therefore the overall corroding potential of pore water, with or without oxygen, needs to be considered in terms of Eh and pH variability, as well as other chemical factors such as salinity and HS^-.

- Piping and erosion of the buffer has been recognised only recently as a phenomenon that could compromise the integrity and performance of the buffer, especially during a period of anomalously high groundwater fluxes. Therefore the presence of intact buffer as a hydraulic and chemical barrier should not be invariably assumed in PA. A scenario where the buffer 'failed' in this way would place emphasis back on the geosphere to assure that the probability of oxygen contacting the canister will be kept as low as possible.

- Geochemical modelling is used for simulating various aspects of EBS evolution. In addition, as discussed in this report, geochemical modelling is used to simulate the long-term response of the geosphere to changing environmental conditions and scenarios, such as dissolved oxygen penetration. It is important that geochemical modelling concepts (e.g. kinetic versus equilibrium assumptions, ion exchange versus dissolution reaction), methods and thermodynamic databases are appropriate for the task and consistent with those used for other modelling tasks.

3.2. Dissolved oxygen and other hydrochemical influences on corrosion

3.2.1. Dissolved oxygen

The Pourbaix type of diagrams informs about stability of species in a chemical system in the pH/E_h -plane. There is, however, no information to be found directly on the dissolved, molar O_2 concentration (DO) in a pH/E_h point of such a diagram. E_h is determined by pH and the predominating redox couple in that point, which in a specific case of course could be the O_2/OH^- couple, but most probably is a modified version of the Fe(II)/Fe(III) couple, or some other couple in the geological system. However, the formal chemical activity of oxygen, which <u>at equilibrium</u> is also valid for the water phase, can be calculated from Nernst's equation and the redox equilibrium data between oxygen and water. The following set of equations can be written at 25 ºC:

$$4OH^- = O_2 + 2H_2O + 4e^- \ ; E_0 = 0.401 \text{ V}$$

$$E_h = E_0 + 0.059/4\log[\{O_2\}/\{OH^-\}^4]$$

$$pH + pOH = 14$$

From these equations the chemical activity for oxygen dissolved in the water, $\{O_2\}$ can be derived:

$$\{O_2\} = 10^{67.797Eh+4pH-83.186}$$

From $\{O_2\}$, DO or the molar concentration of oxygen, $[O_2]$ can be calculated from the formula:

$$[O_2] = k_*\{O_2\}$$

If k is known at the repository conditions it is thus possible to calculate $[O_2]$ for any "background" E_h/pH point in the Pourbaix diagram. If k were equal to 1, the oxygen concentration would in a case of E_h = -0.2V and pH = 7.5 (see Figure 3) be of the order of 10^{-67} M. Even if 'background' E_h/pH points can be calculated from other, dominating redox couples, it is thus difficult and perhaps meaningless to discuss true, dissolved O_2 values at equilibrium in such low E_h cases. However, as an illustration, in Figure 1 the calculated concentration of O_2 (log[O_2]) is plotted as a function of E_h in the actual interval of about -0.4 to +1 V for the simple case of pH = 7.5 and k = 1. E_h is here supposed to be determined exclusively by the couple O_2/OH^-, which is in many cases irrelevant.

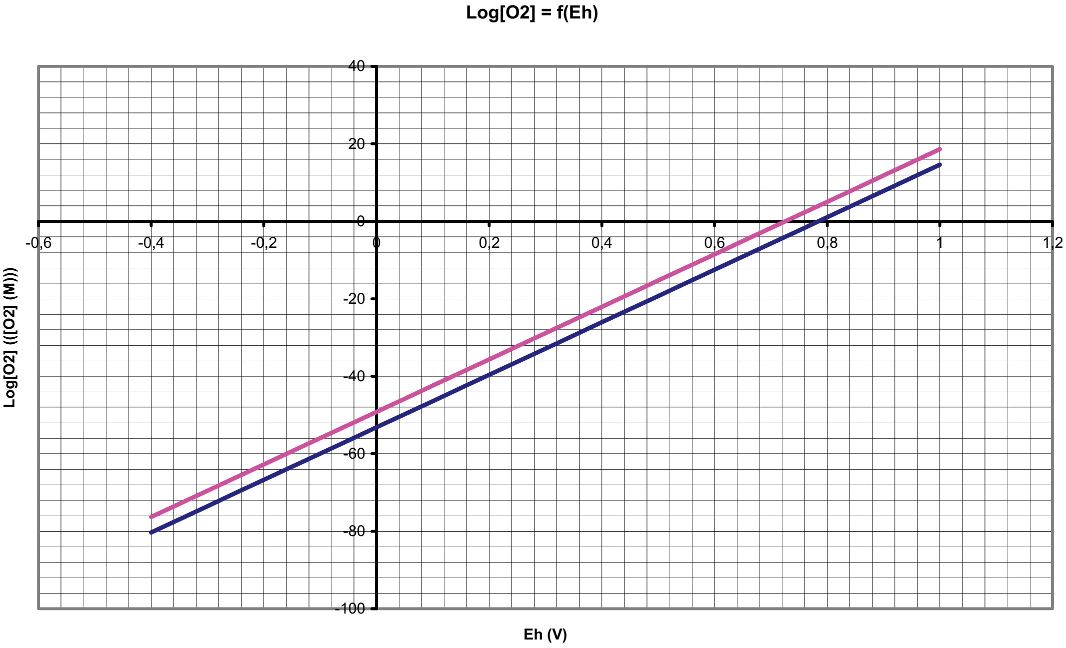


Figure 1. Calculated dissolved concentration of log[O_2] as a function of E_h. See the text for conditions and limitations. Red is pH = 8.5 and black is pH = 7.5.

3.2.2. General chemical background to copper corrosion

A part of this work is to sketch a background to what will happen in the repository especially at a glaciation. Important information to rightly judge this is to have knowledge about the environment itself, the nature of canister corrosion and the thermodynamic limits for corrosion in the repository environment. A rough overview of the thermodynamics for the whole system Cu-Fe-Cl-S-C-H-O is therefore given to form a general background for the review work. Data are normally presented as Pourbaix diagrams that are valid at indicated conditions and, if not otherwise indicated, at 25 ºC.

Some of the conclusions are that general corrosion on copper will probably not be of significant importance in a repository at normal conditions. However, there are specific conditions, for example at glaciation, as there could be a status of no passivation of copper in a highly saline and oxidative environment. In a previous research plan from SKB [21] a decrease of the importance of the multi-barrier principle was implied as only a small emphasis was put on geology. Therefore the engineered barriers and especially the canister are rendered a much larger importance for the system integrity. This implies that it is reasonable to put much higher emphasis on all functions of the canister. The proof burden of the canister lifetime thereby increases strongly and should cover up to 1,000,000 years as there are no guarantees for example that oxidising conditions combined with high salinities will not return at a later stage, for example at periods of glaciation. A combination of a mechanical fault, materials stress and localised corrosion in an oxidising, chloride containing environment would be especially dangerous and is not at all just hypothetical.

There are many studies of canister corrosion accounted in literature. This work is, however, not intended as a literature survey and the reader is therefore suggested to find such information directly in literature or in already existing surveys. However the mechanisms for corrosion can be expected to differ greatly for different situations, the general conclusion of the repository oriented literature is that copper is an excellent canister material. It is foreseen to have a very long lifetime in the intended environment. There are, however, uncertainties in the estimation of the lifetime indicated in literature, especially at deviating conditions like those supposed to prevail at glaciation (chloride, oxygen, transportation patterns) and at the uncertain influences of agents like sulphides and bacteria.

The layout of the planned Swedish repository for spent nuclear fuel is described in general terms in several older and recent sources [6, 22, 23] and is not treated here.

3.3. The chemical environment around a repository

The limits of possible pressures in the repository are 5 MPa (no glaciation) and 35 MPa (glaciation). There is an estimation of a probable maximum of 14 MPa. The pressure influences mechanical and chemical systems but also groundwater flow and thereby solute transport patterns.

The temperature in the repository will roughly vary with time in a manner, which could give a maximum close to a canister of about 85 °C a short time after the sealing. Thereafter the temperature decreases and will after some time adopt the surrounding rock temperature, about 15 °C. Lower temperatures can appear in connection with glaciation. The calculations in this section of the report have been performed at 25 °C as input data are normally given at that temperature. The difference of 15 °C is judged to be negligible for the intended purpose.

The groundwater flows slowly through the repository and its composition can vary with time for different reasons, for example in connection with glaciation and as a function of other climate and environmental changes. The water is supposed to contain e.g. chloride, carbonate and sulphide/sulphate in concentrations and relations that could vary. Furthermore there will exist very low concentrations of reducible species, for example Mn(III, IV) and Fe(III), bound as complexes together with e.g. chloride and organic complexing agents. The latter species can exist in the organic material in the bentonite and are supposed to have a large influence on the prerequisites for copper corrosion.

It is also of interest for corrosion processes which kind of water will fill the repository after the sealing. Would it be fresh surface water or chloride-containing deep water? In [24] there is a discussion to use salt water or brine for hydrodynamic retrieval of canisters. This is an obvious example of anthropogenic actions that could add to the risk of corrosion.

At sealing, the repository environment will be oxidising. It is of course of importance to estimate how long oxidising conditions can prevail. In a shorter perspective just after the sealing, free oxygen will decide the redox potential. It is probably going to be relatively high. The total amount of free oxygen in the aerated repository consists of oxygen left in pockets of air and oxygen dissolved in water (DO), for example in the bentonite pore water. The bentonite has also an open porosity, which is filled with air. The air and thereby the oxygen can have entered into the bentonite pore water and porosity during the relatively lengthy and extensive handling period in connection with excavation, transportation and storage of the bentonite.

As an example of calculation, it could be supposed that the bentonite pore water would be oxygen saturated (8 mg/l at normal pressure and temperature). Then the bentonite in a deposition hole (about 12 m^3 of bentonite) is going to contain about 10 g DO in water if the bentonite moisture content is about 10 vol. %. If this oxygen were consumed in some mechanism of attack, it would correspond to dissolution of about 70 g of copper metal. It should simultaneously be pointed out that the amount of oxygen, which is found initially in the open pores of the bentonite, is much bigger than what is dissolved. SKB have from certain laboratory experiments and considerations estimated the oxidising time in the repository to be about 100 years. The uncertainty is judged to be large. Perhaps oxidising conditions can prevail under considerably shorter or longer periods of time. As long as porosity in the bentonite is open and not filled with water, oxygen can still reach the canister hole from the tunnel refill, which would extend the oxidative period.

After the oxidising period relatively large amounts of reducible species are still present in the masses of bentonite. Those can serve as electron sinks in combination with other processes, for example formation of copper sulphide. The repository pH is buffered by the bentonite, which implies a pH of about 7-9. The bentonite itself consists of clay minerals as montmorillonite and can be supposed to vary in composition. It can also contain many of the elements in the periodic table as impurities. For example pyrite (FeS_2) will occur and also residuals of organic materials.

The repository will probably be subject to variations of groundwater salinity. There can also be events which result in crack formation in or peptisation of the bentonite. Such events can, if they would happen, be supposed to strongly influence the chemical environment of the repository. Furthermore, it shall be pointed out that if the rock fracture system is not already biologically contaminated, the very opening and construction of the repository will imply a biological contamination. Therefore it is probable that microbes will exist in the repository after the sealing. Their survival and biological activity has been discussed extensively [25].

Human incursion in the repository can be supposed to happen in a multitude of ways and will, if it would happen, probably influence the chemical and the physical environment very strongly. Acidification, deposition of chemical waste in the proximity of the repository, and climate changes are all examples of anthropogenic events that can be considered to influence water chemistry. Different types of alien material will probably unwittingly be left at the sealing of the repository. The alien material can thereafter influence in several ways. For example it could sustain biological processes and thereby contribute to sulphate reduction, formation of sulphide and in the prolongation copper corrosion. Furthermore the alien substances themselves can have chemical and mechanical properties which directly would influence corrosion and transportation processes.

As a summary it can be said that the global pH in the repository will be in the range of 7-9, buffered by the bentonite. The redox potential will probably run through an initial period of oxidising conditions and gradually turn into a reducing. Oxidising and reducing conditions might alternate e.g. during glaciation periods. A very rough estimation based on Figures 6 and 7 and also other information indicates that the redox potential would vary in the interval $-0.5 < E_h \text{ (V)} < 0.7$. The global concentrations of Cl^- can rise to the order of 1.5 M and O_2 to $3x10^{-4}$ M (~10 mg/L).

As a first approximation the same conditions will prevail initially on the canister surface. However, the change with time on micro sites on the surfaces can differ slightly from position to position and from the global environment in the rest of the repository. One example of this is the higher temperature (and the temperature distribution) during the first, hot time after the sealing at the canister. This could cause transportation effects not occurring in other parts of the repository. Components could by the temperature gradient be concentrated on the canister surface or in the proximity of the canister and cause a chemistry that differs strongly from the repository in general. For example chloride and other water borne components can be suspected to concentrate in such a process, at least within certain zones of vicinity of the canister. Circulation in the immediate proximity of the canister through convection is, however, less probable. If it still occurs, it can imply that the local environment close to the canister have access to a supply of considerably more oxygen than foreseen from global environmental data. This implies that the redox potential can decrease more slowly on the surface of the canister than foreseen from pure diffusion data.

Mechanical and chemical inhomogeneities in the adjacent bentonite as well as on the copper surface itself can also be foreseen. Such inhomogeneities can be present from the beginning, but also be created by the described circulation process or by external events. For example the canister will initially have an oxide layer which could be locally disturbed and made unstable by high chloride concentrations. This could happen through the influence of the handling equipment and by the fact that the oxide layer locally can to be exchanged for a sulphide layer or by local concentration effects. Further, defects in the copper material can be present from the production process, for example pores as well as welding and handling faults.

The most important chemical entities related to copper corrosion in the repository would be:

Metals: Cu and Fe
Simple anions: Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, and HS^-
Simple cations: Na^+, Ca^{2+}, Mg^{2+}, Cu^+, Cu^{2+}, Fe^{2+}, and Fe^{3+}
Complexes: $CuCl_n^{1-n}$, $CuCl_n^{2-n}$, $FeCl_n^{2-n}$, $FeCl_n^{3-n}$, $Cu(OH)_n^{1-n}$, $Cu(OH)_n^{2-n}$, $Fe(OH)_n^{2-n}$, $Fe(OH)_n^{3-n}$, $Cu(CO_3)_n^{1-n}$, $Cu(CO_3)_n^{2-n}$, $Fe(CO_3)_n^{2-n}$, $Fe(CO_3)_n^{3-n}$, $Cu(HCO_3)_n^{1-n}$, $Cu(HCO_3)_n^{2-n}$, $Fe(HCO_3)_n^{2-n}$, and $Fe(HCO_3)_n^{3-n}$
Solids: CuO, CuO_2, Fe_2O_3, Fe_3O_4, $CuFe_2O_4$, $CuFeO_2$, $CuCl_2{:}3Cu(OH)_2$, $CuCO_3$, $Cu_2CO_3(OH)_2$, Cu_2S, $Cu_{1.75}S$, $Cu_{1.93}S$, CuS, and $\approx FeS_2$
Colloids: Peptized bentonite, organic material
Organic matter: for example humic and fulvic acids
Surfaces: Bentonite minerals and metals

Gases: Dissolved O_2, N_2 and other chemical components that at proper pressure and other circumstances might generate gas (i.e. 'geogas' or methane).

Typical expected concentrations for some of the above species and total concentrations of their systems can be found, i.e. in Tables 1 and 2.

After closing the facility, groundwater has access to the whole system and there will be a groundwater flow through the repository. The flow rate and composition of the water is determined by the surrounding conditions as well as by the repository conditions.

The ranges for main parameters of groundwater compositions given in SR-Can [1] are summarised in Table 1 as 'general orders of magnitude'. These values might of course be modified by future results from ongoing groundwater analyses.

Table 1. Typical compositions of groundwater in the near field. Estimates are made on the basis of extensive field investigations and bentonite water interaction tests.

pH		6.5 - 9.0
E_h {V}		-0.35 to -0.15
HCO_3^-	mg/dm^3	40 - 500
SO_4^{2-}	“	40 - 60
HS^-	“	0.1 - 1
HPO_4^{2-}	“	0.1 - 0.2
NO_3^-	“	0.01 - 0.6
NO_2^-	“	0.01 - 0.1
Cl^-	“	1 - 17000
F^-	“	0.2 - 10
Ca^{2+}	“	5 - 3200
Mg^{2+}	“	1 - 50
Fe^{2+}	“	0.1 - 3
Fe^{3+}	“	<0.1
Mn^{2+}	“	0.2 - 0.5
K^+	“	1 - 25
Na^+	“	10 - 4000
Al^{3+}	“	0.01 - 0.2
SiO_2	“	2 - 20
TOC	“	1 – 8

A discussion of microbial influences can be found in [25]. A major concern for the performance of the canisters is that sulphate-reducing bacteria (SRB) may be present in the clay and induce canister corrosion by production of hydrogen sulphide. Water activity would be a strong limiting factor for activity of bacteria in compacted bentonite. It is demonstrated that a chemical water activity ≤ 0.96 prevents SRB from being active in the clay. Sulphate-reducing bacteria seem to thrive when the Cl^- concentration of the groundwater is 4000-6000 mg/l. Sulphate reduction is an in situ process but it should be noted that the resulting hydrogen-sulphide rich water can be transported to other locations. A more vigorous sulphate reduction takes place when the organic content in the groundwater is high (>10 mg/l DOC), which is the case in the sediments and in the groundwaters under the sea.

Chemical parameters in Table 2 have been used as the background for calculations of Pourbaix diagrams.

Table 2. Selected chemical parameter ranges for background to Pourbaix calculations of copper corrosion.

Parameter	Unit.	Selected value	Min value	Max value
pH		8	7	10
E_h	V	-0.3	-0.1	-0.5
HCO_3^-	mg/l	100	100	300
SO_4^{2-}	mg/l	8	5	500
Cl^-	mg/l	200	170	6500(50000)
HS^-	mg/l	0.1		0.5
Ca^{2+}	mg/l	80	40	2000
Na^+	mg/l	100	60	2000
Fe^{2+}	mg/l	0.1		1
K^+	mg/l	5	5	20
Mg^{2+}	mg/l	9	20	130
Logp_{O2}	(bar)	-2.8		-2.8
(O_2	mg/l			8)
S^{2-}	mg/l	0.1		0.5

There are several chemical environments around and also inside the canister that can be foreseen. It is also well known that chemical components like copper, iron, chloride, sulphide and carbonate are present at varying concentrations. Beside those there is of course a residual probability of significant chemical components appearing that either cannot be foreseen at the present or are misjudged as being unimportant. In all cases the environment is framed by the presence of the surrounding rock and of the bentonite that could be inhomogeneously composed, wetted, heated and mechanically loaded by an anisotropic pressure field. The conclusion is that the total system is very complex and could therefore not be described in a simple way. A thermodynamic description therefore has to be simplified and will cover only the most important parameters as seen in the following.

The relationship between E_h and pH values and equilibrium for the HS^-/SO_4^{2-} redox couple was examined for data from the Forsmark site in ref. [2] and is shown here in Figure 2.

It was concluded in this case that:

- Most measured pH/E_h points are located close to the HS^-/SO_4^{2-} line, also as a function of pH. This would be expected if the couple HS^-/SO_4^{2-} determines E_h.

- Exceptions are for KFM04A/234, for which HS^-/SO_4^{2-} data are absent and for KFM03A/990 for which HS^-/SO_4^{2-} concentrations are very low.

- It thus seems as if the HS^-/SO_4^{2-} couple determines E_h at ‘normal’ concentrations (above about 0.5 mM and around 5 mM).

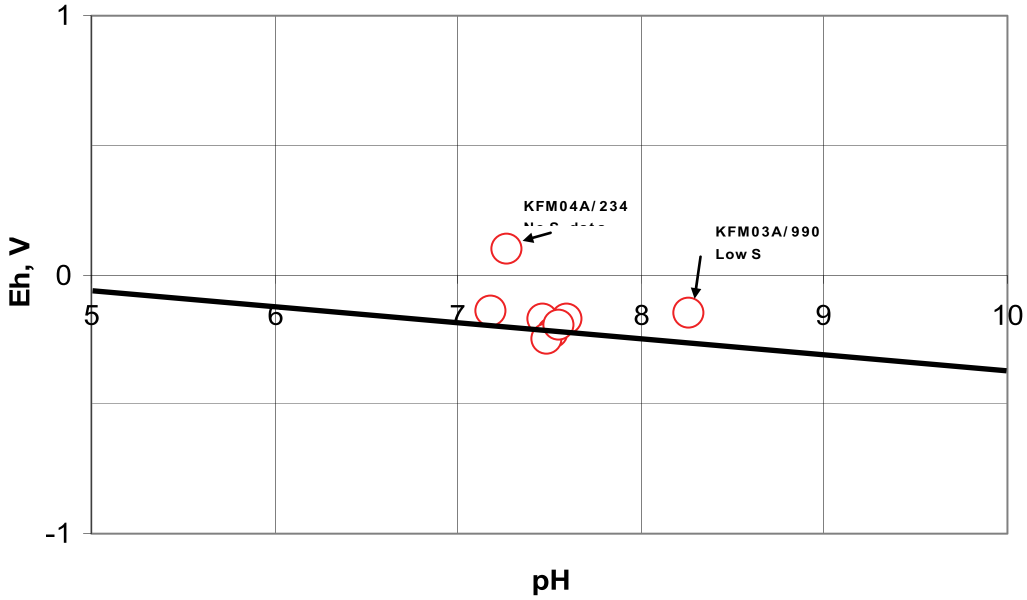


Figure 2. Compilation of pH/E_h data points from the selected set of groundwater data for Forsmark [2]. The line represents the equilibrium of the couple HS^-/SO_4^{2-} when pH > 7.

- If extreme data (KFM04A/234, KFM03A/990) are excluded, the spread in E_h would be around 150 mV. The spread in pH would be around 0.5 units.

- This spread in data would indicate that measured values fall within acceptable limits compared with what would be expected.

- If extreme values are included the spread is larger. Such values, however, seem in the selected cases to be a result of deviating/extreme conditions and not necessarily a result of bad sampling/analysis/data handling.

A compilation of estimated, calculated, proposed and otherwise used E_h/pH couples as found in SR-Can [1] and related documents is shown in Figure 3.

If extremes are excluded, the values of pH/E_h found in Figure 2 are included in the envelope of those in Figure 3. The envelope defined in Figure 3 can be written as the intervals $6.85 < \text{pH} < 9.8$ (main: $6.85 < \text{pH} < 8.0$) and $-310 < E_h\ (\text{mV}) < -150$, which then could be expected to be the 'should be' values of these main chemistry parameters in the repository environment. This work will examine much broader intervals: $7 < \text{pH} < 10$ and $-0.5 < E_h\ (\text{V}) < 0.5$ respectively.

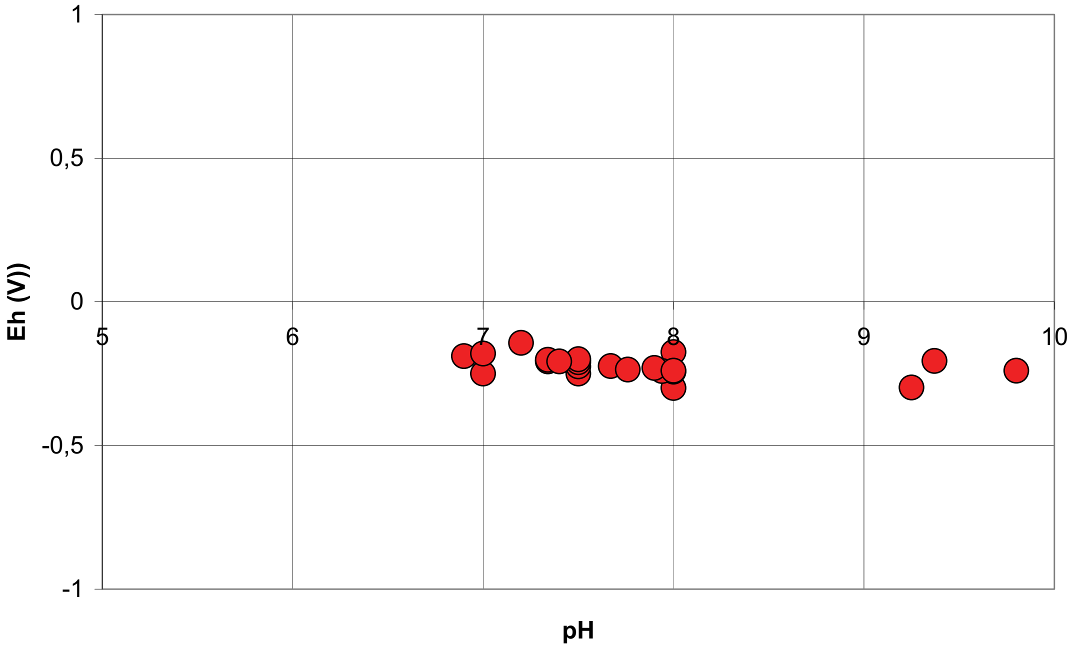


Figure 3. A compilation of estimated, calculated, proposed and otherwise used pot/pH couples as found in SR-Can and related documents.

Those values of the main chemical parameters together with the concentration values of main species found in Table 2 can be considered as the 'standard' values in the following calculations.

3.4. General framework for Pourbaix calculations for copper corrosion reactions

The thermodynamics of copper specifically in saline environments form an important part of the basis for this work. It gives the framework for subsequent modelling discussions. It should be described in relation to as many environmental parameters as possible of those mentioned above. Thermodynamic data are available from many sources and in many shapes and qualities. A convenient way to present calculated data is as Pourbaix diagrams, each calculated for a given set of conditions. They can act as chemical maps and background for the review work. Because of the complexity of the total chemical system, the calculations are limited to the chemical system Cu-Fe-Cl-S-C-H-O at 25 ºC and some of its subsystems [26].

3.5. The system Cu-Fe-Cl-S-C-H-O

3.5.1. General

The material accounted in [26] tries to complete the picture from other investigations (as in [27 and 28]) for the system Cu-Fe-Cl-S-C-H-O. This is done by including iron, sulphide and carbonate as well as performing calculations for very high salinities. Calculations were also performed at an elevated temperature of 150 °C for the subsystem Cu-Cl-H-O in [27], but these are not accounted here. The calculations have been done using Puigdomenech´s set of programs and also in part the database, appearing on the web page at the Royal Institute of Technology, KTH, Stockholm. Our calculations performed on the system Cu-Cl-H-O to higher salinities and temperatures (150 °C) were, however, partly done using data published in [28].

3.5.2. The sub-system Cu-Cl-H-O

In [28] three different total concentrations (10^{-4}, 10^{-6}, and 10^{-8} molal) for dissolved copper were used for the calculations.

It says in [28] that copper is a noble metal, but corrodes with hydrogen evolution at low pH, both at a concentration level of 10^{-6} m at $T \geq 125$ °C, and at a concentration of 10^{-8} m from $T \geq 50$ °C. The oxides (Cu_2O (cr) and CuO (cr)) are stable at all temperatures and concentration levels $\geq 10^{-8}$ m, with the exception of 10^{-8} m at $T \geq 100$ °C. The copper (II) hydroxide, $Cu(OH)_2$(cr), is not thermodynamically stable in the interval investigated. Cu^+ predominates at $T > 80$ °C at all concentrations levels. CuOH (aq) appears in the Pourbaix diagrams only at the lowest concentrations, and in the predominance diagram for dissolved species at 125 and 150 °C. $Cu(OH)_2^-$ predominates at all temperatures and concentrations investigated for high pH values (>11).

At acidic pH, an increasing temperature decreases the immunity area, and therefore the risk for corrosion of copper increases. At alkaline pH-values corrosion also increases with temperature due to decrease of both the passivity and immunity areas.

Examples of Pourbaix diagrams calculated for the subsystem Cu-Cl-O-H at 25 °C and $[Cl]_{tot}$= 0.001, 0.1 and 1.5 M, respectively are shown in Figures 4, 5 and 6.

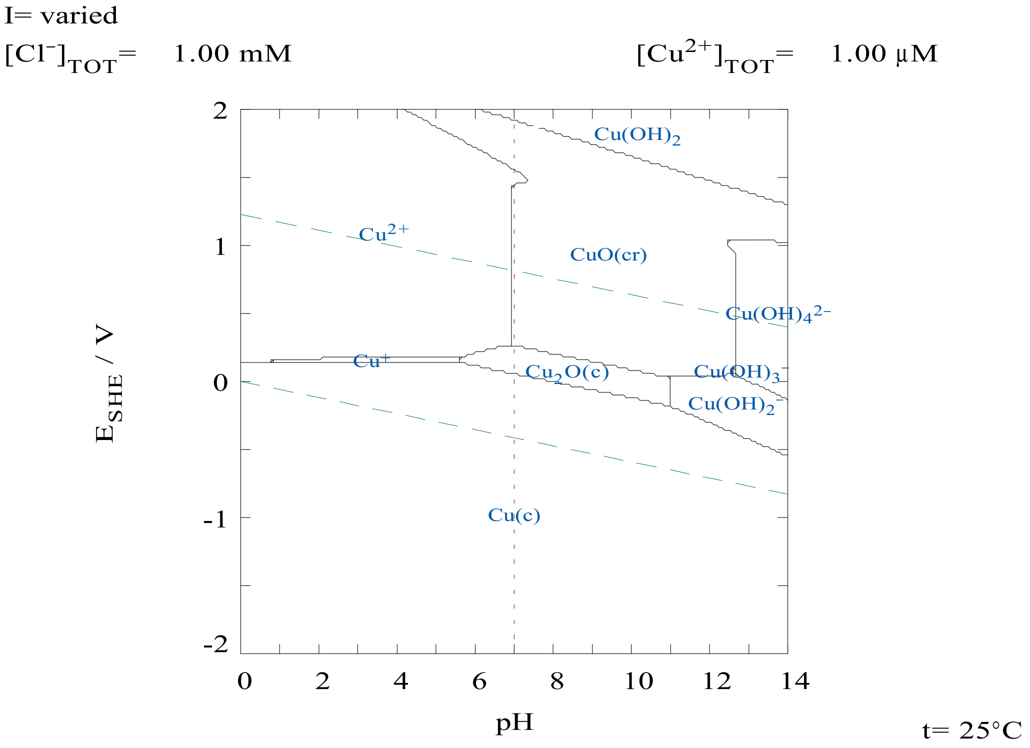


Figure 4. Pourbaix diagram for the system Cu-Cl-H-O at indicated conditions.

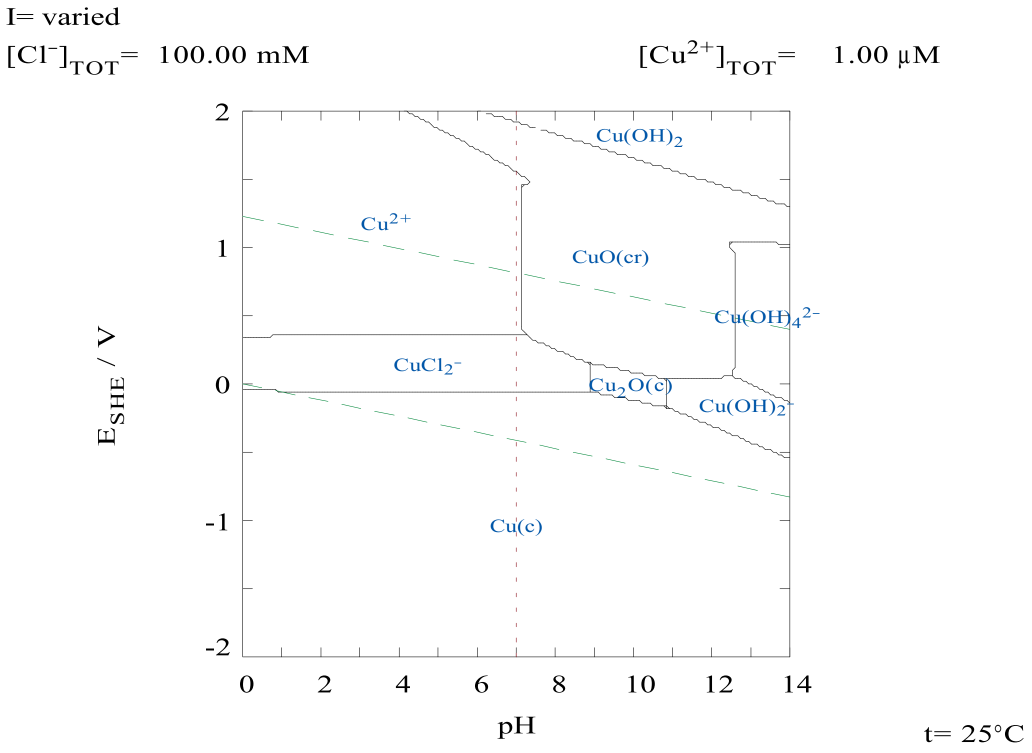


Figure 5. Pourbaix diagram for the system Cu-Cl-H-O at indicated conditions.

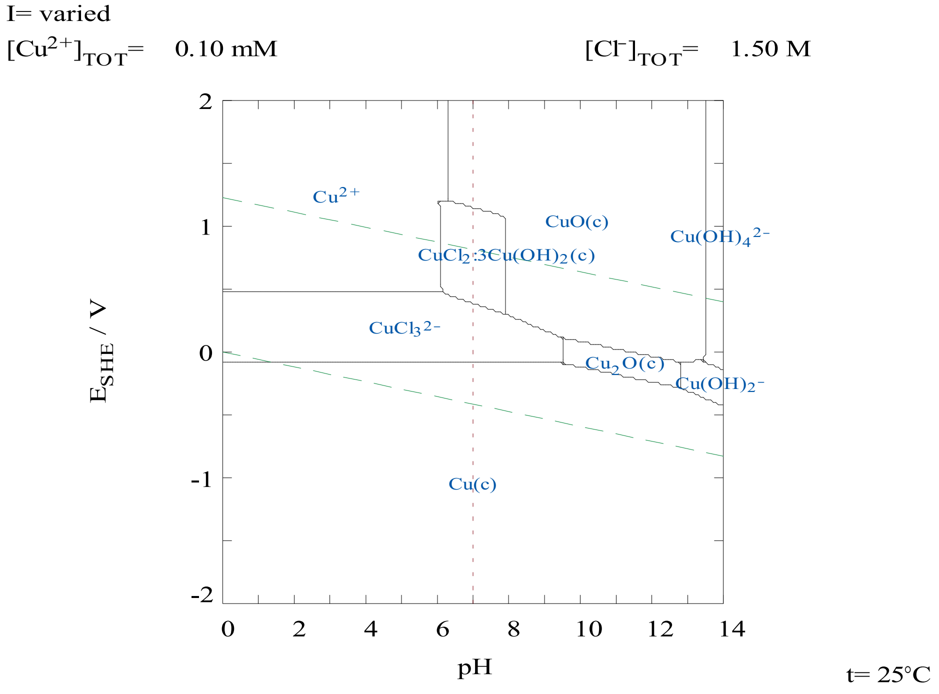


Figure 6. Pourbaix diagram for the system Cu-Cl-H-O at indicated conditions.

It is interesting to see in the previous figures that in the simple system of Cu-Cl-H-O there is no protecting, passivating layer on copper in highly saline media in large pH/E$_h$ regions. This 'vulnerability' of copper develops rapidly as a function of [Cl$^-$] and should be remembered when discussing the risk of introduction of saline waters into the repository. If the diagram in Figure 6, which is calculated for 25 °C, is compared with such for higher temperatures as presented in [27, 28], it can be seen that the immunity limit for copper also descends as a function of temperature at high chloride concentrations. This means a risk that copper could be neither noble (immune), nor passive at elevated temperatures in the repository environment, containing large concentrations of chloride. Higher reaction rates related to the increased temperature will of course add to the risk of corrosion.

3.5.3. The sub-system Cu-S-H-O

A selected set of diagrams shown in Figures 7-9 were calculated at indicated conditions in order to be able to find critical concentrations for copper sulphide formation. A comparison of those and not accounted diagrams show that copper behaviour depends on sulphide and chloride concentrations and the variation of the pH and E_h. The ionic strength itself has very little or no influence.

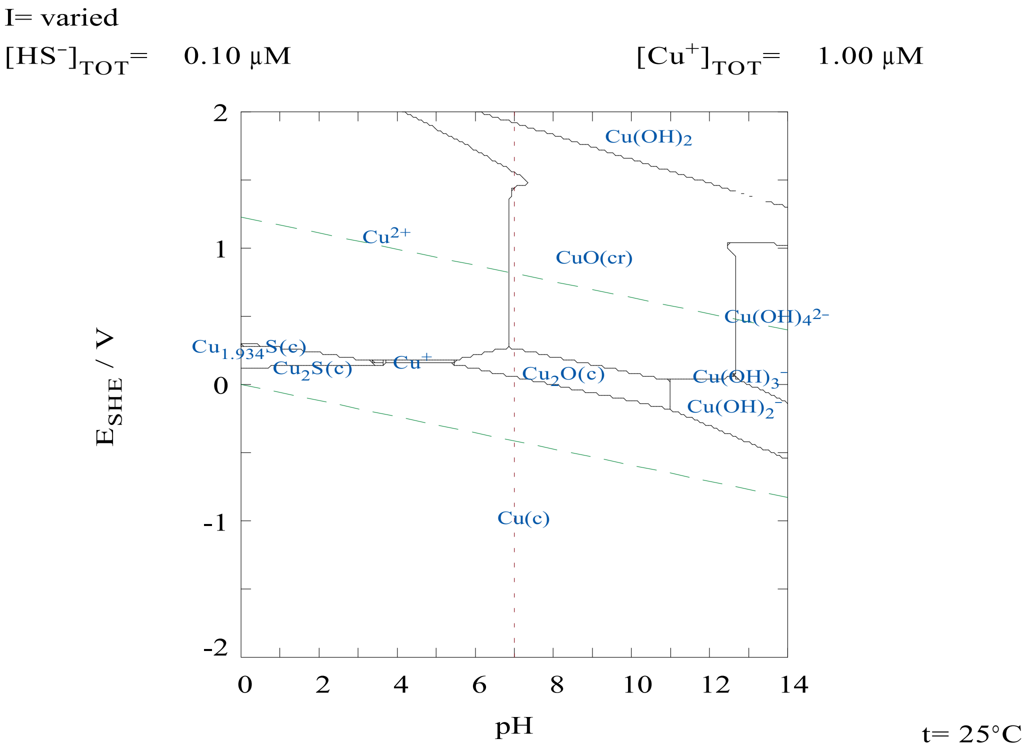


Figure 7. Pourbaix diagram for the system Cu-S-H-O at indicated conditions.

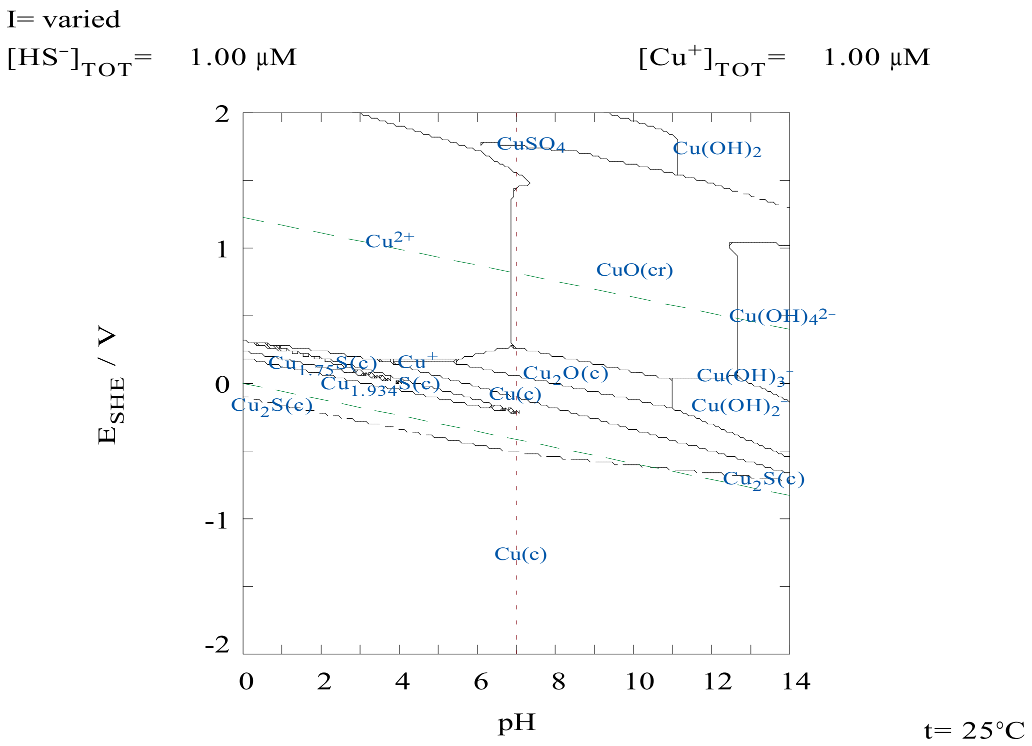


Figure 8. Pourbaix diagram for the system Cu-S-H-O at indicated conditions.

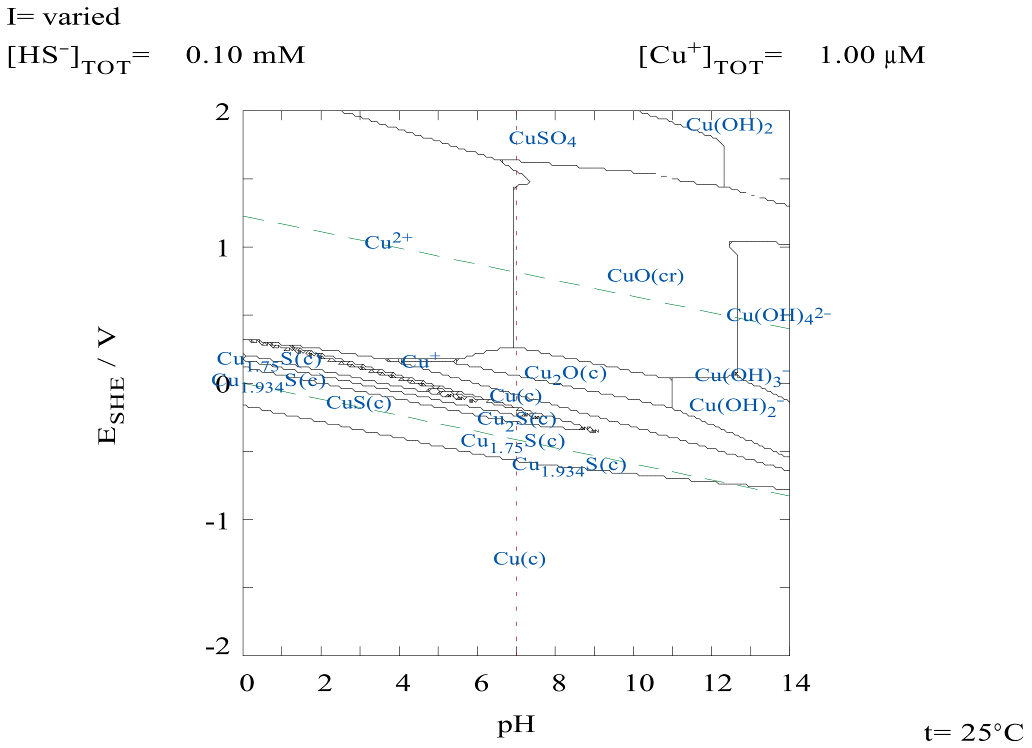


Figure 9. Pourbaix diagram for the system Cu-S-H-O at indicated conditions.

3.5.4. The sub-system Cu-Fe-S-H-O

Pourbaix diagrams for part of the system Cu-Fe-S-H-O were calculated [27]. In certain types of environment sulphide and also iron would have an influence on copper stability. Sulphide is important at low potentials. Iron is important for example if there would be a break through of the copper. Iron is also present in the repository environment.

Depending on conditions, two bi-metallic oxides can be found in the chemical system beside the metals and simple oxides. The bi-metallic oxides are delafossite, $CuFeO_2$ and cuprospinel, $CuFe_2O_4$. There is also a bimetallic sulphide, $CuFeS_2$. The solubility of copper varies between 10^{-7} M and 10^{-5} M, depending on environment. Examples of Pourbaix diagrams for this sub-system are displayed in Figures 10 and 11, showing copper containing species and iron containing species, respectively.

It can be seen that $CuFeS_2$ and Cu_2S both appear in the pH/E_h area of interest.

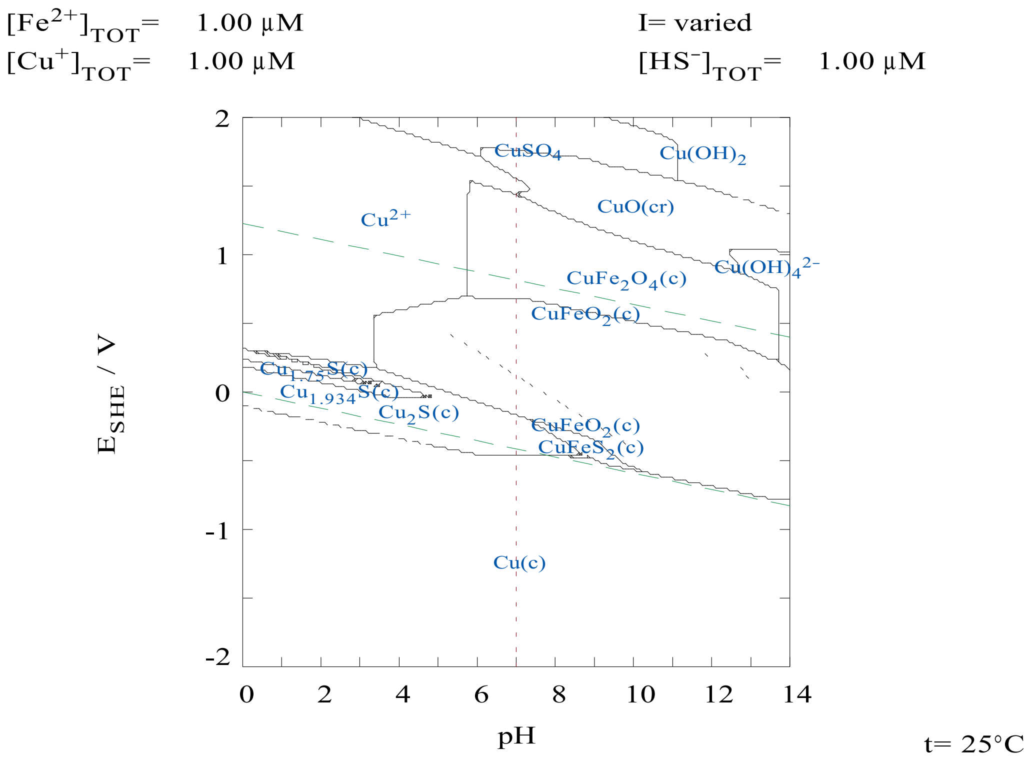


Figure 10. Pourbaix diagram for the system Cu-Fe-H-O at indicated conditions. Copper containing species are shown.

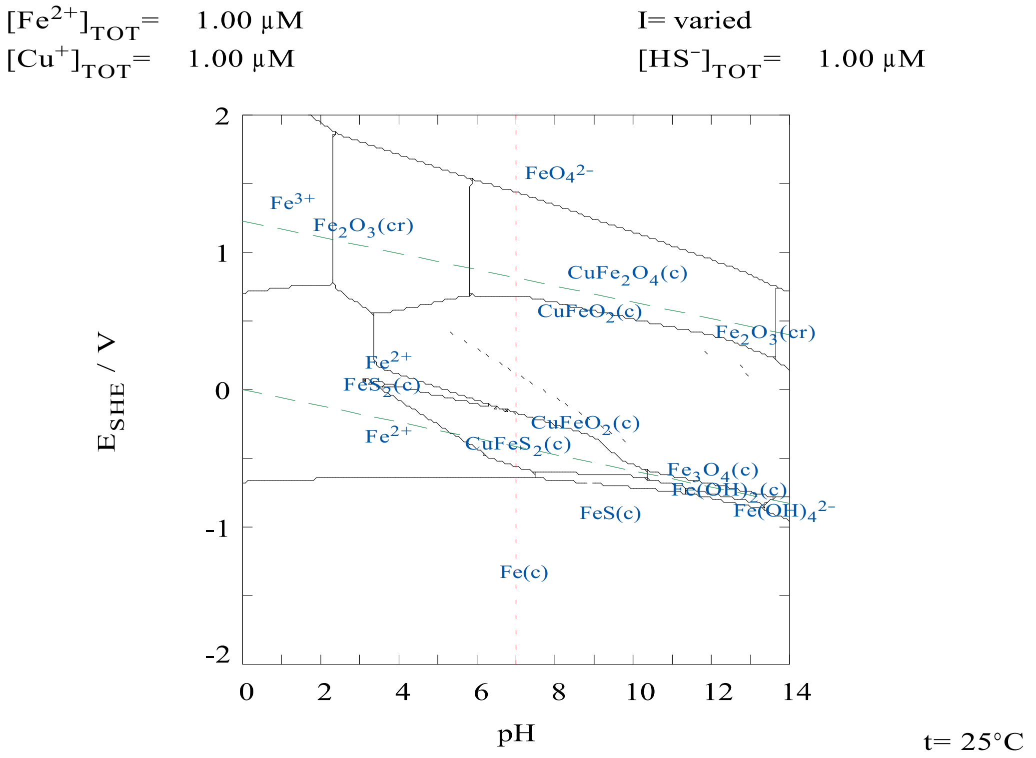


Figure 11. Pourbaix diagram for the system Cu-Fe-H-O at indicated conditions. Iron containing species are shown.

3.5.5. The sub-system Cu-Fe-S-Cl-H-O

An example of a Pourbaix diagram calculated for the system Cu-Fe-S-Cl-O-H at 25 °C and $[Cl]_{tot}$=1.5 is shown in Figure 12.

One important feature that can be observed in Figure 12 is that the immunity limit of copper is further lowered in the S-Cl containing system compared with systems not containing sulphur. This could have consequences for copper corrosion in a reducing environment as a formed sulphide film probably would have a disputable passivating ability.

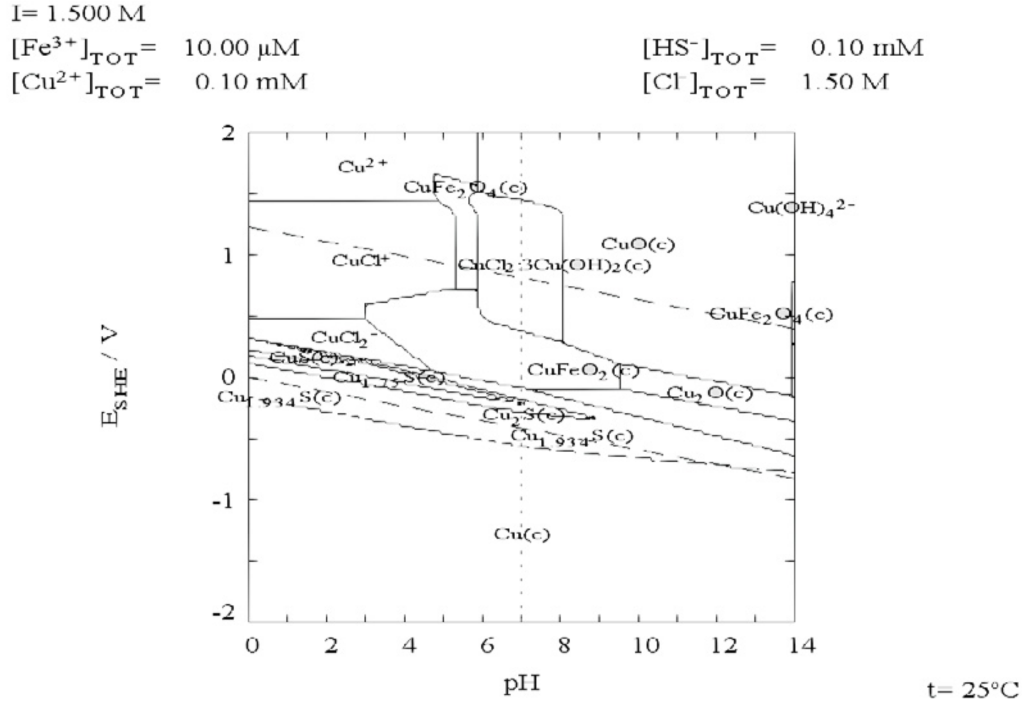


Figure 12. Pourbaix diagram for the system Cu-Fe-Cl-S-H-O at indicated conditions.

3.5.6. The sub-system Cu-Cl-C-H-O

In Figure 13 the system Cu-Cl-C-H-O is shown for indicated conditions at chlorine and carbonate concentrations precisely at which copper species containing those components are starting to appear. It is found that the first chlorine containing species to appear is $CuCl_2^-$ at a total chlorine concentration slightly above 1 mM. The first carbonate containing specie is $CuCO_3$, appearing at a total carbonate concentration of 0.5 mM.

The same system is also shown in Figure 14 at the total concentrations chosen for the repository model system as shown in Table 2. It can be seen that at those slightly higher concentrations of chlorine (2 mM) and carbonate (6 mM), $CuCl_2^-$ is still the predominating copper species containing chloride. Among copper carbonates, malachite ($Cu_2CO_3(OH)_2$) appears beside the simple copper carbonate $CuCO_3$.

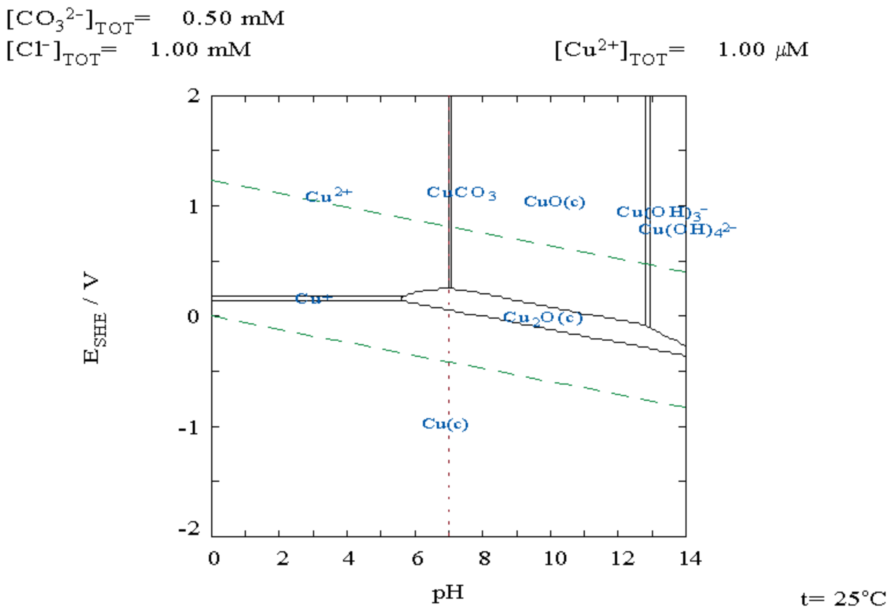


Figure 13. Pourbaix diagram for the system Cu-Cl-C-H-O at indicated conditions.

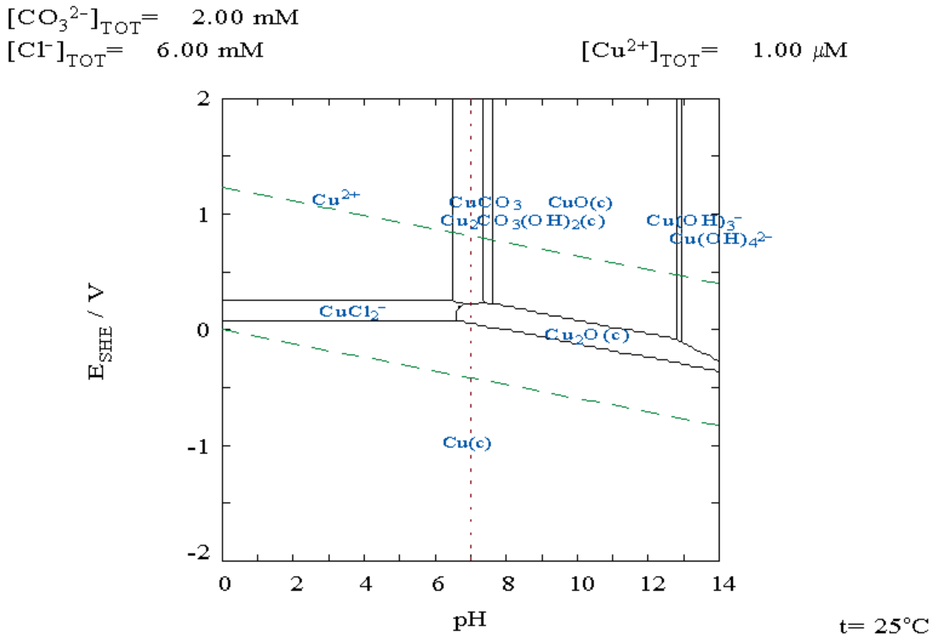


Figure 14. Pourbaix diagram for the system Cu-Cl-C-H-O at indicated conditions.

3.5.7. The sub-system Cu-Cl-S-C-H-O

In Figure 15 a diagram for the subsystem Cu-Cl-S-C-H-O is shown for 25 °C. It could be seen (roughly) that sulphides and oxides predominate at low potentials, chloride at intermediate and carbonates at high. Sulphide is clearly decreasing the immunity area of copper in a way that seems independent of the total sulphide concentration within the calculated range. An increased chloride concentration does not influence the sulphide predominance very much.

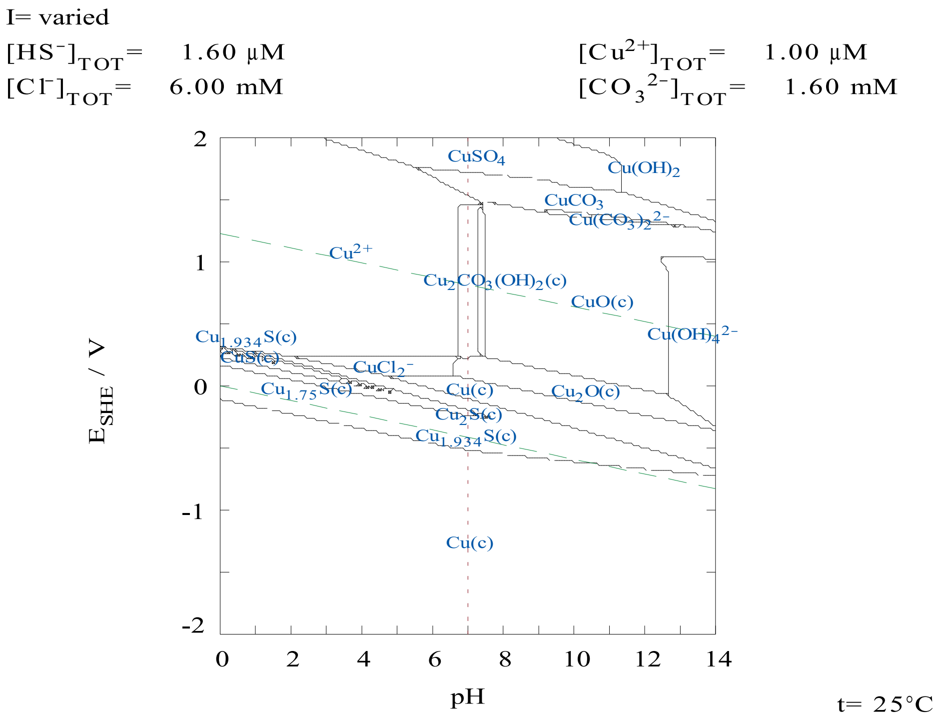


Figure 15. Pourbaix diagram for the system Cu-Cl-S-C-H-O at indicated conditions.

3.5.8. The total system Cu-Fe-Cl-S-C-H-O

In Figure 16 a diagram for the full system of Cu-Fe-Cl-S-C-H-O is shown for 25 °C at the conditions given in Table 2. In Figure 17 the same system is shown at a higher chloride concentration of 5 M. Only copper containing species are shown in the diagrams. These are the most generalised diagrams for the repository system when also iron is present. However, to calculate the diagrams it has been necessary to reduce the number of species participating in the calculation. The way of selecting species to be included in calculations can of course be debated. Essentially, species with a low probability of appearing within the environmental envelope of the repository have been excluded.

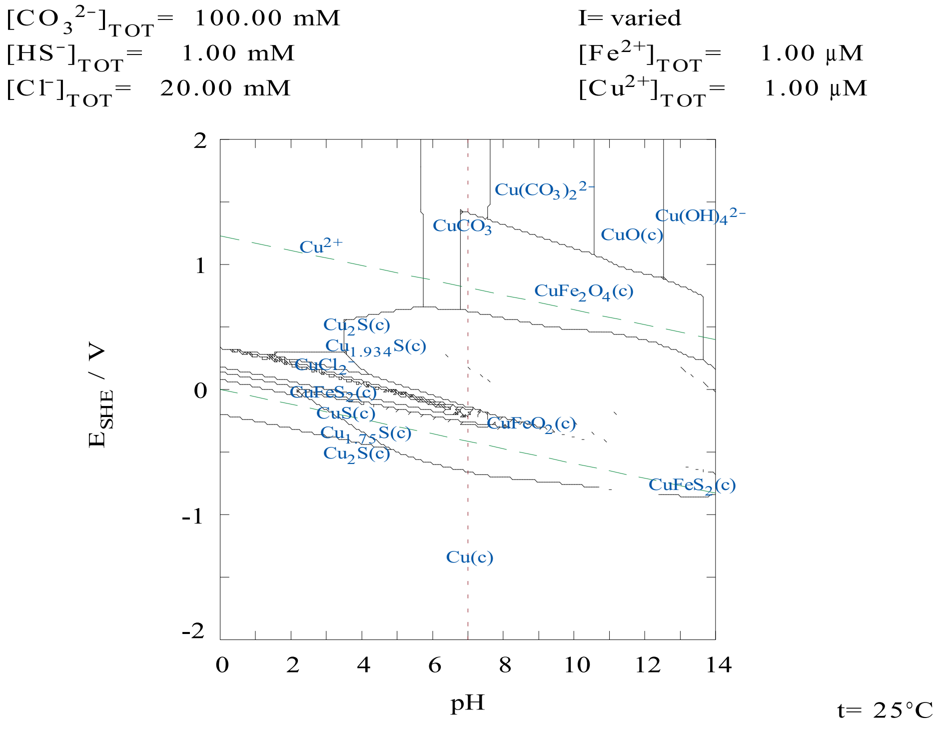


Figure 16. Pourbaix diagram for the system Cu-Fe-Cl-S-C-H-O at indicated conditions. Low salinity. Cu-containing species are shown.

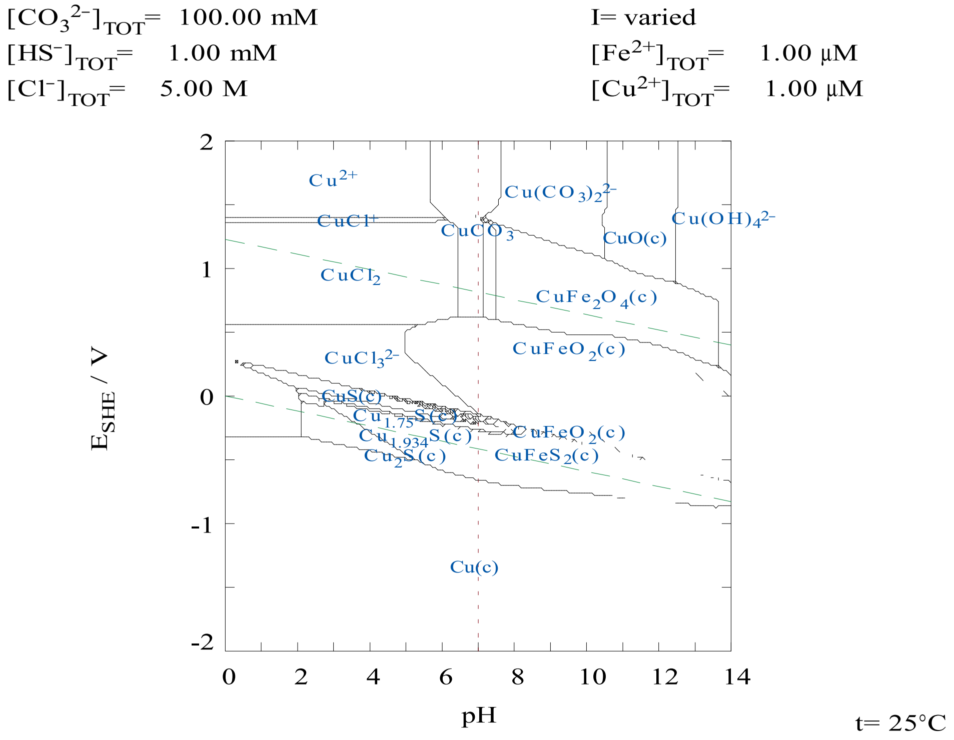


Figure 17. Pourbaix diagram for the system Cu-Fe-Cl-S-C-H-O at indicated conditions. High salinity. Cu-containing species are shown.

Figure 16 demonstrates that copper sulphides dominate at low chloride concentrations in the central parts of the diagram. There are also indications in the diagram that the program cannot properly select the predominating species in every location. The information should therefore be used with caution.

Figure 17 demonstrates that copper sulphides still dominate in central parts of the diagram at high chloride concentrations but only at low potentials. At intermediate potentials $CuFeO_2$ predominates. The program had obvious difficulties to converge at this calculation and the information should be used with the same caution as for that found in Figure 16.

3.6. Comments about copper corrosion

Copper can be exposed for both general and different kinds of localised corrosion in the repository. The complex mechanical, chemical and microbial environment with high pressures varying in time and location and with oxygen, chloride, sulphur and carbon bearing compounds present will cause different types of attacks that are going to prevail during different time periods. The procedures of production, handling and treatment of the canister throughout the processes of filling, transportation and deposition are crucial for its later, corrosion-related integrity throughout the storage period in the repository. There is also a risk that due to systematically induced faults, many canisters may have later corrosion related problems of the same kind.

There will certainly be an introductory period with an oxidising environment followed by a reducing. There is a low probability that oxidising conditions could return at a later stage, during a glaciation. At such an event the hydraulic pressure field could have a complex gradient, which would cause surprising directions and velocities of the groundwater flow, resulting in intrusion of oxygenated and/or chloride containing water into the repository and subsequent replenishment of the oxidising conditions. During such periods, oxygen will provide the driving force for the corrosion processes. Different mechanisms can prevail during different periods of time but also simultaneously in different geometrical parts of the non-homogeneous pressure, heat and chemistry fields that could form in the repository. A non-homogeneous environment is a good starting point for corrosion.

There will probably be long reducing periods between oxidising. During such periods corrosion processes are generally considered to come to a halt. However, mechanisms for e.g. sulphide based attacks should be considered during reducing conditions.

Different periods of the repository lifetime are going to be exposed to different transportation mechanisms for the groundwater. As a consequence the reacting chemical species transported by the water will be transported with different velocities. This is valid both on a global and a local scale. A couple of mechanisms for such variable transportation mechanisms could be mentioned, but others are probably also possible. Normal ground water flow during normal conditions is a first. Change of flow gradients due to different pressure gradients during glaciation periods is a second. Anthropogenically-caused change is a third. Gas evolution due to processes in the repository as well as a flow of substances that at some stage might evolve geogas is a fourth possible mechanism for transportation. A fifth is the presence of temperature gradients.

All procedures of production, filling, transportation and deposition of the canister are crucial for its later integrity throughout the storage period in the repository. There are risks of metallurgical and mechanical faults in the canister due to any of those processes that can influence the corrosion integrity at a later stage. Also buckling of the copper onto the iron insert due to the pressure field of the closed repository and also changes of that field could cause subsequent corrosion related problems.

3.7. General copper corrosion

As already mentioned there are several chemical environments around and also inside the canister that can be foreseen. During oxidising conditions in a highly concentrated chloride solution, which will prevail for example during the initial period after closure of the repository, there will be general corrosion of copper in a situation of rather homogenous environmental conditions. According to thermodynamic calculations copper is not stable in such an environment. Such a homogeneous attack is, however, not very harmful for copper integrity, as long as transport rates of reacting matter are low.

The immunity limit for copper descends as a function of rising temperature at high chloride concentrations. This means a risk that copper is neither noble nor passive, at least at higher temperatures, in a repository environment containing high concentrations of chloride. Thus, in such an environment copper is protected from serious general corrosion only by keeping transport rates of reacting species very low. Increased transport rates would, however, be very harmful for copper integrity. This situation of general corrosion should be addressed for cases of higher transport rates of reacting species above the immunity limit.

In a 'normal' case, E_h has to go far above the envelope values (Figure 2) before there is any risk for the canister to corrode or up to Eh values about +250mV. An increasing pH value will protect from this effect as CuO is stabilized. There is no essential problem for copper canister corrosion to be foreseen till sulphide concentration reaches the same level as the copper solubility at the relevant temperature. Chloride combined with other poor conditions (like rapid transport through buffer) would be detrimental for the canister integrity. Thus upconing of brine water or downflow of out-frozen brine water could be very harmful if the buffer is destroyed and the brine comes in contact with copper at oxidising conditions and with high solute transport rates.

3.8. Localised copper corrosion

However, different types of localised corrosion that can occur as a result of any inhomogeneity in the system are probably more dangerous than the general corrosion outlined above. The inhomogeneity could be of a chemical nature (concentration gradients), or mechanical (pressure load gradient), as a temperature gradient (different heat conducting conditions from the canister surface) and also as materials faults and inhomogeneities in the copper metal itself caused by inadequate manufacture, transportation and handling processes.

All of those cases can be disastrous to canister integrity if they prove to be able to cause a rapid break through of the copper layer. Pitting of copper in an oxidising environment is well known from several applications and environments and could also appear in the repository during the oxidising periods. Localised attacks could be a dangerous reality at the right combination of environment chemistry and material faults as cracks, pores, welding faults etc.

A localised attack could in a worst case result in exposing the underlying iron insert. In an oxidising environment such an event could be followed by galvanic corrosion as well. The exposed iron insert would then be the dissolving, anodic electrode. An electrochemical cell with a very large copper cathode, short-circuited with a very small iron anode would develop and could rapidly generate an opening to the inner parts of the canister and the fuel. Only retarded transportation of reacting species would hinder such a dangerous situation to develop.

A combination of a mechanical fault, materials stress and localised corrosion in an oxidising environment would be especially dangerous as it could appear simultaneously in many canisters. As already mentioned there could be systematic and undetected mechanical damages on many canisters due to handling procedure faults. It is therefore essential to further evaluate these combined risks and also to extend the QA system to cover all of the chain down to the final closure of the repository.

At lower potentials copper sulphides are formed on the copper surface in environments containing sulphide and also high chloride concentrations. The sulphide film formed could be of a rather complex nature consisting of several phases. The micro-composition of the sulphide could under such circumstances depend very much on local micro-conditions close to the metal surface. For example variations in pyrite and bacteria+sulphate concentration would probably have an influence on the local copper sulphide composition. A slight variation of the potential over the copper surface could also have a dramatic influence on the composition of the copper sulphide film. Calculations show that the immunity of copper decreases as the sulphide and chloride concentrations increase. This results in low immunity and a complex copper sulphide film of variable and disputable ability to passivate.

3.9. Microbially-enhanced processes

Microbes accelerate redox reactions by mediating the electron transfer processes between electron donor (the reducing agent) and the electron acceptor (the oxidising agent) [18]. In the present case, copper is the electron donor and oxygen or other oxidant would be the electron acceptor. Microbial acceleration of this process is stated by SKB to be prevented by the exclusion of microbes from the canister-buffer interface due to the sub-micron pore size of compacted bentonite. This is supported by a limited amount of empirical evidence. Therefore, accepting the validity of exclusion by the buffer, microbial enhancement needs to be considered in relation to processes outside the buffer, i.e. at the rims of deposition holes and beyond that in the geosphere.

3.10. Some conclusions for this review

- ♦ A passivating oxide film is formed on copper only at a low chloride concentration in a more or less sulphide free environment.
- ♦ High chloride concentrations can prevent formation of a passive film and destabilise a passivating oxide film present from the beginning.

- Copper sulphides can be formed at low potentials. Copper sulphides give poor passivating films.
- Both chloride and sulphide lower copper immunity.
- At high chloride and sulphide concentrations copper could be neither passive nor immune in certain potential/pH intervals. The only protection against dangerous general corrosion would then be a shortage of oxidising agents and low transportation rates of reacting species.
- There is a risk of pitting and other localized types of corrosion.
- Pitting in oxidative environments is slowed down by chloride in the long run.
- Pitting/localised corrosion at lower potentials can proceed as whisker growth if sulphide is present. There are at least two mechanisms available, depending on circumstances. One pure sulphide whisker growth mechanism and another oxide/hydroxide mechanism.
- Other whisker growth mechanisms in the repository environment like carbonate/malachite growth would also be possible.
- The film formation on the copper surface in groundwater is a relatively slow process taking weeks or months.
- The chloride concentration affects the rate of film formation and the morphology of the film formed.
- The chloride concentration also affects the formation of whiskers in sulphide containing groundwaters.
- In the presence of sulphide the surface processes are much faster and sulphide film formation takes only minutes to hours.
- No signs of localised corrosion on copper were detected in sulphide-free groundwaters.

4. Comments on the uncertainties and robustness of SKB's approach

SKB make the case that the assumptions, simplifications and uncertainties in the processes and parameters for their models of oxygen attenuation are conservative. The processes and parameters that are discussed below are:

– Hydraulic gradient through rocks due to ice sheet leads to maximum downwards flow velocity of 10^{-5} m/s (315 m/y);

– Warm-based ice sheet conditions occur only at edge of ice sheet and anomalous infiltration persists for maximum 2000 years;

– Dissolved oxygen concentration in melt water has a maximum of 45 mg/L (1.4mM) corresponding to $Po_2 = 0.68$ atm;

– Dissolved oxygen is attenuated by reaction with Fe^{2+} released by dissolution of minerals in fractures and/or rock matrix, the Fe^{II} minerals being biotite, chlorite, pyrite;

– Fe^{II} minerals (biotite/chlorite ± pyrite) are present in fractures and matrix and are accessible for reaction with groundwater;

- Minimum amount of biotite in fractures is 1.125 mol/L and in rock matrix is 15.58 mol/L, and minimum surface areas for biotite are 1 m^2/L and 0.086 m^2/L respectively;

- Dissolution of biotite and release of Fe^{2+} occurs according to the pH-dependent formula as reported in [29] which corresponds to a rate of 10^{-5} to 10^{-4} mol $m^{-2}y^{-1}$ in pH range 6 to 9.5;

- Diffusion of oxygen into the rock matrix and reaction with matrix Fe^{II} minerals can occur in addition to attenuation of oxygen by fracture minerals, or as an alternative process;

- Microbial mediation ensures that the kinetics of oxygen consumption reactions are much faster than kinetics under abiotic conditions where reactions may not occur despite being thermodynamically favourable, e.g. reduction of oxygen by methane.

Maximum infiltration velocity of meltwater
Higher sub-glacial groundwater velocities than 315 m/y would be a scenario with other significant implications, e.g. erosion of buffer and massive turnover and freshening of groundwater. Reactive transport modelling carried out for this review (see Section 5) suggests that, with this water velocity and other parameters as in the basic model, O_2 would penetrate to 400 m depth in 1-2 years. If biotite dissolution kinetics were slower, or if biotite and other Fe^{II} minerals were absent or inaccessible, then O_2 breakthrough to repository depth would occur in a shorter timescale.

It is reasonably pessimistic for SKB to have assumed 315 m/y as the maximum infiltration velocity for SR-Can. However SKB have stated in the Qs&As ('questions and answers') prior to the SR-Can Hearing that they will aim to achieve a better understanding of how transmissive fracture zones respond to ice loading. It therefore seems that there is greater uncertainty arising in the geochemistry and kinetics of O_2-consumption (see below) than in the hydraulics, although their impacts in the glacial cycle scenario are interdependent.

Maximum duration of infiltration
The duration of sub-glacial melting could be greater than 2000 y for various scenarios, e.g. warm-based glacial conditions persist for some reason such as ice front halting near to the site. The duration of the second future glaciation, ca.10 thousand years at 100 ka into the future, is longer than that of the next glaciation, ca.50 thousand years, according to SR-Can and therefore the probability of a prolonged period of sub-glacial melting may be greater at that time.

Sub-glacial melting rate (estimated at 50 mm/y maximum) also imposes a limit on the flow velocity that could be sustained for a long period. SR-Can estimates the maximum duration for fast infiltration to be 40 y, based on the duration of a warm-base to the ice sheet as its edge advances or retreats over the site.

In the Qs&As prior to SR-Can Hearings, SKB stated that a duration of 1300 y for fast glacial water infiltration is unlikely, although slower infiltration will occur for a longer period. The possibility that faster-than-normal infiltration might occur for several thousand years, coupled with slower than expected oxygen consumption reactions, needs to be considered further as a slightly more pessimistic scenario than already considered in SR-Can and R-06-105 [4].

Maximum concentration of dissolved oxygen in meltwater

Dissolved O_2 concentration in melt water is likely to be controlled by the partial pressure of O_2 at the base of the ice sheet. It is assumed that this limit is set by atmosphere equilibration in snow/ice/fern at the surface of the ice sheet and not by a discrete gas phase under the ice sheet in which partial pressures would be much higher. There seems to be no source of sub-glacial O_2 that could sustain a high pressure.

A literature survey on sub-glacial hydrochemistry suggests that hard data are sparse. Upper sections of the 3.5km-thick ice sheet over Lake Vostok in Antarctica contain air bubbles which transform to an air clathrate hydrate by 1300 m depth. Melting basal ice has been found to contain typically 113 mg/L of air, of which 27 mg/L is O_2 [33]. Other observations on meltwaters from Arctic and Antarctic glaciers suggest that pCO_2 is usually rather high, promoting weathering of rock fragments, and that SO_4 is sometimes high with sulphate reduction occurring in some cases suggesting anoxic conditions. There is no specific evidence suggesting elevated dissolved O_2.

The assumed maximum of 45 mg/L, estimated by Ahonen and Vieno [9] on the basis of gas occlusion in ice and release during subsequent melting, is reasonable although a more pessimistic maximum should be considered as an illustration. Modelling suggests that an increase of oxygen concentration by a factor of x2 or x5 is unlikely to make a significant difference to the model outcome compared with the impact of kinetic and other geochemical uncertainties which have order of magnitude effects.

Attenuation of oxygen by reaction with Fe^{2+} released from Fe^{II} minerals

Attenuation of dissolved O_2 by water-rock reaction as groundwater infiltrates downwards in an almost ubiquitous process. The primary reductant in soils is organic carbon. In bedrock, the reductants are likely to be dissolved organics, as shown by the fracture zone experiment at Äspö HRL [16, 31, 32, 33], and Fe^{2+} released from minerals. The most reactive mineral with respect to O_2 is likely to be pyrite [34]. Other Fe^{II}-containing minerals are chlorite and biotite, but there is little direct evidence of the rate and its variability with which Fe^{2+} is actually released and the mineral itself is altered.

In terms of natural system evidence, there is a report of deep oxygenated groundwaters in deep (to 1000m) aquifers in the USA, which might be attributable to the carbonate-rich, Fe^{II}-poor, aquifer formations [35]. Deep (>200m) groundwaters at the Okélobondo uranium deposit in Gabon have also been reported to be oxidising [36].

In general, much of the evidence in support of Fe^{2+} being released from minerals and being an effective buffer of redox and against oxygen penetration is inferential or circumstantial (e.g. thermodynamic modelling and observations of iron oxides). There are few direct observations of the process. In situ evidence of alteration of Fe^{II} minerals and formation of secondary Fe^{III} minerals as a direct result of O_2 consumption is sparse and/or unclear.

Using fracture fills from the Äspö HRL, lab experiments have been carried out to measure the kinetics of O_2 reduction by Fe^{II} in ferrous silicate minerals [37]. The mineral samples had varying amounts of biotite and chlorite, plus many other minerals. The experimental results were interpreted as showing that O_2 was reduced at both surface and matrix sites of Fe^{II}. Results were interpreted in terms of rate constants for 2nd order rate equations, i.e. a rate equation involving the concentrations of Fe^{II} on mineral surface and of oxygen in solution. Characteristic times for O_2 concentrations to be halved were in 100's of hours, though the water:mineral ratios were considerably higher than those in natural systems. These experiments were part of the 'REX' project at Äspö [17].

The reaction mechanism inferred for the REX experiment is a reaction of O_2 with structural Fe^{II}. It is therefore distinct from the mechanism inferred by modelling reaction of O_2 with Fe^{2+} from biotite dissolution. Adjusting to the lower in situ water:mineral ratios, it was inferred that the characteristic time for O_2 attenuation would be seconds, i.e. effectively instantaneous [37].

In an unrelated study of the reductive capacities of soil minerals with respect to inorganic and organic contaminants (i.e. not O_2), biotite was found to have a low reductive capacity of a few microequivalents per gram, about 10x less than the reductive capacity of pyrite [38].

Overall, these sparse bits of data for reactivity of Fe^{II} minerals towards O_2 indicate that it can be highly variable, depending on many factors. Further study of the mineralogical alterations that can be associated specifically with oxygen infiltration and consumption in relevant natural systems would be helpful. The REX experiment seems to have achieved as much as is possible from in situ experimentation. A rather greater degree of uncertainty in the mechanism and kinetics of reaction between O_2 and reducing minerals in the fracture assemblage is advised.

Distribution, accessibility and compositions of Fe^{II} minerals

It is assumed by the model that biotite and/or chlorite and/or pyrite are distributed fairly widely in fracture fillings so that it is very unlikely that there could be downwards flow paths that could 'bypass' contact with these Fe^{II} sources. Further, it is assumed that biotite or other Fe^{II} minerals in the rock matrix will be accessible by matrix diffusion to provide an additional redox buffer.

At Simpevarp/Laxemar, chlorite is a common fracture minerals and pyrite also occurs, but biotite is not reported [39, 40]. Similarly, at Forsmark, chlorite is the most abundant fracture mineral whilst biotite is not reported [41]. Drillcore samples of Ävrö granite from Laxemar boreholes have between 0.2-44% biotite by modal analyses (mostly in the range of 8-15%) [42]. In some samples, it is noted that the biotite has been chloritised. Similarly, it has been noted that altered wallrock adjacent to fractures at Forsmark contains chloritised biotite and also contains hematite which accounts for the reddening [43, 44]. It is noted that the redox capacity of these altered rocks is only slightly lowered with most Fe remaining as Fe^{2+}.

A summary of the mineralogy of rock types for SR-Can has reported that [45]:

- At Forsmark:
    - pyrite is <0.3% in the main granite and <1% in other rock types
    - biotite is 0.8-8% in the main granite and 0.23% in other rock types
    - chlorite is 0-1.2% in the main granite and 0-2.4% in other rock types

  - chlorite has been identified in 71% of open fractures, pyrite in 9% and hematite in 15%, whilst biotite is not observed.
- At Laxemar/Simpevarp:
  - pyrite is 0-0.2% in the Ävrö granite (but <0.1% in reddened granite) and 0-0.3% in other rock types
  - biotite is 0.4-25% in Ävrö granite (0-3% in reddened granite) and 0-49% in other rock types (but <2% where these are reddened),
  - chlorite is 0-14% in Ävrö granite (3-18% in reddened granite) and 0-18% in other rock types,
  - chlorite has been identified in 70% of open fractures, pyrite in 10% and hematite in 18% whilst biotite is not observed.

The oxidation ratio (Fe^{3+}/Fe_{tot}) is unaltered rock from Laxemar/Simpevarp is reported to be 40.7% average, with only a slightly higher ratio (43.0%) in altered rock. The main alteration reactions are magnetite to hematite and biotite to chlorite. Oxidation ratio is not yet reported for Forsmark rock but is likely to be lower because of lower relative abundances of Fe^{3+} minerals [45].

In conclusion it is evident that biotite is present and abundant in the matrix of most, but not all, rock types at both sites. Observed contents of biotite appear to be reduced in altered rocks, which tend to support the concept of rock matrix diffusion operating, though it is noted that the observed alteration is primarily hydrothermal and not evidence of active in-diffusion of oxygen.

Chlorite and lesser amounts of pyrite are the Fe^{II} minerals in fractures at both sites. Chlorite is very widespread, although actual amounts in fracture-fillings are not reported. Fe/Mg ratio in chlorite is reported to vary between generations of chlorite, and is typically between 1 and 4 in bulk samples of fractures fillings [45]. A few analyses of chlorite from Forsmark show values of 0.33-0.44 for the Fe^{3+}/Fe_{tot} ratio, implying that more than half of total Fe in Fe^{2+} in these cases.

SKB's modelling of O_2 attenuation [4] should have simulated the dissolution of chlorite rather than biotite as the source of Fe^{2+} in fracture-flow groundwater.

Kinetics of Fe^{2+} release from Fe^{II} minerals

There is a substantial degree of uncertainty in the rate at which biotite dissolves to produce Fe^{2+} or reacts directly with O_2. Uncertainty derives from chemical influences such as pH dependence, proximity to equilibrium, and inhibiting solutes, and also from physical factors such as surface area, grain size and biotite-water contact. These latter factors are more difficult to quantify and potentially have a bigger effect. Uncertainty in dissolution rate is likely to be orders of magnitude.

A zero order pH-dependent rate is used in SR-Can [29]:

$$R_{Fe} = 6.96.10^{-2}[H^+]^{0.51} + 5.28.10^{-11}[H^+]^{-0.65} \text{ mol. m}^{-2}.\text{y}^{-1}$$

which, with a conservative value for surface area of 8.64 m^2/L, gives a Fe^{2+} release rate at pH 9 of about 2.7×10^{-11} mol s^{-1} L^{-1}.

A second order equation for kinetics of O_2 reaction at the biotite surface is [37]:

$$R_{O2} = -k[Fe_s^{II}]\ [O_2] \text{ mol s}^{-1}\text{ L}^{-1}.$$

The way that experimental results are presented in this paper does not indicate values for k in the right units. However graphic presentation of experimental data suggests that R_{O2} is about 2 x 10^{-10} mol $s^{-1}L^{-1}$. The experimental results also indicate that the uncertainty in kinetics is typically 1-2 orders of magnitude in the k value, in addition to being dependent on pH and particle size.

In a compilation of 'reduced' (i.e. simplified) rate parameters for water-mineral reaction kinetics by the USGS, a dissolution rate for biotite in neutral pH conditions is given as [46]:

$$R_{biotite} = 10^{-12.55} = 2.8 \times 10^{-13} \text{ mol } m^{-2} s^{-1}$$

Taking the same surface area as above, this gives a Fe^{2+} release rate of 2.4 x 10^{-12} mol $s^{-1} L^{-1}$.

Overall, it seems that an uncertainty of about 2 orders of magnitude for biotite dissolution rate, other factors such as water chemistry, particle size and accessibility of mineral surface being constant, would be reasonable to use in geochemical modelling.

Diffusion of oxygen and reduction in the rock matrix

The effectiveness of oxygen being attenuated by reaction with Fe^{II} minerals in the matrix depends on there being some sort of interconnected 'micro-porosity' in the matrix and there being diffusive connection between that and oxygenated water flowing in fractures. There are various lines of evidence that diffusion does operate as a mechanism for solute exchange between fracturing and rock matrix in these rocks (e.g. observations in the TRUE experiments at Äspö and observed distribution of salinity between groundwaters and matrix water), and there is also evidence from natural analogues (e.g. Poços de Caldas uranium deposit).

In theory, there are greater concentrations of Fe^{II} minerals in the matrix than in fractures. As discussed previously, mineralogical studies show that the dominant Fe^{II} matrix mineral at both sites is biotite whereas chlorite dominates the secondary minerals in fractures. However there is little direct evidence of oxygen diffusion and reaction in terms of identified alteration and iron oxide formation in the rock matrix. Such alteration would be 'proof positive' that matrix diffusion is an effective attenuating process for oxygen. Sidborn and Neretnieks [14, 47] make calculations of diffusion rates and reaction rates for oxygen diffusion and reaction between fractures and matrix and conclude that the rate limiting process is matrix diffusion of oxygen. A review of modelling of reactive transport with matrix diffusion in fractured crystalline rock, carried out by Macquarie and Mayer [48], highlights the lack of data for the key parameters for reactions in both fractures and matrix.

In summary, diffusion and reaction in the rock matrix would be the process that offers the greatest reduction capacity (RDC) to attenuate oxygen in infiltration due to glacial meltwater, as asserted by Sidborn and Neretnieks [14]. For this process to be effective, matrix diffusion has to provide access for dissolved oxygen to the reactive surfaces of Fe^{II} minerals. More evidence that dissolved oxygen in infiltration under normal climate conditions has had diffusive access to the rock matrix and has altered matrix minerals would increase confidence. Equally, the case where infiltration velocity is so fast that there is insufficient residence time in fractures for effective diffusive access to the matrix should be considered. This is a very similar 'worst case' to that considered in the modelling of oxygen consumption by fracture Fe^{II} mineral.

Microbial mediation of kinetics of oxygen attenuation reactions, e.g. reduction by methane

Microbial intervention in redox reactions in the biosphere and shallow geosphere is a major aspect of biogeochemistry. The general availability of organic carbon in soils is the energy source so that many redox reactions that would otherwise be kinetically inhibited go rather faster towards equilibrium. It is now accepted that similar microbial activity may influence the deeper geosphere. The importance of this for redox reactions in the environment where a repository would be constructed has been highlighted by work by Pedersen et al. [25] including site-specific microbial analyses for Laxemar/Simpevarp and Forsmark. Among the constraints on microbial activity at repository depth in low permeability rocks are the transport and establishment of microbial communities, their viability in terms of availability of nutrient and energy, and the general hydrochemical conditions such as salinity. A major limitation is the concentration and flux of organic carbon as the energy source. Organic carbon is present in the rocks only as very minor traces of asphaltite, whilst dissolved organic carbon concentration is very low, and the flux downwards from soils would be expected to decrease further during a glaciation when soil cover would be absent. In the Geosphere Process Report [15], it is suggested that a flux of deep-sourced abiogenic CH_4 (with lesser amounts of H_2) could be the energy source in the absence of an adequate supply of other organic material. There is a lack of knowledge and a degree of ambiguity in SR-Can about (a) the relative importance of methane-driven and Fe^{2+}-controlled attenuation of oxygen, and (b) the relative importance of Fe^{II} in fracture and matrix minerals in attenuating oxygen. It can be noted that, for (a), the interpretation of the REX experiment supported the importance of methane, and, for (b), that evidence for either process in natural analogues and natural systems is still not particularly clear. It can be remarked also that, for the present sites, chlorite should be modelled as the source of Fe^{II} in the fracture mineral assemblage rather than biotite. It may be the case that redox systems involving both Fe^{II} and CH_4 could play a role in oxygen attenuation in the natural sub-glacial system, the balance depending on the local hydro- and bio-chemical environment at the time. SKB needs to develop a more integrated model for the thermodynamics, kinetics, biochemistry and mineralogy of the processes, supported by a breadth of natural system and natural analogue evidence.

5. Summary of SKI modelling of oxygen consumption by Fe^{2+} release from minerals

A PHREEQC reaction-transport model has been set up to replicate the modelling of oxygen consumption that has been carried out by Guimerà et al. [4]. The model comprises a 1-D column of cells, 200 or 400 in number and 2 or 4 metres in length respectively. The column of cells represents a 400 metre interval above a repository located at 500 metres depth, i.e. the base of the upper 100 metres is taken as the upper boundary of the reaction-transport column which is assumed to be initially a rock profile with low vertical hydraulic conductivity and initially homogeneous hydrochemistry with reducing conditions.

Fresh oxygenated water enters at the top and travels down the column through the fractures, reacting with fracture minerals in each cell as it passes through. The assumptions used by Guimerà et al. [4] were replicated: biotite is assumed to be the source of Fe^{II} (although as stated above chlorite rather than biotite is observed in the fracture mineral assemblage):

$$KFe^{II}_3AlSi_3O_{10}(OH)_2 + 10H^+ \rightarrow K^+ + 3Fe^{2+} + Al(OH)_4^- + 3H_4SiO_4 \quad \log K = 35.88$$

The rate of biotite dissolution is dependent on pH and surface area, and is represented by the kinetic expression of Malmström et al. [29]:

$$R_{Fe} = 6.96 \times 10^{-2} [H^+]^{0.51} + 5.28 \times 10^{-11} [H^+]^{-0.65} \text{ mol m}^{-2} \text{ y}^{-1}$$

Fe^{2+} in solution then undergoes a redox equilibration with O_2 and precipitates $Fe(OH)_3$:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$$

The amount of biotite in fractures and the resulting surface area of biotite were assumed by Guimerà et al. to be 1.125 mol per litre of groundwater and 8.64 $m^2 L^{-1}$ respectively, the latter being claimed to be conservatively low by up to two orders of magnitude. Values used in the present modelling are 0.1125 mol biotite L^{-1} and 8.64 $m^2 L^{-1}$, but sensitivity to the surface area was investigated by decreasing the dissolution rate.

Downwards water velocity through the column of reaction cells is set in the model according to the size of time step for water to move from one cell to the next (i.e. 2 or 4 metres depth increments). The vertical water velocity in the base model here is 2 metres per year (~6×10^{-8} m s^{-1}). This was varied upwards to test the sensitivity of oxygen consumption to water velocity. There are two basic alternative limiting conditions for oxygen penetration: (i) for higher water velocities, that O_2 consumption is controlled by the rate of Fe^{2+} release from biotite (or other Fe^{II} source mineral), or (ii) for lower water velocities, that O_2 consumption is controlled by the availability of unoxidised biotite. The first case is essentially a kinetic control, whereas the second case is a Fe^{II} budget control. In the first case, O_2 penetration is an interplay between the rate of oxygen movement and the rate of Fe^{2+} release, and this has to be simulated with the multi-cell kinetic reaction model. The second case can be estimated by simple mass budget calculation, as was done by Guimerà et al. [3].

The code used was PHREEQCI v 2.13.2 with the default PHREEQC thermodynamic database. A value for log K (= 35.88) for biotite was added, and also the kinetic rate expression for biotite dissolution as above. Modelled solution compositions (O_2, pH, pe, Fe^{2+} and Fe^{3+}) and mineral amounts (biotite and Fe-oxide) were printed out to a spreadsheet for selected cells and timesteps. From the spreadsheet data, variations in the key variables (dissolved O_2 and biotite) versus time could be graphed for the selected cells in the depth column.

A single simulation of oxygen transport and reaction in the column (200 or 400 cells) for 2500-5000 years (typically 0.2 to 0.5 years time steps) took 2-3 hours to run on a 3 GHz Pentium 4 CPU.

Although the basic model is quite straightforward, getting the PHREEQC geochemical kinetic and equilibrium calculations to converge on mass balances has proved difficult. The problem arises from the potentially unstable mass balances at the redox front. The model set-up including length and time-step discretization and convergence tolerances have to be 'tuned' for each set of parameters to obtain a stable model. In many of the runs the model failed to converge before the planned total number of time steps (the total of which varied from 200 to 5000 years as the full model timescale).

Findings from the model runs are summarised in Table 3 where the approximate timings of oxygen breakthrough at various depths are given for various values for biotite.

Table 3. Summary of oxygen consumption modelling results

Vertical water velocity, metres y^{-1}	Biotite dissolution rate	Depth, metres	Time of oxygen breakthrough, years
2	Base case	50	2500
2	Base case x 0.1	200	100
2	Base case x 0.01	400	190
20	Base case	200	10
315	Base case	400	1.2

Results of the modelling can be summarised as follows:

- The base case model run by Guimerà et al. [4] can be replicated reasonably closely, suggesting at least that the two PHREEQC models, with identical thermodata and reaction kinetics, are comparable in terms of basic construction. This increases confidence that the calculations do not contain fundamental ‘operator’ errors in either model set-up.

- With the base case parameters and kinetics of Guimerà et al. [4] and a vertical water velocity of 2 m y^{-1}, the modelled O_2 front penetrates to about 50 metres depth in the column after 2500 years.

- If the Fe^{2+} release rate is decreased by x0.1 (e.g. due to lowered reactive accessible surface area of biotite or due to pH-dependence), then the modelled O_2 front reaches 200 m in about 100 years. For a decrease of reaction rate by x0.01, the O_2 front reaches 400 m in about 190 years.

- Increasing the water flow velocity to 20 m y^{-1}, the modelled O_2 front reaches 200 metres in about 10 years. A further (improbable) increase of sub-glacial water velocity to 315 m y^{-1} (the maximum infiltration velocity assumed by SR-Can)would cause oxygen to penetrate through the entire 400 meter profile in just over a year, i.e. the rate of oxygen transport in infiltration would be such that attenuation by reaction with Fe^{2+} would be ineffective due to the slow rate of release of Fe^{2+} from biotite.

The conclusion to be drawn from the modelling is that, given the assumptions and parameters in the SKB model, dissolved oxygen is very likely to be consumed by redox equilibration before it would reach a repository located at 400-500 metres depth. The conditions under which this probability would be lowered would be (a) exceptionally high hydraulic gradient and downwards water velocity, and/or (b) markedly slower reaction of biotite due to geochemical factors, including uncertainty in the reaction kinetics, or physical inaccessibility. Combining an uncertainty of two orders of magnitude in the kinetics such that there is a bias in modelling towards faster reaction than in reality, with a transient elevated sub-glacial hydraulic gradient, is the most plausible scenario that would raise the probability of oxygen breakthrough.

The overall significance for repository performance of the scenario of oxygen transport into the geosphere at repository depth needs to take account of the additional barriers to oxygen reaching copper canisters. These barriers are provided by the fracture-free low permeability rock conditions around deposition holes and by the diffusive medium of the bentonite buffer.

6. Assumptions, data and uncertainties in other aspects of glacial geochemistry in SR-Can

This section has comments on other aspects of hydrochemistry and biogeochemistry at repository depth during glaciation and permafrost periods of the reference scenario: (i) formation and downflow of saline water due to freeze-out from permafrost, (ii) upconing of saline water due to glacial advance and post-glacial recovery, (iii) methane hydrate associated with permafrost, (iv) general issues of microbial activity at repository depth including sulphate reduction.

Formation and downflow of saline water due to freeze-out from permafrost
Literature reviews by Vidstrand [49] and Gascoyne [50] identified the probability that salt rejection occurs when permafrost forms. Consequently, saline waters or brines which have lowered freezing points due to their salt content may form. These saline waters could remain in soils and shallow sub-surface, or they could flow downwards along the density-dependent hydraulic gradient. The latter process has been modelled by Vidstrand et al. [12] (see Section 2.3.4 above). In coastal areas, it is also possible that brines may derive from salt freeze-out from seawater and then flow downwards into bedrock beneath the sea bed [51, 52]. These are modelling and experimental studies and there are few if any direct observations of these processes in situ.

Research investigations of intra-permafrost and sub-permafrost groundwater in permafrost conditions (to ca. 500m depth) at the Lupin Mine in Nunavut Territory, Canada, found brackish and saline waters within and below deep permafrost [53]. However it was thought that these compositions were dominated by contamination from saline drilling water, and that any natural 'freeze-out' salinity could not be reliably distinguished on the basis of chemical and isotopic compositions.

There have been various other studies of saline groundwaters in north American and Russian permafrost formations but none seem to be conclusive about, for example, the maximum salinities achieved by freezing out and the volumes of saline waters produced. It has to be concluded that the production of saline water by freeze out is probably a site-specific process.

SKB's SR-Can evaluation concludes that saline water formation due to freeze-out is a possibility and that the maximum salinity in a 10 metre layer at the base of a 300 m permafrost column would be ~12000 mg/L chloride [1]. This is a reasonable estimate for in situ permafrost formation.

The freezing of Baltic seawater in bulk could also result in residual brackish or saline waters, perhaps in greater volumes than under permafrost although the maximum salinity might be only moderate due to the low salinity of Baltic water. This process has not been considered in SR-Can and should be considered in addition to terrestrial permafrost for its potential impact on water salinities and flow directions near to the coast.

Upconing of saline water during glacial advance, post-glacial recovery and during permafrost

Upconing of saline water during glacial advance and post-glacial recovery has been modelled for SR-Can by Jaquet and Siegel [13]. Saline groundwater could also rise to relatively shallow depths during a period of permafrost. SR-Can [1] considers this briefly in a qualitative sense and discounts its possible impact on a repository because upconing would occur only in transmissive deformation zones which would be avoided by a repository, as suggested by Jaquet and Siegel's modelling.

Asserting that saline upconing, should it occur due to changed hydraulic conditions at these stages of the glacial cycle, will not affect a repository is inadequate justification for discounting it from PA. Evidence needs to be sought from past fluctuations of salinity in deep groundwaters that might be attributable to these processes. Mineralogical and geochemical methods for obtaining this evidence have been evaluated in [54, 55] and are summarised in [56]. Very limited amounts of evidence from other sites that have experienced permafrost and glaciation tend to indicate that large fluctuations of salinity have not occurred at those sites.

Methane hydrate associated with permafrost

Trapping of methane as a 'clathrate' (i.e. the structure formed by methane hydrate) is mentioned in SR-Can. The amount of methane that could accumulate by this process cannot be quantified in the absence of data for methane fluxes, though low dissolved methane concentrations suggest that flux is also low. Methane hydrate can exist in permafrost at depths where the temperature is low enough and the hydrostatic/lithostatic pressure is high enough to stabilise it. A typical depth range for methane hydrate stability in present-day Arctic conditions is 300-1000 metres in bedrock, as illustrated by occurrences in Canadian and Siberian permafrost which are being investigated as resources.

Potential accumulation of methane hydrate over the duration of a permafrost period would depend on upwards methane flux, minus the flux that is lost out of the ground to atmosphere and via groundwater pathways that remain active (e.g. discharges at taliks).

Methane would participate in redox reactions, notably the reduction of sulphate to sulphide (HS^-). HS^- is corrosive with respect to copper. SR-Can (SKB 2006) asserts that HS^- concentrations would anyway be controlled at low levels (e.g. $\leq 10^{-5}$ M) due to equilibration with iron sulphide (FeS). It is possible that a release of methane, e.g. when permafrost and methane hydrate thaw, could cause transient high concentrations of methane and sulphide due to redox reactions being mediated by enhanced microbial activity. However the local accumulation of HS^- would be limited by the supply of sulphate.

At present there is rather large uncertainty in these hypothetical and speculative scenarios connected with permafrost. There is no evidence that the coupled permafrost-methane-sulphide processes have been significant during glacial cycles in the past. Positive confirmation that this is the case should be sought.

General issues of microbial activity at repository depth, including sulphate reduction
SR-Can considers that HS^- concentration is limited, for both glacial and non-glacial conditions, by equilibration with FeS (see above). Anomalously high HS^- concentration can be envisaged only in the condition where high sulphate concentration would be coupled with negligible supply of Fe^{2+} and with rapid sulphate reduction mediated by microbial activity. Microbiological research indicates that microbes including sulphate reducers (SRBs) are not viable in compacted bentonite [25]. Therefore the question is whether the conditions could exist in glacial or non-glacial conditions for rapid production of HS^- in the geosphere at repository depth. A period of transient high microbial activity would require a carbon source in the form either of methane (see above) or of dissolved organic carbon (which is likely to be lowered in sub-glacial recharge [25]). Reduction of sulphate in the undisturbed natural system is therefore likely to be slow, as evidenced by the concentrations of dissolved sulphate in groundwaters sampled from repository depth. Attention therefore should be focused on scenarios that could increase the population or activity of microbes.

There is no palaeohydrogeological evidence that suggests that periods of glaciation or permafrost have been associated with such conditions in the past. It is unlikely that glacial conditions could enhance microbial activity in the geosphere at repository depth above that which is presently observed.

7. Summary of review conclusions

- Freshening of groundwater at repository depth will almost certainly occur at some time during a glacial cycle, most probably due to glacial meltwater infiltration. The effect on bentonite stability, colloidal erosion/dispersion of the clay, and on the mobility and maximum concentrations of colloids, is not well enough constrained in SR-Can.

- ‘Glacial melt water’ from past glaciations is identified palaeohydrogeologically as a dilute water originating in cold climate conditions because it has a light isotopic composition and also perhaps a carbon-14 age corresponding to the time of the last glaciation. The depth of glacial melt water penetration seems to be rather site-specific, judging from comparison of data from various Fennoscandian Shield sites. Factors controlling this depth need to be better understood. Reasonable confidence about the possible range of penetration depths and the flow directions for future glacial conditions is needed in PA. It underpins all of the hydrochemical and hydrogeological scenarios for long-term PA.

- The physical model for permafrost formation in SA-Can is quite sophisticated, but there is still a substantial uncertainty about the hydrochemical and hydrogeological effects of permafrost, especially if permafrost develops as far down as repository depth. The uncertainty is potentially significant because permafrost will develop sooner in the PA timescale, and would have longer duration, than ice sheet cover. SKB’s model suggesting only limited salinization of non-frozen water underlying permafrost is reasonable. However models for hydrochemistry and hydrogeology of these glacial stages of the normal evolution scenario would be viewed with greater confidence if they were supported by more observations of present-day analogues.

- In considering the potential impacts of changes in geochemical conditions at repository depth during a future glaciation, the moderating effect of the low permeability rock locations for deposition holes need to be considered also. Additionally the buffer, if remaining as an intact diffusion medium, would offer some chemical attenuation of oxygen or sulphide, and of variations of redox and pH in general, between the near-field geosphere and the copper canisters. Detailed issues of EBS performance are outside the scope of this report, but they clearly need to be coupled with geosphere changes when considering overall implications for PA.

- A further EBS issue, in addition to the moderation of impacts due to geosphere chemistry by the physical environment of the deposition hole and buffer, is the possibility of chemical heterogeneity in the vicinity of the canisters. In other words, when considering the overall geochemical environment for corrosion and passivation/depassivation, it would be most appropriate to assume a range of redox, pH and salinity conditions for each of the stages of post-closure evolution.

- Potential influx of dissolved oxygen in sub-glacial infiltration, and penetration to repository depth, is of concern with respect to corrosion of copper and the possibility of early loss of primary containment of wastes. The general background to copper corrosion suggests that a combination of oxygenated and saline conditions would pose a threat to copper integrity because high salinity reduces the passivation due to oxide formation. However this combination seems to be unlikely because oxygen would probably be associated with dilute glacial melt water. At least, an uncertainty in future oxygen contents and redox, plus additional uncertainty about future salinity variation, would add uncertainty to prediction of long-term performance.

- It is evident from modelling of water data from boreholes that the HS^-/SO_4^{2-} couple is an important component of redox equilibria and E_h control in undisturbed present-day groundwaters. The potential role of HS^- as a corrosive agent for copper also needs to be considered, especially since the prevailing redox conditions at repository depth is reducing. Microbial mediation, via SRBs, of SO_4-HS transformations means that microbial activity is an important aspect of this. The geochemical model for HS^- has its concentration limited by FeS equilibrium and by supply of SO_4. Conditions in which Fe^{2+} would cease to be available in the vicinity of the canisters, coupled perhaps with high SRB activity, might promote higher HS^- than currently observed. However such a scenario does not seem to be linked with evolution through a glaciation so is not considered further here.

- In addition to E_h dependence, chemical equilibrium calculations and Pourbaix diagrams show that corrosion of copper is sensitive to pH and temperature. In the diagrams, presence of significant amounts of dissolved oxygen corresponds to a hypothetical E_h value of around +0.4 V, assuming that E_h would be controlled by the OH^-/O_2 couple which does not happen in reality. Depassivation and risk of corrosion increases at both low and high pH and in both cases raised temperature increases risk further. Calculations for the Cu-Cl-O-H system also show that increasing salinity decrease the size of the passivated area in the Pourbaix diagram (due to Cu_2O or CuO). The concentration of O_2 involved at that E_h is, in theory, many orders of magnitude below normal analytical detection limit. Pourbaix calculations also suggest that additional factors that may influence the passivating behaviour are HS, HCO_3, and Fe concentrations in water. In summary, the corrosion of copper in the hydrochemical environments considered here is a complex process as also is the formation and stability of passivating solids. Distinct corrosion processes occur in oxidising and reducing chemical conditions – due to oxygen and sulphide respectively, and the rates of these processes will depend on E_h, pH, salinity, temperature, other trace solutes and microbial activity (though this has been shown to be inhibited in compacted buffer).

- The arguments in SR-Can for the low probability of dissolved oxygen penetrating to repository depth in sub-glacial water make various assumptions and simplifications. Consequently uncertainties may be underestimated. Although the assumed maximum infiltration rate appears to be pessimistic, the duration over which moderately high infiltration rates might prevail could be higher than has been assumed. This is evidently an area of uncertainty due to the absence of observations in real systems to constrain the hypothetical model.

- Uncertainty in the possible range of dissolved oxygen concentrations is much less significant than the hydrogeological and geochemical (i.e. oxygen-consuming reactions) uncertainties. Some of the evidence in support of a general model for Fe^{2+} release from minerals is inferential and there is little direct observation, especially for relevant rock types. SKB's REX experiments at Äspö are the exception in providing compelling direct evidence. Overall, however, a rather greater degree of uncertainty in the mechanism and kinetics of O_2-consuming reaction would be realistic. The relevant Fe^{II} minerals in fractures are chlorite and, sparsely, pyrite, whereas biotite is the Fe^{II} source in the rock matrix (with reference to the Sidborn and Neretnieks model for attenuation of oxygen by matrix diffusion and reaction). An uncertainty range of about two orders of magnitude in the kinetics of Fe^{2+} release from these minerals is probably reasonable. This is significant as shown by the modelling.

- In view of oxygen attenuation being a continuous natural hydrogeochemical process in non-glacial conditions, at least in shallow rocks where the normal oxidising-reducing redox front is located, some confidence that Fe^{II} release and reaction really does occur should be obtained from direct observation of the oxidising reaction products in fractures and/or in rock matrix. Alteration patterns in such rocks would be strong supporting evidence for the oxygen consumption model.

- Microbial reactions in the geosphere at repository depth are likely dependent on various hydrogeochemical factors, one of which is the flux of deep-sourced methane, CH_4, as a potential energy source. Methane oxidation, microbially mediated, could also consume oxygen. A more integrated biogeochemical redox model for the system would identify whether this could be significant.

- It has been possible to replicate SKB's geochemical modelling from which it is concluded that, given the model assumptions and parameters, it is likely that oxygen will be consumed by redox equilibration before it could reach repository depth. However there are significant uncertainties, namely in the maximum downwards sub-glacial water velocity and in the kinetics of release of Fe^{2+} from biotite or chlorite. Along with the uncertainties about the duration of anomalous sub-glacial hydraulic conditions, it can be concluded that there is a low but non-negligible probability of oxygen reaching repository depth. Whether that oxygen could have any impact on copper canisters would depend on the performance of the near-field rock barrier and of the bentonite buffer.

- SR-Can makes various assumptions and uses models to estimate the limits on variations of salinity at repository depth through the glacial cycle. These are mostly reasonable, though the uncertainties generally are not constrained by observations on present-day or palaeohydrogeological analogues. In addition to the freshening effect of glacial melt water inflow, there are also possibilities of salinization due to freeze-out by permafrost or by sea freezing, or due to upconing of deeper groundwaters during glacial advance/recovery or permafrost.

- Other aspects of sub-glacial and sub-permafrost geochemistry also have rather large uncertainties – for example, the possibility of methane hydrate accumulating and then being released. These would be significant if they affected redox equilibria at depth, especially with respect to sulphate reduction and sulphide production. The inorganic redox equilibria and microbial involvement in such processes have been discussed above. At present, there is no evidence that these types of processes coupled to the physicochemical impacts of glaciation or permafrost have occurred in the past. As with all of these uncertain hypothetical impacts of environmental processes at climate stages in the distant future, it would build confidence if there were more evidence of what happened in past glaciations.

8. References

[1] SKB (2006) Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation. Main Report of the SR-Can project. SKB Report TR-06-09.

[2] Bath A and Hermansson H-P (2007) Variability and Uncertainties of Key Hydrochemical Parameters for SKB Sites. SKI Report 2007:03

[3] Guimerà, J., Duro, L., Jordana, S. and Bruno, J. (1999) Effects of ice melting and redox front migration in fractured rocks of low permeability. SKB Report TR-99-19.

[4] Guimerà, J., Duro, L. and Delos, A. (2006) Changes in groundwater composition as a consequence of deglaciation. Implications for performance assessment. SKB Report R-06-105.

[5] SKB (1999) SR-97 – Post-closure safety. Deep repository for spent nuclear fuel. Main Report Volume II. SKB Report TR-99-06.

[6] SKI SITE-94. Deep Repository Performance Assessment Project Volume I and II. SKI, Stockholm (Sweden), 1996.

[7] Glynn, P. and Voss, C. (1996) SITE-94. Geochemical characterization of Simpevarp ground waters near the Äspö Hard Rock Laboratory. SKI Report 96:29.

[8] Grenthe, I., Stumm, W., Laaksoharju, M., Nilsson, A.-C. and Wikberg, P. (1992) Redox potentials and redox reactions in deep groundwater systems. Chemical Geology, 98, 131-150.

[9] Ahonen, L. and Vieno, T. (1994) Effects of glacial meltwater on corrosion of copper canisters. Report YJT-94-13, YJT, Helsinki.

[10] Gascoyne, M. (1999) Long-term maintenance of reducing conditions in a spent nuclear fuel repository. SKB Report R-99-41.

[11] Auqué, L. F., Gimeno, M. J., Gómez, J. B., Puigdomenech, I., Smellie, J., Tullborg, E-L. and Wallin, B. (2006) Modelling of groundwater chemistry over a glacial cycle. Background data for SR-Can. SKB Report TR-06-31.

[12] Vidstrand, P., Svensson, U. and Follin, S. (2006) Simulation of hydrodynamic effects of salt rejection due to permafrost. Hydrogeological numerical model of density-driven mixing, at a regional scale, due to a high salinity pulse. SKB Report R-06-101.

[13] Jaquet, O. and Siegel, P. (2006) Regional groundwater flow model for a glaciation scenario. Simpevarp subarea – version 1.2. SKB Report R-06-100.

[14] Sidborn, M. and Neretnieks, I. (2007) Long term redox evolution in granitic rocks: Modelling the redox front propagation in the rock matrix. Submitted to Applied Geochemistry.

[15] SKB (2006) Geosphere process report for the safety assessment SR-Can. SKB Report TR-06-19.

[16] Samper, J., Molinero, J., Yang, C. and Zhang, G. (2003) Redox Zone II. Coupled modelling of groundwater flow, solute transport, chemical reactions and microbial processes in the Äspö island. SKB Report TR-03-16.

[17] Puigdomenech, I., Ambrosi, J-P., Eisenlohr, L., Lartigue, J-E., Banwart, S.A., Bateman, K., Milodowski, A.E., West, J.M., Griffault, L., Gustafsson, E., Hama, K., Yoshida, H., Kotelnikova, S., Pedersen, K., Michaud, V., Trotignon, L., Rivas Perez, J. and Tullborg, E-L. (2000) O_2 depletion in granitic media. The REX project. SKB Report TR-01-05.

[18] Kotelnikova, S. and Pedersen, K. (1999) The Microbe-REX project. Microbial O_2 consumption in the Äspö tunnel. SKB Report TR-99-17.

[19] King, F., Ahonen, L., Taxén, C., Vuorinen, U. and Werme, L. (2001) Copper corrosion under expected conditions in a deep geological repository. SKB Report TR-01-23.

[20] Bruno, J., Arcos, D. and Duro, L. (1999) Processes and features affecting the near field hydrochemistry. Groundwater-bentonite interaction. SKB Report TR 99-29.

[21] SKB FUD-PROGRAM 92 Kärnavfallets behandling och slutförvaring. SKB, Stockholm, September 1992.

[22] Anon. Kärnbränslecykelns slutsteg. Använt kärnbränsle - KBS-3. SKBF, 1984.

[23] SKI SITE-94. Deep Repository Performance Assessment Project. Summary SKI, Stockholm (Sweden), 1997.

[24] Anon SKB FUD-PROGRAM 98. Kärnavfallets behandling och slutförvaring. SKB, Stockholm, September 1998.

[25] Pedersen, K. (2000) Microbial processes in radioactive waste disposal. SKB Report TR-00-04.

[26] Hermansson H-P and Eriksson S. (1999) Corrosion of the copper canister in the repository environment. SKI-R-99:52

[27] Hermansson H-P. Theoretical evaluation of the stability of steam generator sludge containing copper and magnetite. STUDSVIK/M-97/6

[28] Beverskog, B. and Puigdomenech, I. (1995) SITE-94. Revised Pourbaix diagrams for copper at 5-150 C. SKI Report 95:73.

[29] Malmström, M., Banwart, S., Duro, L., Wersin, P. and Bruno, J. (1995) Biotite and chlorite weathering at 25°C. SKB Report TR 95-01.

[30] Lipenkov, V., Istomin, V., Bulat, S., Raynaud, D. and Petit, J. (2002) An estimate of the dissolved oxygen concentration in subglacial Lake Vostok. B21A-06, Abstracts, Spring Meeting, American Geophysical Union.

[31] Banwart, S., Gustafson, E., Laaksoharju, M., Nilsson, A-C., Tullborg, E-L. and Wallin, B. (1994) Large-scale intrusion of shallow water into a vertical fracture in crystalline bedrock: initial hydrochemical perturbation during tunnel construction at the Äspö Hard Rock Laboratory, southeastern Sweden. Water Resources Research, 30, 1747-1763.

[32] Banwart, S., Tullborg, E-L., Pedersen, K., Gustafsson, E., Laaksoharju, M., Nilsson, A-C., Wallin, B. and Wikberg, P. (1996) Organic carbon oxidation induced by large-scale shallow water intrusion into a vertical fracture zone at the Äspö Hard Rock Laboratory (Sweden). J. Contaminant Hydrology, 21, 1-4, 115-125.

[33] Banwart, S.A. (1999) Reduction of Fe(III) minerals by natural organic matter in groundwater. Geochimica et Cosmochimica Acta, 63, 2919-2928.

[34] Tarits, C., Aquilina, L., Ayraud, V., Pauwels, H., Davy, P., Touchard, F. and Bour, O. (2006) Oxido-reduction sequence related to flux variations of groundwater from a fractured basement aquifer (Ploemeur area, France). Applied Geochemistry, 21.1, 29-47.

[35] Winograd, I.J. and Robertson, F.N. (1982) Deep Oxygenated Ground Water: Anomaly or Common Occurrence? Science, 216, 4551, 1227-1230.

[36] Salas, J., Ayora, C. and Bitzer, K. (2000) The redox control of groundwater around the Okélobondo uranium deposit (Gabon): 1D reactive transport modelling. J. Geochemical Exploration, 69-70, 189-193.

[37] Perez, J.R., Banwart, S.A. and Puigdomenech, I. (2005) The kinetics of O2(aq) reduction by structural ferrous iron in naturally occurring ferrous silicate minerals. Applied Geochemistry, 20.11, 2003-2015.

[38] Lee, W. and Batchelor, B. (2003) Reductive capacity of natural reductants. Environ. Sci. Technol., 37.3, 535-541.

[39] Byegård, J., Gustavsson, E. and Tullborg, E-L. (2006) Bedrock transport properties – evaluation of transport data and retardation model. Preliminary site description Laxemar subarea – version 1.2. SKB Report R-06-27.

[40] Wahlgren, C-H., Hermanson, J., Curtis, P., Forssberg, O., Triumf, C-A., Tullborg, E-L. and Drake, H. (2005) Geological description of rock domains and deformation zones in the Simpevarp and Laxemar subareas. Preliminary site description, Laxemar subarea, version 1.2. SKB Report R-05-69.

[41] Byegård, J., Gustavsson, E., Tullborg, E-L. and Selroos, J-O. (2005) Bedrock transport properties. Preliminary site description Forsmark area – version 1.2. SKB Report R-05-86.

[42] Wahlgren, C-H., Bergman, T., Ahl, M. and Ekström, M. (2006) Oskarshamn site investigation. Modal and geochemical analyses of drill core samples 2006 and updated bedrock map of the Laxemar subarea. Classification of rock types in KLX08, KLX10, KLX11A, KLX12A, KLX18A and KLX20A. SKB Report P-06-279.

[43] Sandström, B., Savolainen, M. and Tullborg, E-L. (2004) Fracture mineralogy. Results from fracture minerals and wall rock alteration in boreholes KFM01A, KFM02A, KFM03A and KFM03B. Forsmark site investigation. SKB Report P-04-149.

[44] Sandström, B. and Tullborg, E-L. (2006) Forsmark site investigation. Mineralogy, geochemistry, porosity and redox capacity of altered rock adjacent to fractures. SKB Report P-06-209.

[45] Drake, H. Sandström, B. and Tullborg, E-L. (2006) Mineralogy and geochemistry of rocks and fracture fillings from Forsmark and Oskarshamn: Compilation of data for SR-Can. SKB Report R-06-109.

[46] Palandri, J.L. and Kharaka, Y.K. (2004) A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. Open File Report 2004-1068, U.S. Geological Survey.

[47] Sidborn, M. and Neretnieks, I. (2004) Modelling biochemical processes in rocks: Analysis and exploratory simulations of competition of different processes important for ferrous mineral oxidation and oxygen depletion. Mat. Res. Soc. Symp. Proc. Vol. 807, 829-834..

[48] MaQuarrie, K.T.B. and Mayer, K.U. (2005) Reactive transport modelling in fractured rock: A state-of-the-science review. Earth-Science Reviews, 72, 189-227.

[49] Vidstrand, P. (2003) Surface and subsurface conditions in permafrost areas – a literature review. SKB Report TR 03-06.

[50] Gascoyne, M. (2001) A review of published literature on the effects of permafrost on the hydrogeochemistry of bedrock. SKB Report R-01-56.

[51] Herut, B., Starinsky, A., Katz, A. and Bein, A. (1990) The role of seawater freezing in the formation of subsurface brines. Geochimica et Cosmochimica Acta, 54, 13-21.

[52] Starinsky, A. and Katz, A. (2003) The formation of natural cryogenic brines. Geochimica et Cosmochimica Acta, 67, 1475-1484.

[53] Ruskeeniemi, T., Ahonen, L., Paananen, M., Frape, S., Stotler, R., Hobbs, M., Kaija, J., Degnan, P., Blomqvist, R., Jensen, M., Lehto, K., Moren, L.,

Puigdomenech, I. and Snellman, M. (2004) Permafrost at Lupin (Phase II). Report YST-119, Geological Survey of Finland.

[54] Bath, A., Milodowski, A., Ruotsalainen, P., Tullborg, E.-L., Cortés Ruiz, A. and Aranyossy, J.-F. (2000) Evidence from Mineralogy and Geochemistry for the Evolution of Groundwater Systems During the Quaternary for Use In Radioactive Waste Repository Assessment (EQUIP Project). Final Report, Contract No FI4W-CT96-0031. Euratom/EC DG Research Report EUR 19613EN. European Commission, Luxembourg, 157pp.

[55] Degnan, P., Bath, A., Cortés, A., Delgado, J., Haszeldine, S., Milodowski, A., Puigdomenech, I., Šilar, J., Torres, T. and Tullborg, E-L. (2005) PADAMOT: Project Overview Report. PADAMOT Project – EU FP5 Contract No FIKW-CT2001-20129, 85 pp. UK Nirex Ltd., Harwell.

[56] Bath, A. (2005) Geochemical Investigations of Groundwater Stability. SKI Report 2006:12.

9

Review of the SR-Can project regarding microbial processes

Rolf Hallberg

Department of Geology and Geochemistry
Stockholm University
106 91 Stockholm
Sweden

Table of contents

1. General views

In the main report of the SR-Can project (SKB TR-06-09) the corrosion of the copper canister is modeled with data input according to different scenarios. That is, first the scenarios are set up and thereafter the model is predicting the possible corrosion effect.
All scenarios presume an uneven general corrosion and chemical input data to the models are average data from field observations and/or chemical equilibrium calculations. The models used are assuming a homogenous environment around the canister. This approach is not consistent with natural environments where variations in data are the most common and where a mean value seldom is observed.

Conservative estimates on the corrosion of copper should be retrieved from models where not only average numbers but also end members of each data set are used.

I would also like to see another approach to the corrosion problem. First answer the question "What are the prerequisites to corrode the canister to such an extent that a penetration of the 5 cm copper is achieved in 1,000,000 years?". Thereafter look for necessary scenarios and find out whether they can be expected from a realistic point of view.

In the main report (p. 361) it is stated that corrosion from sulphate-reducing bacteria cannot be ruled out, but it is not clear that this has been taken into account in any of the models. The microbes' impact is ruled out and they are assumed to have a negligible effect on the copper coverage of the canisters. The evidences presented for such an assumption are far from convincing.

1.1. General aspects on bacteria

Bacteria can be found in almost all type of environments. The species diversity is large and their distribution scattered. Below a temperature of 120° C the most important limitation is the availability of water, which can be expressed as water activity (a_w, see below).

Bacteria form micronisches and biofilms where they create optimal conditions for growth and activity. We can thus not use overall redox and pH conditions to exclude the activity of certain bacteria. Microbiologists believe that we may have catalogued 1% of all types of bacteria in natural and man-made environments. The one we have catalogued are those we can cultivate in the laboratory. When we count the numbers of viable bacteria in a natural environment or sometimes even in the laboratory experiments we seldom get representative numbers of those that are attached to solid material. A very large number is attached as this conserves energy compared to be in a motile state.

1.2. Bacterial activity in the repository

The bacterial activity in the compacted bentonite has been debated for many years. Among the factors that are raised to support a non bacterial activity or 'sterile' environment, I will bring up the most common, like desiccation, swelling pressure and no formation of biofilms. There are many factors regulating the activity of bacteria but water is probably the most important factor.

1.2.1 Water activity

In the modeling of copper canister corrosion Liu and Neretnieks (2004) state "The water activity is low enough to exclude all bacteria that do not form spores." This statement is based on findings reported by Pedersen and co-workers. The bentonite will reach the planned full compaction density of 2g cm^{-3} (5Mpa), and have a water content of around 26%. The water activity (a_w) is low, probably around 0.92.

a_w is related to the water concentration through an activity coefficient times the mole fraction of water in the system (%RH/100).

Bacterial cells are membrane bound bags of water. In the compacted bentonite the bacteria are exposed to a process of desiccation.

Potts (1994) has published a thorough review, "Desiccation tolerance of Prokaryotes", on the subject with 433 references. Many of his statements are worth taking into consideration before we exclude the bacterial activity in the bentonite. Especially in the long time perspective, which according to SKB TR-06-09 is one million years. I will here list some citations from Potts paper.

> *There are numerous biophysical and physiological components that contribute to, interact in, and require consideration with respect to desiccation tolerance of bacteria.*
>
> *The anhydrobiotic cell is more than simply a collection of dried components.*
>
> *The lipid biosynthetic machinery, as well as the proteins required for the uptake and phosphorylation of glycerol and the uptake of sulphate remains functional during desiccation.*
>
> *A biofilm provides the largest surface area for rewetting, and a film with a clay envelope, especially montmorillonite* [bentonite]*, may protect bacteria from excessive desiccation. Cells that express desiccation tolerance undergo drying at much lower water potentials, and it would appear that they must withstand the most extensive perturbations of V_b (quantity of bound water) for their various cellular constituents over the long term – the absolute lower limit beyond which no reactivation can occur is unknown.*
>
> *The water potential of a system is proportional to a constant times the absolute temperature and a_w. The term represents the work involved in moving 1 mole of water from some point in a system to a pool of pure water at atmospheric pressure and at the same temperature as the system under consideration.*
>
> *The sensitivities of soil bacteria to relatively small negative water potentials have been attributed to the restriction of movement as the soil*

> *water drained. Pseudomonas a. requires water-filled pores 1 to 1.5 µm in diameter or larger to move readily in soil, so it is easy to understand how a matrix deficit could influence viability if the latter is dependent on motility.*
>
> *... not all cells in a population respond in a similar fashion to a water deficit. The physiological status of the cell at the time of drying, and the time of the drying event, seem to be potential sources of this variation in sensitivity.*
>
> *Studies suggest that cells in the stationary phase are structurally, physiologically, and functionally distinct from those in the log phase. Stationary-phase cells of E. coli show a marked enhancement of resistance to air drying, ...*
>
> *Surface structures of the sulphate reducing bacteria Desulfurococcus mobilis, another archaebacterium, have an unusual protein lattice at the surface, providing almost an exoskeleton that has been speculated to afford protection from water stress.*
>
> *Bacteria respond to desiccation by channeling energy and nutrients into polysaccharide production. For example, Pseudomonas sp. contains more EPS (extra cellular polysaccharides) than protein when desiccated.*
>
> *What is remarkable about desiccation tolerance is not what is known but what is not known.*
>
> *.... ecological studies, for the most part, include a good deal of phenomenological and anecdotal observations that shed little light on the mechanism of desiccation tolerance.*

1.2.2 Swelling pressure

SKB TR-06-09 p.186. “The buffer should furthermore have a sufficient swelling pressure to prevent bacteria from surviving in it. Past and ongoing studies ……”

The bacteria originally present in the repository have adopted to the hydrostatic pressure of about 5MPa. If this pressure is doubled due to the swelling pressure of the bentonite it is most probable that the bacteria will adapt to this new pressure. We can allow the adaptation time to be decades, which is a short time compared to the assessment time of 1 million years. No study of bacterial survival at high pressure will be able to guaranty the elimination of bacterial activity in the repository. Such studies can easily be met with the argument that the study time was too short. We know that bacteria like sulphate reducing bacteria (SRB) are as active at the bottom of the ocean at a water depth of 4000 m as they are in surface waters.

In SKB TR-06-18 (pp. 127-132, 186-187) it is stated that SRB occur abundantly down to depths of at least 600 to 700 m. Also microbes are generally very robust and can withstand harsh conditions. The potential for sulphide production is significant at repository depth and possible effects on the repository function must be considered in safety assessment. Most microbes tolerate large variations in hydrostatic pressure and flow.

Data from several laboratory and field experiments are presented among which "Field experiments exploring microbial copper sulphide production in buffer" can be considered the most reliable though it suffers from several uncertainties.

It was a closed system and did not take into consideration the contribution of nutrients and sulphate from diffusion processes and water flow in cracks etc. Also the experimental time was very short, only 70 days.
Other uncertainties listed are

> *...water content and heat stress must be clarified and defined.*
> *...restrictions due to a low pore size may need to be experimentally defined.*
> *...survival of microbes ... not fully understood.*
> *...mechanisms for the observed disappearance of viability of microorganisms remain to be clarified.*

"Model simplification uncertainties and Input data and data uncertainties" are classified as "Not relevant since a model for microbial processes in the buffer is lacking."
When effects from microbial processes in the backfill are discussed they are eliminated with the comment that "Microbial effects in the backfill are not considered in SR-Can."

1.2.3 Biofilms

The joints between the bentonite packages and between the bentonite and the canister will allow the bacteria to form biofilms, including EPS (exopolysacharides), where they can tolerate desiccation and have enough space for motility in case they seek for nutrients. The SRB (sulphate-reducing bacteria) are motile by means of a polar flagellum. Masurat and Pedersen, report that SRB were present in a dormant state in the commercial bentonite tested. The dormant SRB produced hydrogen sulphide after activation by groundwater and in the presence of added carbon sources. SRB exists in nature as components of consortia of organisms. Hamilton (1985) states that these consortia often take the form of biofilms and allow for the creation of anaerobic microenvironments within a bulk aerobic environment. It has been estimated that when a biofilm of aerobic or facultative bacteria and their associated EPS reaches a thickness of 10-25 µm, then conditions at the base of the biofilm will be anaerobic. Other estimates suggest that in most natural biofilms the depth required for anaerobiosis may be closer to 100 µm. That is to say that even within aerobic environments, thin bacterial slime growth, or biofilm, can generate ideal conditions for the growth of the obligatory anaerobic sulphate-reducing bacteria, with all the attendant problems of sulphide production and corrosion.

At the present state there are no evidences that can allow us to exclude the activity of bacteria in the repository, especially not in the compacted bentonite barrier. Bacteria are present in the backfill and bentonite from the beginning of the repository, and need not to be introduced from the ambient rock.

Whenever there is a positive effect from bacterial activity it is used in the arguments for the safety of the repository. SKB TR-06-19 p. 159, "Microorganisms ….. may mediate reactions that stabilise the redox potential in ground water at a low and, therefore, beneficial values for the repository."

"Oxygen is a corrosive component and microbial activity is beneficial for its reduction. E.g. Hydrogen, and … will reduce oxygen if it is introduced." Contradictory to this the negative effects of the secondary metabolites are not taken into consideration.

SKB should accept the fact that microbial activity will be present in the repository and include their relevant positive as well as negative processes in the assessments and the modelling.

SKB TR-06-18 p.129. "The relevant boundary conditions in order to treat the (microbial) processes quantitatively are those of the transport processes that control the exchange of solutes (microbe nutrients) between the buffer pore water and the water in the adjacent components. i.e. the boundary conditions of the processes diffusion and advection."

1.2.4 pH and Eh

Bacteria form microniches and biofilms where they create optimal conditions for growth and activity (e.g. Hallberg, 1968, Jörgensen, 1977). pH is regulated by chemical and microbial processes in microniches of the buffer. Such local pH conditions may at the surface of the canister govern the corrosion processes.

We can thus not use overall redox and pH conditions to exclude the activity of certain bacteria. pH should not be considered as an average pH of the entire repository but more representative of local environments in the barrier.

The proposed final pH of 7-7.5 is probably somewhat higher then what can be expected. The governing factor is the microbial processes that dominate and buffer the pH at a level most acceptable for these bacterial species. It is most probable that it will be the SRB, and if so the pH will stabilize at a value close to 6.8. That is, a final pH is probably just below than above 7.
The redox state is likewise regulated by the dominating chemical/microbial processes. It is buffered at two dominating levels. The Eh of Fe(II)/Fe(III) at about +220 mV and that of SO_4^{2-}/HS^- at about -250 mV. The latter is the most probable for the repository. The Eh given in SKB TR-06-09, fig 9-50 is very close to that value. This figure refers to box-and-whisker plots. The corrosion takes place at the root parts of the whiskers and the Eh at this microenvironment is not considered in the calculations for fig 9-50. The increase in Eh at 9000 years is only valid for the macroenvironment.

It is the buffering power of the microbial processes that will determine the pH and Eh of the microbial microenvironment of the canister and not dilution processes of the macroenvironment.

2. Mobility of radionuclides

SKB TR-06-09 p.189. "… slow transport in the buffer, in the backfill, in the near field host rock…" Microbial activities have not been considered in this context. However, the influence of microbial processes on radionuclide transport is discussed in SKB TR-06-19 and presented in Table 5-7 of that report.

The mobilization processes are of most concern for the distribution of radionuclides to the ambient environment. The outer part of the bacterial cell wall is generally anionic. Thus, a cell surface in contact with metal ions will change their electronegative surface to an electropositive when metal ions are fixed to the surface. Bacteria are supposed to be poisoned by metals and have their propagation inhibited. According to textbooks As should have a toxic effect on the bacterium *Thiobacillus* at concentrations >200 ppm . However, in our own laboratory experiments we could grow these bacteria at As concentrations of 4000 ppm. Another toxic metal, Mo, inhibited the bacterial growth at concentrations of 8 ppm. The cells increased in size but they could not multiply. The plasmatic membrane of the bacterial cell seem to have the ability to isolate the more vital cell content from toxic metals but the cells ability to multiply was inhibited. When the cells were transferred to a metal free solution they started to divide and multiply in a normal way.

SKB TR-06-09 p.223. "During the excavation and operation phases, substantial amounts of colloids may be formed due to microbial activities,… Other processes contributing to the elimination of colloids are microbial decomposition of organics,…" These statements are contradictory to each other. In the first place microbes form a substantial amount of colloids and in the second place they eliminate colloids. SR-Can will see the second process to be dominating and the first to be present during a short period when the excavation of rock and deposition of canisters take place. At a leakage of radionuclides they are assumed to bind strongly to the bentonite and in such a way be retained from distribution to the surrounding environment.

The binding of metals to the microbial cell surface is a passive mechanism. However, metals with low concentrations in a solution and with high atomic numbers seem to be attached to the cells in abnormally high amounts (Fyfe 1979, Hodge et al. 1979, Mangini et al. 1979). Accumulation of uranium was studied with *Pseudomonas aeruginosa* (common soil bacterium), Strandberg et al. (1981). The uptake of uranium was so fast that they could not observe the effect of changes in the ambient environment. The fixation of the radionuclide was strong enough to withstand washing with water. Part of the uranium was also accumulated in the cell. This means that ions of radionuclides are transferred into particles with a size of 0.2-1.5 µm or a few µm in diameter and thus act as colloids. Bacteria are generally adsorbed to mineral surfaces and then also the radionuclide will be immobilized. If the cells are suspended, their mobility is dependent on the transmissivity of the soil. However, the binding between the cell material and the metal is increased when the bacterium is starving or after the death of the cell (Dawson et al. 1981, Humphrey et al. 1983). This is because starving bacteria increase in number faster than a normal population and thereby the surface/volume of the cell material is increasing. The same is true when they die as the cell material from a lysing cell represents a much larger surface/volume ratio then a living cell. Bacteria can also move by means of flagella.

Laboratory studies have demonstrated that motile SRB move about 3 mm/day in sediments (Oppenheimer 1960). We have observed “diffusion coefficients” to be about 20% larger in microbial active sediments compared to sterile (Östlund et al. 1989).

The anionic surface of bacteria and other microorganisms is a strong agent for binding of metals.
The binding of metals to the cell material is increased when the bacterium is starving or after its death.
Metals can be transported on bacterial fragments and consequently radionuclides can be suspended as colloids on particles with a size from an organic molecule to an aggregate of bacteria (5-10 μm).

Solubility of radionuclides.

Can radionuclides be dissolved in the water of the repository? The answer is yes if they form a complex or chelate with organic compounds. This is discussed in SKB TR-06-19 p.163 and Table 5.7.2. References are made to Arlinger et al. (2004), where they in experiments have found bacterially produced complexing agents.

Chelating organics are formed during the degradation of organic material at aerobic and anaerobic conditions (Mooney et al., 1978 and Hallberg, Larsson, 1999). In experimental sedimentary systems copper formed soluble metal-organic complexes that made copper stay in solution in the presence of sulphide (Hallberg et al. 1980). We have, in a Norwegian fjord, observed metal chelating compounds that are very stable at reducing conditions (Hallberg and Larsson 1999). The dominating chelating agent was 2-mercaptobenzothiazole (MBT). MBT is known as an efficient chelator and is used for solvent extraction of metals in industrial processes (Turel and Haldar 1982, Rajadhyaksha and Turel 1985).

2.1. The microbial impact on corrosion of copper

Liu and Neretnieks (2004) state that during the period of glaciations, groundwater containing high concentrations of oxygen might penetrate into the depth of the repository. The duration of those periods is in the order of a few hundred years and can be considered as instantaneous and these events are deemed not to cause significant corrosion.

During the last million years, the Baltic shield has experienced at least 8 glaciation cycles. Oxygen may penetrate into the bedrock during glaciations but I do not know to what depth and to what extent. There may be observations from the Polar Regions that will allow us to make some conclusions on that subject. The presence of oxygen is an important factor for pitting corrosion to take place. However, the concentration of oxygen necessary to create pitting corrosion can be debated. Hardy and Bown (1984) suggested that the most aggressive conditions associated with SRB were those, which were not entirely anaerobic, but where small quantities of oxygen might be present from time to time. My own observations from studies of bronze canons from the sunken battleship ‘Kronan’ showed that the most severe corrosion had taken place at the interface between the anoxic and oxic environment. To create an anode/cathode system you need a combination of both. These results and those of Zhu et al. (1994) show that SRB though being strictly anaerobic can survive and contribute to metal corrosion problems in environments with the presence of oxygen. The total time needed for construction and operation of the repository will probably be about 40 years. During that time oxygen will be introduced into the repository. For how long times will the oxygen that is trapped in the repository be available for pitting corrosion processes? (300 years, SKB TR-94-02). This together with a high probability that during an extensive time, the repository will be subject to glacial conditions, means that oxic conditions may be prevailing during which, there is a high risk for pitting corrosion.

During the interglacial time anoxic conditions is the most plausible and it seems to be a consensus that pitting corrosion can be excluded. Liu and Neretnieks (2004) have modeled the general corrosion of a canister where water is entering the repository from a horizontal fracture in the ambient rock. They base their transport processes on the vague argument that “Inside the bentonite buffer, no bacteria are assumed to exist or be active.” They continue “Corroding species like sulphide will be transported only by molecular diffusion through the bentonite buffer to the canister surface.” They do not take into consideration the possibility of biofilms on the canister surface where SRB can be active. They conclude “This means that in this example 41% of the produced sulphide enters the clay, and the rest is carried away by the water. During 10^5 years a general corrosion opposite the fracture would be 2.45 mm.” If we extrapolate this to 10^6 years it would correspond to 24.5 mm. If all sulphide reaches the canister surface 60 mm is a more appropriate number.

SKB TR-06-09 pp. 222-223
Organic matter is present in the backfill and buffer of the repository. It may also be in the form of geogases entering the repository from the ambient rock. These gases are supposed to escape from the repository.

The safety function to prevent canister sinking is a swelling pressure of the buffer to be >0.2 MPa. The safety function to eliminate microbes is >2 MPa, which is expected to be the case for all deposition holes. However, in order to allow gases to escape from the repository a low swelling pressure would be an advantage. These prerequisites are contradictory to each other and no solution to this is presented in SR-Can.

Bacteria can use hydrogen as an energy source. Nikitinsky (1907) suggested from field observations that certain sulphate-reducing bacteria oxidized hydrogen. However, it was not until 1931 that Stephenson and Strickland (1931) established the utilization of molecular hydrogen by SRB. Sisler and ZoBell (1950) give an excellent review of the subject. Hydrogen can escape from the lower part of the crust to the surface through fissures in the basement. There are many small pits in the bottom sediments of the Stockholm archipelago. These are created by gas leakages from below. Presently I do not have excess to analytical data from these gases but they contain hydrogen as well as methane. Methane is used as carbon source by SRB, which was documented by Cappenberg (1974) in several papers, eg. Cappenberg and Prins (1974). Liu and Neretnieks (2004) have in their model used methane as carbon and energy source, and applied a value of 1 mol m^{-3}. Finish data show, according to Liu and Neretnieks, concentrations that are one magnitude higher. Why is not the higher concentration used in the model? Data on hydrogen and methane concentrations should be sampled in the rock fracture where the gases are transported.

This is the place where we should expect the highest concentrations and if it coincides with the canister it would be the most conservative number of a model.

The production of sulphide from SRB is limited by access to sulphate and organic matter. Calculations on the amount of organic matter that will be present in the repository is made by Hallbeck et al., SKB R-06-104. Their calculations are focused on stray material in the tunnels and other cavities, which is mainly where the backfill material is deposited. The result from these calculations is a total amount in the order of 10^{-3} kg/m^3. Organic material is also produced by biofilms of mainly iron oxidizing bacteria. This is estimated to be of the same order as the stray material, or 1 ton given as total amount for the repository. Based on these data they have calculated the maximum amount of sulphide produced by SRB to be 1 mg/L and not exceeding the highest concentration found of 7 mg/L. In SKB TR 06-09 p.222, there is a reference to Hallbecks report, which states that the maximum amount of sulphide that can be generated microbially is ≈ 10 moles for each deposition hole. The calculations in SKB R-06-104 do not take into account the organic matter in the bentonite. There is no explanation why this is neglected. The canister will be surrounded by a bentonite with an organic content of 5-6 kg/ton. I have calculated the volume of bentonite in each canister hole to be 12.6 m^3. With a density of 2 kg/m^3 of a saturated buffer it means that 25.2 tons of bentonite with a total content of about 140 kg of organic material will be deposited around each canister. The content of organic material calculated in SKB R-06-104 is negligible in comparison with that in the bentonite. If all 140 kg of organic material was used to produce sulphide it would generate a total amount of 466 kmol sulphide. Thus, the amount of organic material will not be a limiting factor for SRB in the repository but the excess to sulphate. Thus the most conservative estimate of the maximal sulphide concentration is equal to the maximal amount of sulphate that will be available at the canister. Sulphate is a common component in groundwater and thus a concentration of 7 mg/L or more of sulphide is a realistic scenario. However, the most probable scenario is that part of this sulphide is precipitated as FeS (mackinawhite). The sulphide ionic activity on the canister surface is thus regulated by diffusion and Fe activity.

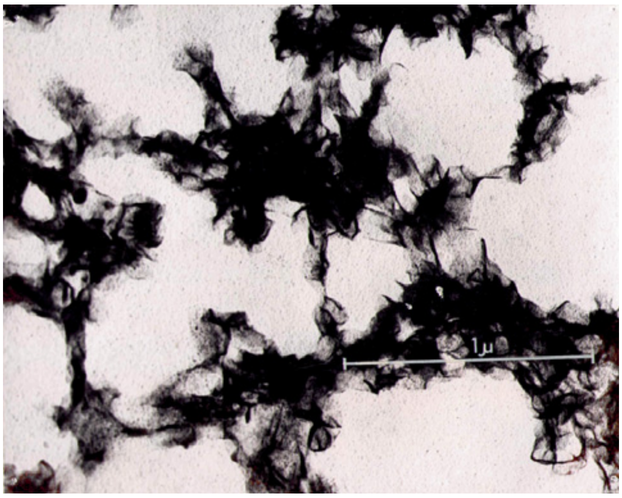


Figure 1: TEM micrograph of an initially stage of FeS formed in a continuous culture of sulphate reducing bacteria.

The corrosive product H_2S is supposed to be eliminated from corrosion of copper by precipitation with Fe to form iron sulphide. The formation of H_2S at normal temperature and pressure can only take place by means of bacterial sulphate reduction. The precipitated iron sulphide is formed on the cell surfaces of the bacterium and as thin sheets close to the cell (Figure 1). If this FeS is precipitated on the surface of the canister does it mean that it can be eliminated from corrosion of copper? In this context I will refer to Weiner and Dove, 2003, p.8.

> *…organisms possess fluids with significant ionic strength. This means that mineralization studies must address the solution chemistry in the terms of ion activity, not concentration. Careful use of activity coefficient models is necessary to estimate the supersaturation of growth environments. For example, calcium ions in a blood plasma with the physiological ionic strength of 0.15 molal has an activity coefficient of approximately 0.3, compared to a value of 1.0 in an infinitely dilute solution (e.g. Langmuir 1997). In high salinity fluids associated with marine environments, the correction to activity becomes greater (and sometimes more ambiguous). In addition to affecting supersaturation, ionic strength mediates the charges of precursor molecules, thus affecting the stabilization of colloids and amorphous gels. (e.g. Iler 1979, Perry 2003).*

Thermodynamic models for the corrosion of the copper canister should use ion activity, not concentration.

3. References

Arlinger, J., Oskarsson, A., Albinsson, T., Anlid, T., and Pedersen, K. 2004. Mobilisation of radionuclides by ligands produced by bacteria from the deep subsurface. In V.M. Oversby and L.O. Werme (eds.) Scientific basis for nuclear waste management XXVII. Materials research society, Warrendale, Pennsylvania. p.823-828.

Cappenberg, Th.E. and Prins, R.A. 1974. Interrelations between sulfate-reducing and methane-producing bacteria in bottom deposits of a fresh-water lake. III. Experiments with ^{14}C labelled substrates. Antonie van Leeuwenhoek. 40:457-469.

Dawson, M.P., Humphrey B., Marshall, K.C. 1981. Adhesion: a tactic in the survival strategy of a marine vibrio during starvation. Curr.Microbiol. 6:195-198.

Fyfe, W.S. 1979. The geochemical cycle of uranium. Philos. Trans. R. Soc. London. A291:433-445.

Hallberg, R.O. 1968. Some factors of significance in the formation of sedimentary metal sulphides. Stockholm Contr. In Geol. Vol. XV 4:39-66.

Hallberg, R.O., and Larsson, C. 1999. Biochelates as a cause of metal cycling across the redoxcline. Aquatic Geochem. 5:269-280.

Hallberg, R.O., Bubela, B., and Ferguson, J. 1980. Metal chelation in sedimentary systems. Geomicrobiology J. 2:99-113.

Hamilton, W.A. 1985. Sulphate-reducing bacteria and anaerobic corrosion. Ann. Rev. Microbiol. 39:195-217.

Hardy, J.A. and Bown, J.L. 1984. Sulfate-reducing bacteria: Their contribution to the corrosion process. Corrosion. 40:650-654.

Hodge, V.F., Koide, M., and Goldberg, E.D. 1979. Particulate uranium, plutonium and polonium in the biogeochemistries of the coastal zone. Nature 277:206-209.

Humphrey, B., Kjelleberg, S., and Marshall, K.C. 1983. Responses of marine bacteria under starvation conditions at a solid-water interface. Appl. Environ. Microbiol. 45:43-47.

Iler, R.K. 1979. The chemistry of silica. John Wiley & Sons, New York.

Jörgensen, B.B. 1977. Bacterial sulfate reduction within reduced microniches of oxidized marine sediments. Mar. Biol. 41:7-17.

Langmuir, D. 1997. Aqueous Environmental Geochemistry. Prentice-Hall, Inc. Upper Saddle Rriver, New Jersey.

Liu, B.J. and Neretnieks, I. 2004. Coupled transport/reaction modelling of copper canister corrosion aided by microbial processes. Radiochim. Acta. 92:849-854.

Mangini, A., Sonntag, C., Bertsch, G., and Műller, E. 1979. Evidence for a higher natural uranium content in the world rivers. Nature 278:337-339.

Masurat, P. and Pedersen, K. Microbial sulphide production in compacted bentonite at the commencement of long-term disposal of high-level radioactive waste. Göteborg university, CBM-Microbiology.

Mooney, J.R., Bubela, B., Ferguson, J., and Hallberg, R.O. 1978. Mathematical modeling of experimental systems simulating metal chelating in reducing sedimentary environments. BMR J. Australian Geology & Geophysics 3:93-100.

Nikitinsky, J. 1907. Die anaerobe Bindung des Wasserstoffes durch Mikroorganismen. Zentr. Bakt. Parasitenk. 19:495-499.

Oppenheimer, C.H. 1960. Bacterial activity in sediments of shallow marine base. Geochim. Cosmochim. Acta 19:244-260.

Östlund, P., Hallberg, R.O., and Hallstadius, L. 1989. Porewater mixing by microorganisms, monitored by a radiotracer method. Geomicrobiology J. 7:253-264.

Perry, C.C. 2003. Silicification: the processes by which organisms capture and mineralize silica. In P.M. Dove, J.J. de Yoreo, and S. Weiner (eds.) Biomineralization. Rev. Mineral. Geochem. 54: 291-327

Potts, M. 1994. Desiccation tolerance of Prokaryotes. Microbiology Reviews 58:755-805.

Rajadhyaksha, M., and Turel, Z.R. 1985. A study of solvent extraction of Cu(II) with 2-mercaptobenzothiazole into chloroform. J. Radioanal.Nucl. Chem. Letters 93:163-172.

Sisler, F.D. and ZoBell, C. 1950. Hydrogen-utilizing, sulfate-reducing bacteria in marine sediments. Contribution from Scripps Institution of Oceanography, New Series No. 490:747-756.

Stephenson, M. and Stickland, L.H. 1931. Hydrogenase. II. The reduction of sulphate to sulphide by molecular hydrogen. Biochem. J. 25:215-220.

Strandberg, G.W., Shumate II, S.E., and Parrott Jr., J.R. 1981. Microbial cells as biosorbents for heavy metals: Accumualtion of uranium by *Saccharomyces cerviseae* and *Pseudomonas aeruginosa*. Appl. Environ. Microbiol. 41:237-245.

SKB R-06-104, Hallbeck, L., Grivé, M., Gaona, X., Duro, L., Bruno, J., 2006; Main organic materials in a repository for high level radioactive waste, Svensk Kärnbränslehantering AB, Stockholm.

SKB TR-94-02, Wersin, P., Spahiu, P. and Bruno, J.; Time evolution of dissolved oxygen and redox conditions in a HLW repository, Svensk Kärnbränslehantering AB, Stockholm.

SKB TR-06-09, Svensk Kärnbränslehantering AB, 2006; Long-term safety for KBS-3 repositories at Forsmark and Laxemar - a first evaluation. Main report of the SR-Can project, Svensk Kärnbränslehantering AB, Stockholm.

SKB TR-06-18, Svensk Kärnbränslehantering AB, 2006; Buffer and backfill process report for the safety assessment SR-Can, Svensk Kärnbränslehantering AB, Stockholm.

SKB TR-06-19, Svensk Kärnbränslehantering AB, 2006; Geosphere process report for the safety assessment SR-Can, Svensk Kärnbränslehantering AB, Stockholm.

Turel, Z.R., and Haldar, B.C. 1982. A study of the solvent extraction of Pt(II) with 2-mercaptobenzothiazole into chloroform. Radiochem. Radioanal. Letters 52:37-42.

Weiner, S., and Dove, P.M. 2003. An overview of biomineralization processes and the problem of the vital effect. In P.M. Dove, J.J. de Yoreo, and S. Weiner (eds.) Biomineralization. Rev. Mineral. Geochem. 54: 1-29.

Zhu, J., Mackie, R.I., Riskowski, G.L., and Day, D.L. 1994. Bacterial colonization on metal surfaces in animal buildings: Implication for microbial-induced corrosion. Transaction of the ASAE. 37:929-937.

www.ski.se
www.ssi.se

STATENS KÄRNKRAFTINSPEKTION
Swedish Nuclear Power Inspectorate

POST/POSTAL ADDRESS SE-106 58 Stockholm
BESÖK/OFFICE Klarabergsviadukten 90
TELEFON/TELEPHONE +46 (0)8 698 84 00
TELEFAX +46 (0)8 661 90 86
E-POST/E-MAIL ski@ski.se
WEBBPLATS/WEB SITE www.ski.se

STATENS STRÅLSKYDDSINSTITUT
Swedish Radiation Protection Authority

POST/POSTAL ADDRESS SE-171 16 Stockholm
BESÖK/OFFICE Solna Strandväg 96
TELEFON/TELEPHONE +46 (0)8 729 71 00
TELEFAX +46 (0)8 729 71 08
E-POST/E-MAIL ssi@ssi.se
WEBBPLATS/WEB SITE www.ssi.se