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# **Hydrogeochemical and microbiological effects on fractures in the Excavation Damaged Zone (EDZ)**

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January 2009

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

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# Summary and conclusions

Due to the disturbances associated with the excavation, construction and closure of the repository for storage of spent nuclear fuel, the saturation state of the groundwaters at repository depth with respect to several mineral phases may change and mineral precipitation/dissolution reactions may take place. In addition, changing groundwater conditions may facilitate microbial growth on fracture walls. These processes are of importance since they may influence the stability and safety of the Excavation Damaged Zone (EDZ) because precipitation and microbial growth may seal the hydraulically conductive fractures caused by the repository construction. This information is not only important from the process understanding and safety assessment point of view but is also useful when designing investigation programmes for the EDZ and when evaluating field data from e.g. hydraulic tests.

Different processes expected to occur in the EDZ during the open repository conditions and after repository closure have been evaluated based on data from Forsmark, Laxemar and Äspö.

**Geochemical modelling** by using PHREEQC was applied to simulate the following cases:

- increase of temperature to 50°C and 100°C to simulate the thermal effects from spent nuclear fuel;
- open repository conditions simulating atmospheric conditions (equilibrium with atmospheric partial pressures of CO<sub>2</sub>(g) and O<sub>2</sub>(g));
- mixing with deep saline water simulating up-coning;
- mixing with shallow infiltration waters simulating down-coning;
- mixing with different proportions of cement dissolution porewater.

The effect of variable temperatures (up to 100°C) on most of the above modelled processes has also been assessed.

Most of the studied groundwaters or the mixtures of different groundwaters are close to equilibrium or even oversaturated with respect to calcite and ferric oxyhydroxides. Therefore, the occurrence of mineral precipitation reactions is thermodynamically feasible in most of the studied cases. Moreover, most of the groundwater compositions do not exhibit any capacity to dissolve calcite or ferric oxyhydroxides and, in the scarce cases of under-saturation with respect to those phases, the effect is very small.

The main mineral phase potentially responsible for the fracture clogging of the EDZ is generally calcite. The precipitated amounts for this mineral are generally between one and three orders of magnitude larger than the amounts of precipitated ferric phases. As a general trend, the largest amounts of precipitated ferric phases are predicted to take place in the scenarios of open repository conditions (i.e. equilibrium with atmospheric partial pressures of O<sub>2</sub>(g)). This can be attributed to the setting of oxidising redox conditions in which Fe(II) transforms into Fe(III) and precipitates. In contrast, under the reducing conditions present if closed repository conditions are assumed (pe values < -2.5) the predicted precipitation of ferric oxyhydroxides is smaller, increasing slightly if the temperature at repository depth is increased, which increases the oversaturation with respect to more crystalline and insoluble ferric phases (mainly goethite or hematite).

Under the assumption of geochemical equilibrium, the largest amounts of precipitated minerals are obtained for the mixtures of groundwaters from the repository depth with shallow infiltration waters.

A preliminary estimation of the effect of mineral precipitation on the hydraulic conductivity of the EDZ has been carried out. For most of the modelling cases, the estimated decrease of the hydraulic conductivity in ten years is smaller than 2%.

**Microbial** evaluation was used to identify the potential for microbial calcite and iron hydroxide formation during various repository conditions. The most important groundwater parameters for microorganisms, are pH and carbonate, ferrous iron, methane and the dissolved organic carbon (DOC) concentrations. The following cases were evaluated:

- The potential for microbial iron hydroxide production will be large in all groundwater with ferrous iron. The production will be significant as soon as the oxygen concentration rises above  $0.3 \text{ mg L}^{-1}$ . This will trigger an increase in the  $E_h$  towards the range where iron oxidation is favourable ( $> 100 \text{ mV}$ ). The potential for microbial calcite formation production will be large in all groundwater with high concentrations of DOC and methane, irrespective of oxygen,  $E_h$  or pH.
- Deep groundwater generally has less ferrous iron and DOC than intermediate and shallow groundwaters. It can, therefore, be assumed that the rate of microbial iron oxide and calcite formation will decrease, relative to the unchanged situation, except for cases where deep groundwater contains a high concentration of methane that mixes with a sulphate or oxygen rich groundwater.
- Shallow groundwater generally has more ferrous iron and DOC (and less methane) than intermediate (unchanged) groundwater. It can, therefore, be assumed that the rate of microbial iron oxide and calcite formation will increase in relation to the unchanged situation.
- The contamination explosives with nitrogen compounds will not influence the concentrations of ferrous iron, DOC or methane and the situation will, therefore, not change in relation to the unchanged situation.
- The increase in pH from cement grouting will not have a large effect on the microorganisms. However, observations made in tunnels elsewhere where low pH cement has been injected reveal vivid microbial growth and formation of up to 5 cm thick slime layers on the tunnel walls, the slime clogged water conducting fractures.
- There is no information available about the potential for microbial growth and activity at  $50^\circ\text{C}$  and  $100^\circ\text{C}$ . As a rule of thumb, biological processes double with every  $10^\circ\text{C}$  increase in temperature. Increasing temperature will then most probably speed up the bio-precipitating processes.

It is important to note that the calculations included in this report correspond to a preliminary assessment of the groundwater sealing potential. More sophisticated calculations are required in order to increase the accuracy of the modelling and especially to be able to quantify the effects from microbial sealing. Some of these improvements include the incorporation of mineral dissolution reactions able to increase the concentrations of dissolved elements, the evaluation of kinetic vs. equilibrium approaches to the dissolution/precipitation reactions, the refinement of the thermodynamic description of the cement and grout constitutive phases and the inclusion of more realistic recipes for the low-pH cement, and probably, the implementation of reactive transport models of the EDZ and its surroundings. Testing and developing a code for microbial modelling and moreover include more site-specific physical and hydraulic parameters from the repository geological system, such as porosities, permeabilities or fracture densities and width, are needed if more accurate results about fracture sealing are required.

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# 1 Introduction

## 1.1 Scope and objectives

One of the critical geochemical issues for repository safety in the short and medium terms is the disturbance created by the construction, operation and subsequent closure of the deep geological environment.

The Excavation Damaged Zone (EDZ) is of special interest since changes in this zone due to clogging or opening may change the flow situation in the repository. During the excavation/construction stage, the rock and groundwaters at repository depth will be exposed to open atmospheric conditions and this exposure will shift their redox character towards more oxidising conditions and will change their carbon content due to reequilibration with atmospheric partial pressures of CO<sub>2</sub>. Moreover, the excavation of underground galleries and the use of pumping will facilitate the access of dilute infiltration waters downwards and deep saline groundwaters upwards to the repository system. Furthermore, the dissolution of the cementitious material used for sealing and stabilizing mechanically the system will generate high-pH waters which can mix with the repository groundwaters. All these processes, which can also take place after the repository closure, will lead to geochemical disequilibria with respect to the original conditions.

Besides these processes, other geochemical changes are expected to occur when closing the repository. Firstly, the repository closure will lead to isolation with respect to atmospheric gases and to the recovery of reducing conditions. Secondly, the temperature will increase due to the thermal impact of spent nuclear fuel on the surrounding rock and this may also influence the hydrochemistry.

The aim of this report is to contribute to the understanding of the potential of fracture mineral/microbial clogging or dissolution of fracture material during prevailing and transient chemical and microbiological conditions based on data from Forsmark, Laxemar and Äspö, mainly to understand how these changes may affect an investigation programme for the EDZ.

Changes due to mixing, pressure and temperature differences, reducing/oxidising conditions, presence of construction materials such as cement and microbial sealing are simulated and discussed based on hydrogeochemical data and understanding from the repository depth at Forsmark and Laxemar. The discussion is based on simplified modelling which can only indicate the potential for fracture clogging/dissolution to occur under different conditions over the lifespan of the repository. Although an estimate of the amount of inorganic clogging is made, this modelling is preliminary and does not take into account the clogging effect from microbes. For more advanced modelling coupled modelling and newly developed models for microbial growth have to be employed but this was deemed to be outside the scope of this project.

Compilation of information and simplified modelling was conducted according to the following steps:

1. Identification of representative groundwater samples from repository depths at Laxemar and Forsmark.
2. Modelling and discussion of the potential for calcite and iron hydroxide and microbial sealing during prevailing conditions.
3. Modelling and discussion of the potential for calcite and iron hydroxide and microbial sealing and dissolution during open repository conditions (atmospheric pressure and oxidising conditions) by assuming: a) the groundwater composition is unchanged (except for E<sub>h</sub> and pH), b) a deep water is 50% mixed, c) a shallow water is 50% mixed, e) the pH is affected by a low-pH cement according to the discussion in SR-Can, and d) the groundwater is contaminated by nitrogen compounds (300 g/m<sup>3</sup> rock) from explosives.
4. Modelling of the temperature effects during emplacement and after closure. This was carried out in three steps: at 100°C, 50°C and at ambient temperature (i.e 15°C). The 100°C and 50°C cases are modelled by simulating closed repository conditions and the 15°C situation by assuming open repository conditions.

## 2 Hydrogeochemical data

For modelling purposes, several groundwaters were selected as hydrogeochemically representative for the repository depth both in Forsmark and in Laxemar (Table 2-1). The groundwater samples were collected in different boreholes at the target areas.

In the case of Forsmark, three different groundwater compositions have been selected as representative of the three main water types present at the planned repository depth; a brackish marine-type composition, a brackish composition from a fractured zone and a brackish composition from a deformation zone. For Laxemar, the two selected groundwater compositions represent a high-salinity and a low-salinity groundwater composition (Table 2-1).

In addition, a deep saline groundwater and a shallow infiltration groundwater have been added for each site in order to be able to perform the mixing calculations for up/down-coning as described in subsection 3.4.1.

The sampling and analytical protocols follow the SKB standard stated for the data in the SKB database SICADA. When possible, pH,  $E_h$  and temperatures were determined in the field. In cases where an accurate  $E_h$  determination was not available, the value of this parameter was approximated as determined by the  $SO_4^{2-}/S^{2-}$  redox couple. This modelling approach has proved to be adequate in earlier work associated with target area groundwaters /SKB 2007/. All the selected representative groundwaters for the repository depth display a slightly alkaline (pH values between 7.4 and 8.4) and reducing (pe below  $-2.50$  in all the cases) character (Table 2-1).

**Table 2-1. Description and analytical data for the repository depth groundwaters from Forsmark and Laxemar. The composition for the selected deep saline groundwater and shallow infiltration groundwater used for the modelling of up-coning and down-coning is also detailed.**

	Site	Description	Borehole	Sample ID	pH	pe	HCO <sub>3</sub>	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	Fe	Sr
Representative groundwaters at repository depth	Forsmark	Brackish marine type water	KFM02A	8016	8.40	-2.50	126	2,040	34.2	934	226	5,410	498	1,850	8.04
	Forsmark	Non-marine brackish waters from fractures	KFM01D	12343	8.30	-4.55	17.1	1,770	7.31	1,840	10.9	5,960	31.1	0.759	20.8
	Forsmark	Non-marine brackish waters from deformation zone	KFM08D	12818	8.10	-4.55	6.98	1,900	5.42	2,740	4.86	7,460	101	b.d.l.	29.3
	Laxemar	Low salinity water with glacial component	KLX03	10091	7.60	-4.72	189	791	5.51	234	10.8	1,390	127	0.435	4.84
	Laxemar	Brackish marine-type water	KLX15A	15008	7.42	-3.71	14.1	2,080	13.8	1,540	54	5,890	425	0.556	27.7
Groundwaters for mixing calculations	Forsmark	Shallow infiltration water	HFM09	8335	7.91	4.00	466	274	5.6	41.1	7.5	181	85.1	b.d.l.	0.38
	Forsmark	Deep saline water	KFM07A	8843	8.04	-4.42	7.36	2,780	13.5	5740	21.5	14,400	103	0.288	68.4
	Laxemar	Shallow infiltration water	HLX28	10231	8.17	4.00	265	110	2.97	11.2	3.6	23	35.8	0.079	0.14
	Laxemar	Deep saline water	KLX02	2731	7.90	-5.25	9	8,030	29	18,600	2.7	45,500	832	0.405	275

All the analytical values expressed in mg L<sup>-1</sup>

b.d.l.: below detection limit



## 3 Hydrogeochemical modelling

### 3.1 Aim of the modelling

The aim of the hydrogeochemical modelling is to address the key inorganic processes of interest to this project. Due to the disturbances caused by the repository excavation, construction, closure and post-closure, the saturation state of the groundwaters at repository depth with respect to several mineral phases may change and mineral precipitation reactions may take place. This implication is especially important for the stability and safety of the EDZ, since mineral precipitation may lead to sealing of the fractures.

### 3.2 Geochemical modelling approach

The geochemical calculations have been done using the PHREEQC computer code /Parkhurst and Appelo 1999/ in its interactive version 2.12.5.669 released on November 16 of 2005 and using the inbuilt thermodynamic database WATEQ4F.dat /Ball and Nordstrom 2001/.

In all the modelling cases assessed in this report, two sets of calculations have been carried out. Firstly, simple simulations were carried out to evaluate the effects of the induced disequilibria on the potential for mineral precipitation (saturation index calculations). Secondly, oversaturated mineral phases have been allowed to precipitate in order to evaluate the amount (and volume) of precipitating minerals and the associated changes in the groundwater hydrogeochemistry.

Within the range of conditions assessed in this report, the main mineral phases able to precipitate are calcite ( $\text{CaCO}_3$ ) and ferric oxyhydroxides. The precipitation of both mineral types has already been predicted in earlier modelling exercises carried out for the same areas /Domènech et al. 2006/. This has also been observed at field scale in Äspö HRL /SKB 2006/, where it is believed to cause a decrease of the overall water inflow of about  $\approx 4\%$  each year. The actual ferric phase included in the conceptual models depends on the temperature used for the calculations.

In the simulations carried out at  $15^\circ\text{C}$ , only amorphous iron oxyhydroxides (generically represented as  $\text{Fe}(\text{OH})_3(\text{a})$  in the WATEQ4F database) have been allowed to precipitate. For the precipitation of amorphous iron oxyhydroxides, a value of  $\log K$  of  $-5$  has been used, following the criterion proposed by /Nordstrom et al. 1990/. The precipitation of other more crystalline ferric phases, such as goethite ( $\text{FeOOH}$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) or other microcrystalline iron hydroxides, has not been allowed in the simulations because those phases are thought to form generally by recrystallisation of the amorphous iron oxy-hydroxides and not by direct precipitation at low temperatures /Cornell and Schwertmann 2003/.

For simplification, goethite has been the only iron oxyhydroxide allowed to precipitate in the simulations carried out at  $50^\circ\text{C}$  and  $100^\circ\text{C}$ , although hematite precipitation is also possible at  $100^\circ\text{C}$  under the simulated conditions /Cornell and Schwertmann 2003, and references therein/. In the light of the fast precipitation rates found in the literature for the mineral phases used in the models /Plummer et al. 1979, Langmuir 1997/ and by comparing to the timeframe of the rest of the considered processes, precipitation reactions have been considered to be in equilibrium.

The discussion below will be based on simplified modelling which can only indicate the potential for fracture sealing to occur under different expected conditions at the EDZ.

### 3.2.1 Ambient conditions

The speciation-solubility calculations for the ambient conditions (Table 3-1) indicate that the groundwaters are generally close to equilibrium with respect to calcite (except the sample 8016 from Forsmark, which is oversaturated) and subsaturated with respect to amorphous iron hydroxides, although oversaturated with respect to other ferric phases of higher crystallinity.

**Table 3-1. Summary of results for the geochemical calculations obtained for the selected groundwater compositions at Forsmark and Laxemar at temperature similar to present downhole conditions (15°C).**

S. I.									
Site	Sam- ple ID	Sample type	pH	Calcite (CaCO <sub>3</sub> )	Fe(OH) <sub>3</sub>	Hematite (Fe <sub>2</sub> O <sub>3</sub> )	Goethite (FeOOH)	log P <sub>CO2</sub>	log P <sub>O2</sub>
Forsmark	8016	Repository depth	8.40	1.32	-0.63	11.97	5.01	-3.6	-63.1
	12343	Repository depth	8.30	0.62	-3.33	6.57	2.30	-4.4	-71.7
	12818	Repository depth	8.10	0.15	-	-	-	-4.6	-72.5
Laxemar	10091	Repository depth	7.60	0.40	-5.72	1.78	-0.09	-2.5	-75.2
	15008	Repository depth	7.42	-0.35	-5.27	2.69	0.37	-3.5	-71.9
Forsmark	8335	Shallow infiltration water	7.91	0.48	-	-	-	-2.3	-39.1
	8843	Deep saline water	8.04	0.30	-4.44	4.36	1.20	-4.6	-72.2
Laxemar	10231	Shallow infiltration water	8.17	0.02	2.26	17.74	7.89	-2.8	-38.0
	2731	Deep saline water	7.90	0.64	-5.31	2.65	0.34	-4.6	-76.1

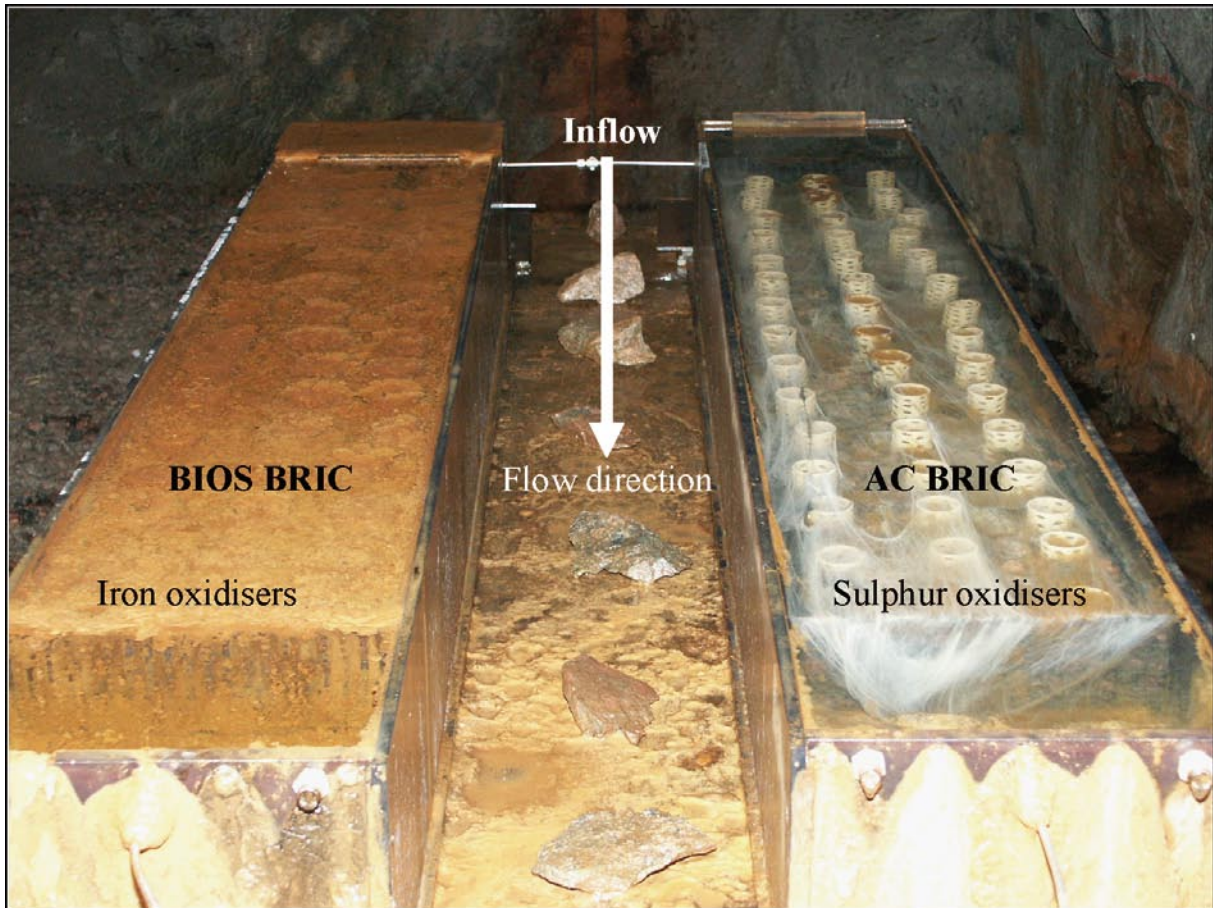
### 3.3 Microbial modelling approach

#### 3.3.1 Background on biological iron hydroxides and sulphur

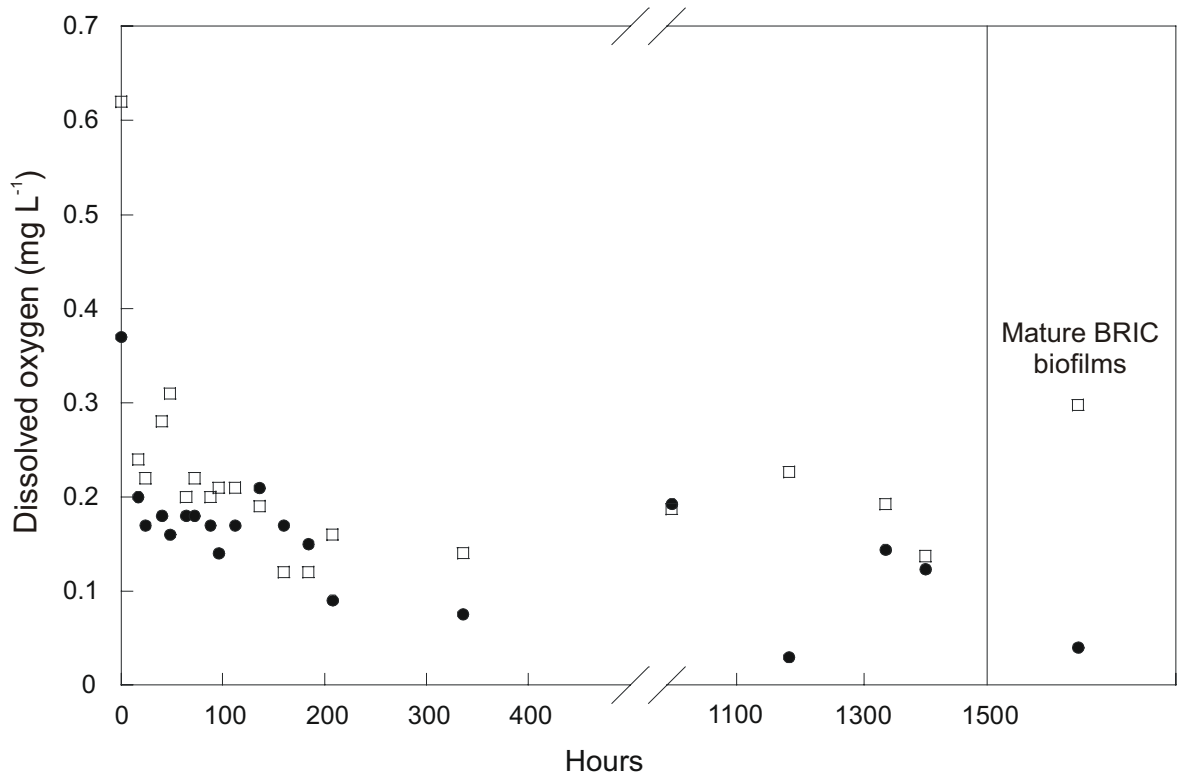
A large group of microbes catalyse the formation of iron oxides from dissolved ferrous iron in groundwater that reaches an oxidising environment /Ferris et al. 1999, 2000/. Such biological iron oxides (BIOS) will have a significant effect on the hydraulic conditions in fractures that open towards tunnels. Typically, microbes form stalks and sheaths that increase the volume of the iron oxides from densely packed inorganic oxides to a fluffy, rust-like material with water contents of up to 99%. The water content, the density of the BIOS and the formation rate are flow dependent /Pedersen and Hallbeck 1985/. The microbes then contribute to the exposure of a large oxide area to ferrous iron flowing with the groundwater and the organic biological material adds a strong oxidation capacity in the addition of iron oxides. The dominating organism in BIOS formation in tunnels is *Gallionella ferruginea*.

*Gallionella ferruginea* is an iron-oxidising chemolithotrophic microorganism that lives in low-oxygen conditions (0.1–1.5 mg l<sup>-1</sup> saturation) /Hallbeck and Pedersen 2005/. It can harvest energy from the oxidation of ferrous iron with oxygen concomitant with the fixation of carbon dioxide into organic cell components /Hallbeck and Pedersen 1990, 1991/. It produces a stalk structure from the concave side of the cell depending on population development, pH and redox conditions /Hallbeck and Pedersen 1990/. After *Gallionella* oxidises ferrous iron and bacteriogenic iron oxides (BIOS) precipitate on the stalk material. Over time, the stalks and/or the precipitated BIOS attenuate more ferrous iron as well as trace metals from surrounding groundwater /Hallbeck and Pedersen 1995, Anderson and Pedersen 2003, Anderson et al. 2006/.

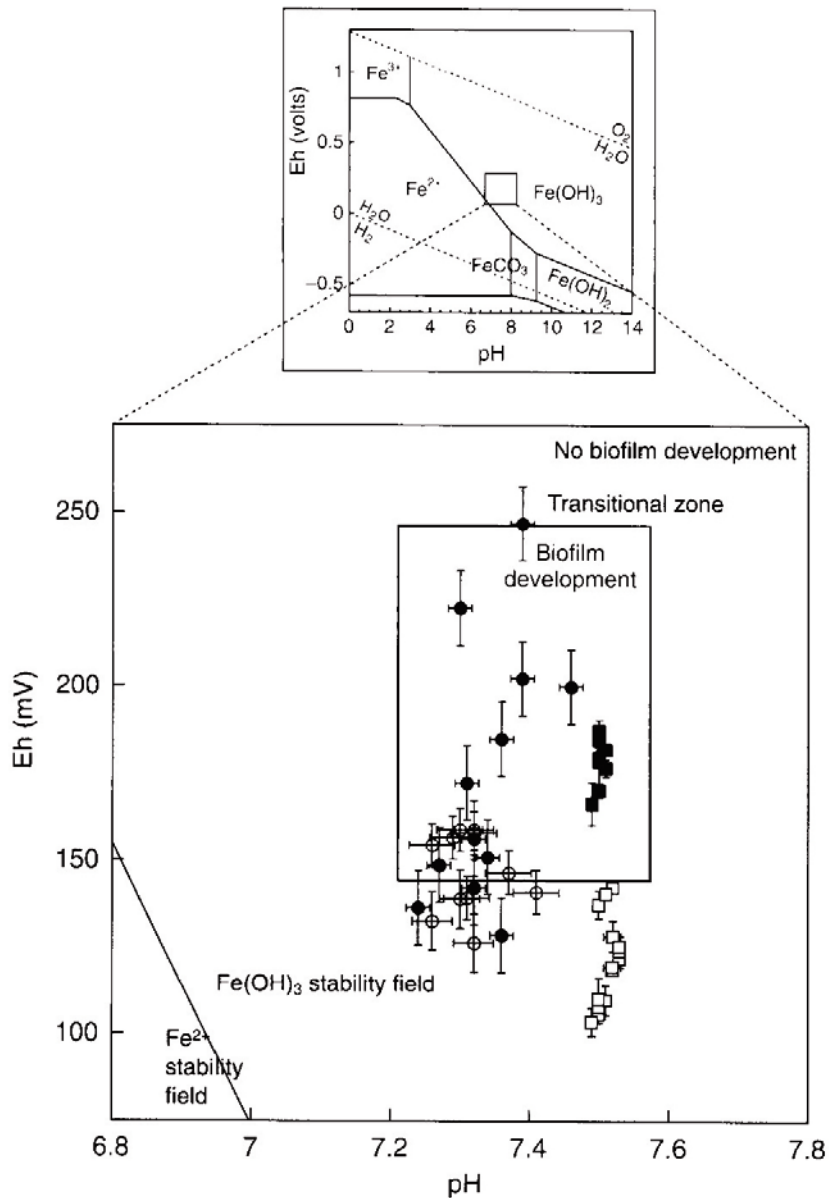
*Gallionella ferruginea* has been investigated *in situ* in the Äspö Hard Rock Laboratory (HRL) tunnel in a pond at 907 m tunnel length /Anderson and Pedersen 2003/ and subsequently in an artificial channel denoted BRIC (2,000 x 300 x 250 mm) using groundwater sourced from a borehole (KA2198A) situated 297 m below sea level (Figure 3-1). The relations between oxygen concentration, E<sub>h</sub>, and pH were first investigated in the 907 m pond and the BIOS and later in the BIOS channels at 297 m. It was found that BIOS formation was circumvented by ranges of oxygen concentration, pH and E<sub>h</sub> (Figures 3-3 and 3-4). The pH of the groundwater that formed BIOS was always between 7.4 and 7.7 with oxygen saturation between 0.3 and 1.5 mg l<sup>-1</sup> and E<sub>h</sub> between 100 and 200 mV. Values outside these ranges terminated prolific BIOS formation /Anderson and Pedersen 2003/. The initial development and diversity of an *in situ* subsurface microbial community producing BIOS was further investigated at the initiation of growth (2 month period) and after a 1 year period of undisturbed growth /Anderson et al. 2006/. Water chemistry data, samples of iron encrusted BIOS material and groundwater were collected from the BIOS channels. Comparisons between the BIOS channels and an anaerobic control (AC) channel (Figure 3-1) revealed that water mixing at the inflow leads to profuse development of BIOS related to a slightly elevated level of O<sub>2</sub> (up to 0.3 mg L<sup>-1</sup> at the transition zone between BIOS development and non-development) and elevated E<sub>h</sub> (> 100 mV) in the first 70 mm of water depth (Figure 3-2). When oxygen was below to 0.3 mg L<sup>-1</sup>, sulphur oxidizing bacteria, mainly *Thiothrix* sp proliferated. It became obvious that a succession of events may contribute to the sealing of fractures that are in contact with tunnel air. Both the iron oxidizers and the sulphur oxidizers produce biomass and precipitate iron oxides and sulphur, respectively, which will clog up the fractures, as a function of oxygen concentration, pH and E<sub>h</sub>.



**Figure 3-1.** The BRIC apparatuses installed at the 2,200 site in the Äspö hard rock laboratory tunnel. The BRIC on the left is the BIOS BRIC the BRIC on the right is the anaerobic control (AC) BRIC. Note the heavy growth of BIOS in the left channel. The BRICs are 2,000 mm long, 300 mm wide and 250 mm deep and are supplied with groundwater from a borehole that intersects a water conducting fracture behind the rock face (KA2198A). Note the prolific growth of sulphur oxidising bacteria within the AC BRIC and masses of iron oxide stained biomass in the BIOS BRIC. This figure represents 8 months of BIOS development. /Image from Anderson et al. 2006/.

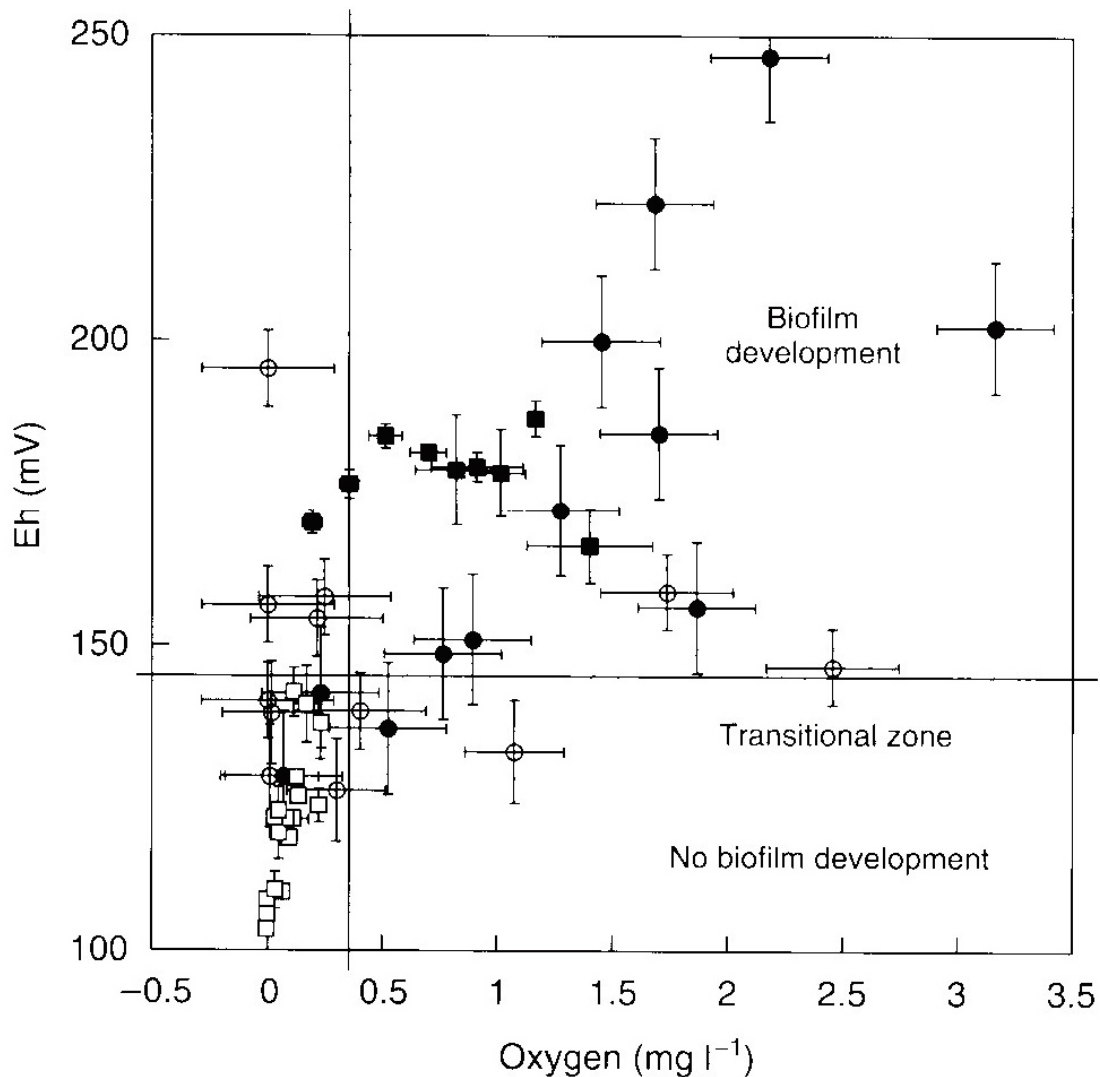


**Figure 3-2.** Dissolved oxygen decline at 70 mm depth over 2,000 hours (3 months) for the BIOS BRIC (□) and the AC BRIC (●). Mature BIOS sampled after 8,700 hours (1 year) indicates that the decrease in oxygen is preserved in the AC BRIC but oxygen levels in the BIOS BRIC can increase. /Image from Anderson et al. 2006/.



**Figure 3-3.** Measurements of the  $E_h$ -pH range for the 907 site and the BRICs at the 2,200 site. The base diagram is for the Fe-CO<sub>2</sub>-H<sub>2</sub>O system (12°C) /recalculated from Stumm and Morgan 1996/. Concentration of soluble Fe species = 10<sup>-5</sup> M and carbon C<sub>T</sub> = 10<sup>-3</sup> M. Error bars represent the standard error of the mean. Measurements are from the open BRIC with BIOS (biofilm) development (■), from both BRICs with no BIOS development (□), from the 907 site with BIOS development (●) and from the 907 site without BIOS development (○). /Image from Anderson and Pedersen 2003/.



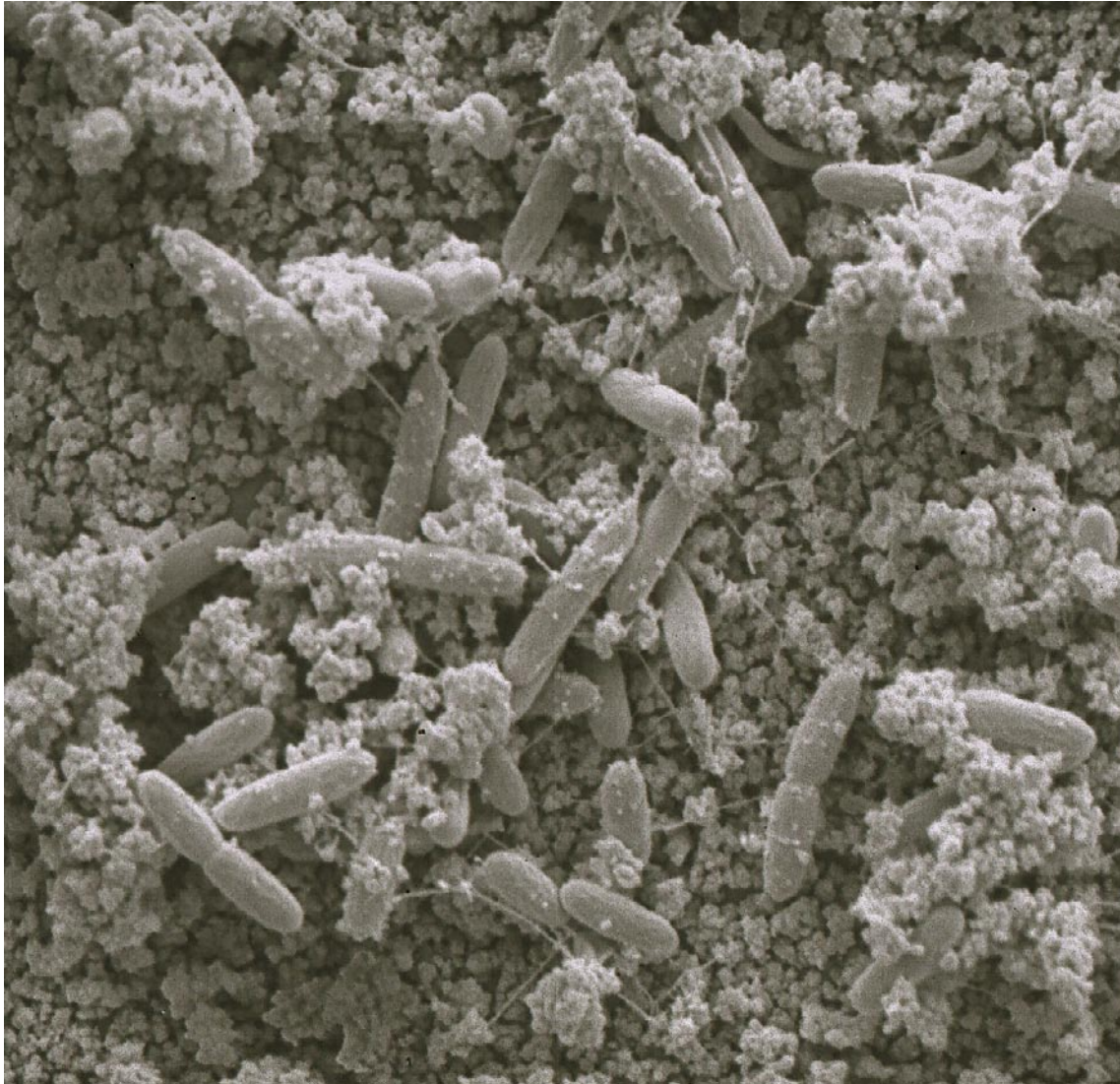


**Figure 3-4.** Redox measurements and oxygen limits for the 907 site and the BRICs from the 2,200 site. Error bars represent the standard error of the mean. Measurements are from the open BRIC with BIOS (biofilm) development (■), from both BRICs with no BIOS development (□), from the 907 site with BIOS development (●) and from the 907 site without BIOS development (○). /Image from Anderson and Pedersen 2003/.

### 3.3.2 Background on microbes and calcite

The effect from microorganisms on calcite formation is mainly due to their production of carbon dioxide during degradation of organic material and oxidation of methane. Observations from the Äspö HRL tunnel suggest that this effect can be significant as judged from heavy calcite formation in the tunnel boreholes SA813B (Figure 3-5) and SA923B /Pedersen et al. 1996/. These boreholes were influenced by intrusion of Baltic sea water with high chloride and sulphate concentrations. They also had carbonate concentrations that were very high. It was assumed that this carbonate originated from biological processes encompassing the degradation of organic carbon from shallow groundwater and sea floor sediments.

The effect of microorganisms on calcite formation will depend on the load of organic carbon and on pressure and temperature. Calcite will form along decreasing pressure gradients in fractures that reach the tunnel. Microorganisms will form biofilms (Figure 3-5) and contribute to the precipitation of calcites by production of carbon dioxides and also by acting as initiation and nucleation sites for the calcite precipitation.



*Figure 3-5. SEM images of attached bacteria in groundwater from SA813B in the Äspö hard rock laboratory tunnel (Image from Pedersen et al. 1996). Amorphous calcites are clearly visible together with growing bacteria.*

### **3.4 Results of the modelling**

#### **3.4.1 Results of the geochemical modelling**

The following modelling cases have been evaluated:

- Case 1: the only change with respect to present conditions is a variation of temperature at depth to 50°C and 100°C.
- Case 2: the present groundwater composition at depth is altered by changing the pressure to atmospheric pressure.
- Case 3: saline water is mixed with the present groundwaters to simulate up-coning.
- Case 4: a shallow non-saline water is mixed with the present groundwaters to simulate down-coning.
- Case 5: the groundwater composition at repository depth is affected by the dissolution of the cementitious material used for sealing and grouting.

Moreover, the effect of variable temperature (up to 100°C) on most of the modelled processes is also discussed below.



### Geochemical modelling case 1: Temperature increase in the repository area

Under present conditions, the undisturbed rock temperature at repository depth is around 11°C and 14°C at the Forsmark and Laxemar sites respectively. However, this temperature will increase throughout the years following the repository construction as a consequence of the thermal impact of the residual radioactivity of the deposited spent fuel /SKB 2006 and references therein/. As shown in Figure 3-6, this will alter the temperature of the engineering barriers and the rock wall for thousands of years.

With the aim of assessing the potential for mineral precipitation to occur due to the expected temperature increase in the near field, geochemical calculations by changing the temperature of the selected waters to 50°C and 100°C were carried out. Closed repository conditions were assumed in all the simulations (i.e. equilibrium with atmospheric gas pressures was not allowed).

The main results obtained for this modelling case are summarised in Table 3-2. As expected (calcite solubility decreases with temperature /e.g. Langmuir 1997/, all the representative groundwaters reach oversaturation with respect to calcite with the temperature increase (except the Laxemar sample 15008 at 50°C). Consequently, calcite precipitation is thermodynamically favoured in most cases. All the studied groundwater compositions are also oversaturated with respect to goethite and hematite.

As listed in Table 3-2, the precipitation of calcite and goethite up to equilibrium with respect to these phases would lead to a decrease of up to one unit in the pH of the groundwaters at repository depth. With regard to the redox conditions, all the repository groundwaters display pe values are very similar to their values at the original conditions (between -3.5 and -4.5).

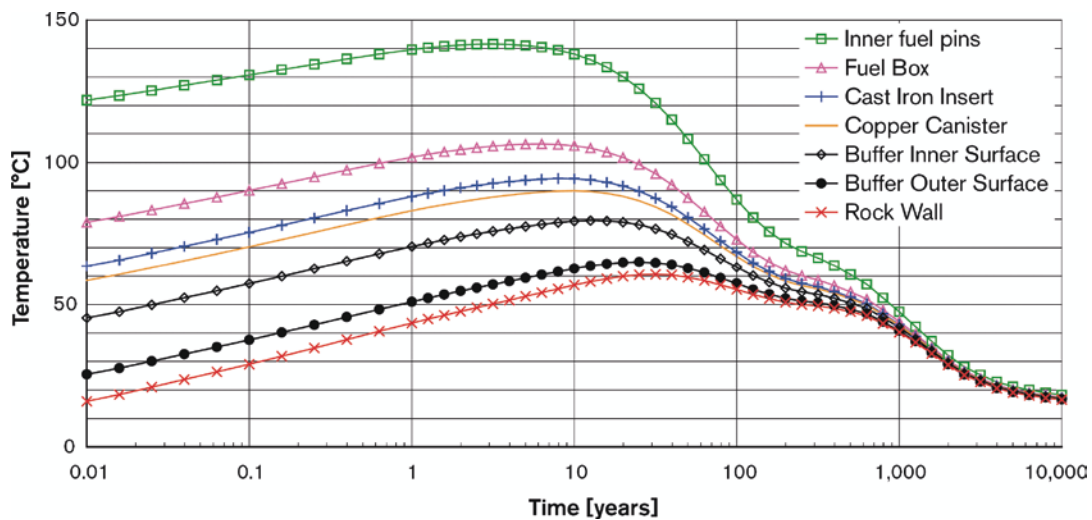


Figure 3-6. Calculated thermal evolution in different parts of the repository near field at Forsmark (SKB 2006).

**Table 3-2. Summary of results for the geochemical calculations obtained for the groundwaters at repository depth in Forsmark and Laxemar for the modelling case number 1 (temperature increase 50°C and 100°C).**

MODELLING CASE 1: TEMPERATURE INCREASE											
T (°C)	Site	Sample ID	S. I. (before mineral precipitation)			Calcite (CaCO <sub>3</sub> )	Amorphous Fe(OH) <sub>3</sub>	Hematite (Fe <sub>2</sub> O <sub>3</sub> )	Goethite (FeOOH)	log P <sub>CO2</sub>	log P <sub>O2</sub>
			pH initial <sup>(1)</sup>	pH final <sup>(2)</sup>	pe final <sup>(2)</sup>						
50	Forsmark	8016	7.88	6.78	-3.51	1.23	-2.67	10.42	4.15	-2.9	-58.9
		12343	7.76	7.26	-4.18	0.49	-3.76	8.25	3.07	-3.6	-60.8
		12818	7.57	7.54	-3.78	0.03	-	-	-	-3.9	-60.4
	Laxemar	10091	7.38	6.87	-3.58	0.62	-4.62	6.51	2.20	-2.0	-60.8
		15008	7.14	6.89	-3.59	-0.21	-4.86	6.04	1.96	-3.0	-59.7
100	Forsmark	8016	7.37	6.43	-3.85	1.22	-4.15	10.26	3.99	-2.0	-51.4
		12343	7.23	6.83	-4.41	0.46	-4.81	8.94	3.33	-2.8	-51.5
		12818	7.06	7.06	-3.66	0.01	-	-	-	-3.0	-49.5
	Laxemar	10091	7.28	6.53	-3.91	1.05	-4.78	8.99	3.35	-1.6	-51.4
		15008	6.91	6.78	-4.19	0.04	-5.32	7.91	2.81	-2.5	-50.6

<sup>(1)</sup>pH before allowing mineral precipitation.

<sup>(2)</sup>pH and pe after mineral precipitation (CaCO<sub>3</sub> + Fe(OH)<sub>3</sub> or FeOOH).

-: Saturation Index not calculated, sample without initial measurable dissolved iron.

### **Geochemical modelling case 2: Exposure of groundwaters to open atmospheric conditions**

Together with the temperature increase, this case represents a scenario that would certainly take place in both sites during the repository excavation/construction. During open repository conditions, groundwaters at repository depth come into contact with atmospheric pressure of oxygen and carbon dioxide and generally dissolve up to equilibrium, producing a shift towards more oxidising and acidic conditions.

For this modelling case, the groundwater compositions considered as representative of the repository depth for Forsmark and Laxemar have been equilibrated with atmospheric partial pressures of carbon dioxide (10<sup>-3.5</sup> atm) and oxygen (10<sup>-0.7</sup> atm).

The resulting saturation state of the selected groundwaters with respect to several relevant mineral phases is shown in Table 3-3. In the Forsmark case, the groundwaters were initially in equilibrium with a partial pressure of CO<sub>2</sub>(g) lower than the atmospheric value (Table 3-2). Therefore, the opening of the system to atmospheric conditions allows CO<sub>2</sub>(g) to dissolve to equilibrium, which decreases the pH and shifts the waters towards subsaturation with respect to calcite (except for sample 8016).

In contrast to Forsmark, the Laxemar representative groundwaters were initially in equilibrium with partial pressures of CO<sub>2</sub>(g) higher (sample 10091) or similar (sample 15008) to the atmosphere (Table 3-2). Thus, the opening of the system to atmospheric pressures of CO<sub>2</sub>(g) would produce a loss of dissolved CO<sub>2</sub>(g) from sample 10091, with the corresponding pH increase and calcite oversaturation and precipitation. On the contrary, the exposure to atmospheric CO<sub>2</sub>(g) pressure would not affect the values of those parameters for sample 15008.

As can be deduced from the comparison of the initial hydrogeochemistry of the waters with the calculations in Table 3-3, the exposure to open atmospheric conditions would cause a shift in the redox character of the groundwaters from clearly reducing under the initial conditions (pe values between -2.5 and -4.5) to very oxidising (with a corresponding pe value around 14). This variation leads to the oxidation of the Fe initially present in the studied groundwaters as Fe(II) to Fe(III), increasing the oversaturation with respect to goethite and hematite and leading to oversaturation with respect to amorphous ferric oxyhydroxide. Therefore, the precipitation of ferric oxyhydroxides is thermodynamically favoured under these conditions.

**Table 3-3. Summary of results of the geochemical calculations obtained for the representative groundwaters at repository depths in Forsmark and Laxemar for modelling case number 2 (repository in equilibrium with open atmosphere).**

MODELLING CASE 2: OPEN REPOSITORY									
S. I. (before mineral precipitation)									
T (°C)	Site	Sample ID	pH initial (1)	pH final (2)	pe final (2)	Calcite (CaCO <sub>3</sub> )	Amorphous Fe(OH) <sub>3</sub>	Hematite (Fe <sub>2</sub> O <sub>3</sub> )	Goethite (FeOOH)
15	Forsmark	8016	8.31	7.70	13.80	1.22	3.65	20.53	9.28
		12343	7.46	7.45	14.05	-0.17	3.14	19.51	8.78
		12818	7.09	7.09	14.41	-0.78	–	–	–
	Laxemar	10091	8.59	7.97	13.53	1.32	2.97	19.17	8.60
		15008	7.39	7.39	14.11	-0.40	2.98	19.20	8.62

(1) pH before allowing mineral precipitation.

(2) pH and pe after mineral precipitation (CaCO<sub>3</sub>+Fe(OH)<sub>3</sub>).

–: Saturation Index not calculated, sample without initial measurable dissolved iron.

### **Geochemical modelling case 3: Mixing with deep saline groundwaters**

Mixing of the groundwaters from repository depth with more saline and deeper groundwaters may take place as a consequence of the groundwater inflow into open tunnel sections. This phenomenon, commonly termed as up-coning has been observed in some boreholes at Äspö /SKB 2006 and references therein/. The interaction of repository groundwaters with more saline solutions may lead to mineral dissolution and precipitation.

In order to assess the potential for mineral precipitation or dissolution under these conditions, the mixing of equal proportions of deep saline groundwaters (groundwater samples 8843 and 2731 for Forsmark and Laxemar respectively) and the repository groundwaters for each site was simulated. The most probable scenario for upconing in the short and medium terms corresponds to the excavation/construction stage, which has been conceptualized by assuming a temperature of 15°C and open repository conditions. Once the repository has been backfilled and closed, it is expected that groundwater inflow to the tunnels will almost cease and that saline waters that had moved upwards will sink due to their higher density. However, the potential for mineral precipitation subsequent to up-coning of deep saline groundwaters in a post-closure scenario has also been evaluated at 50°C and 100°C.

The results obtained in the simulations are summarized in Table 3-4. The saturation states of the groundwaters with respect to calcite and iron oxyhydroxides are very similar to the values obtained when using the same temperatures for the modelling case in open repository conditions (at temperature of 15°C) and with simple temperature increases simulating closed repository conditions (at temperatures of 50°C and 100°C).

As displayed in Table 3-4, most of the groundwaters resulting from mixing are near equilibrium or oversaturated with respect to calcite. At 15°C, the open repository conditions lead to Fe (II) oxidation and oversaturation with respect to all the included ferric oxyhydroxides whereas at 50°C and 100°C only crystalline ferric phases reach oversaturation. Therefore, mineral precipitation reactions of different types are thermodynamically favoured in all the groundwater mixtures.

The pH value of the mixtures after reequilibration with the corresponding mineral phases is generally similar or slightly lower than the initial pH. Regarding the redox conditions, two different situations can be identified (Table 3-4); in the modelling cases considering open repository conditions they determine very oxidising pe values (around 14), whereas in closed repository conditions the groundwater mixtures preserve the reducing character of the groundwaters representative from repository depth (Table 2-1).

**Table 3-4. Summary of results for the geochemical calculations obtained for the repository groundwaters for Forsmark and Laxemar simulating three temperatures (15°C, 50°C and 100°C) for modelling case number 3 (mixing of representative groundwaters with equal amounts of deep saline water).**

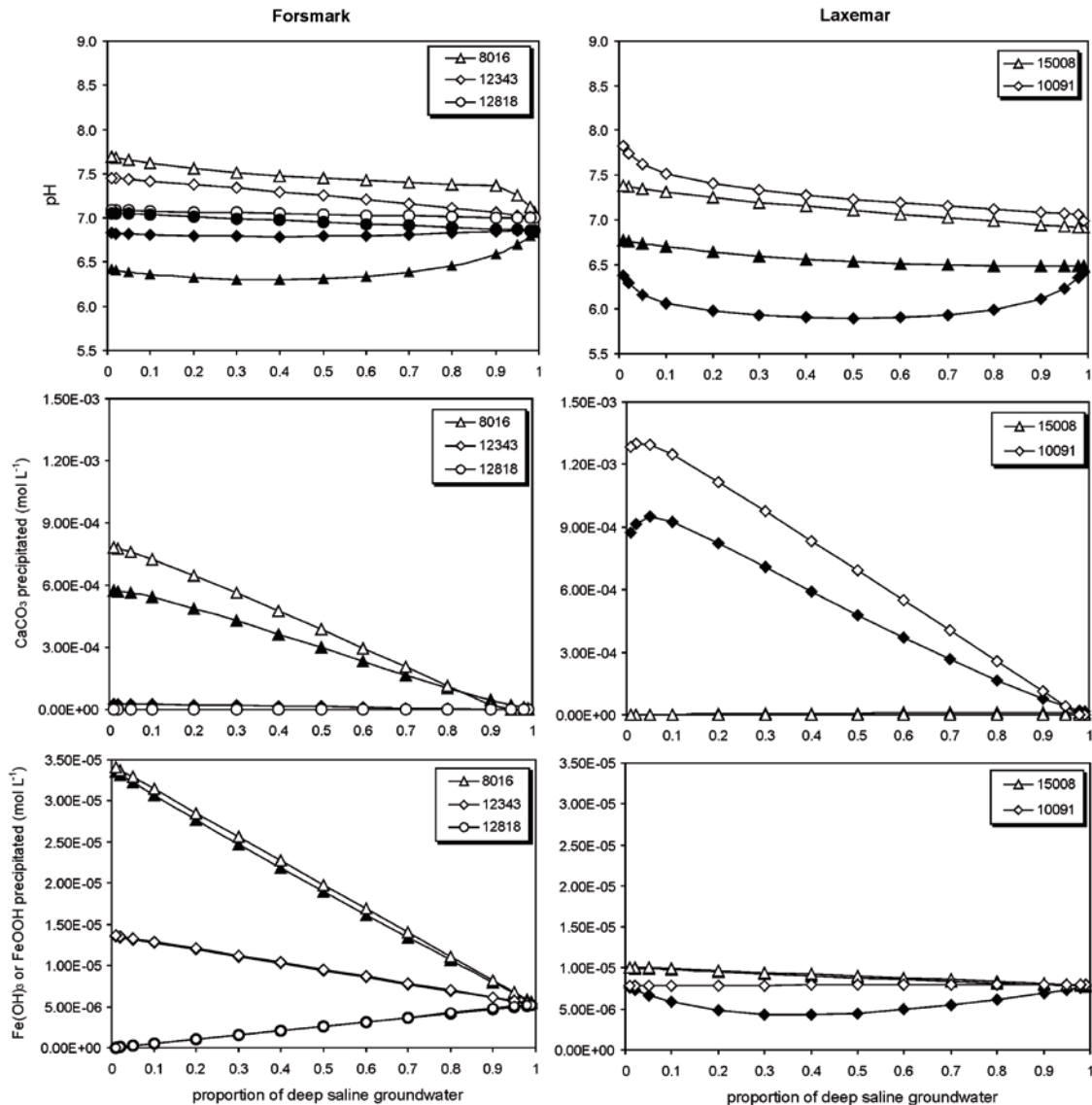
MODELLING CASE 3: MIXING 1:1 WITH DEEP SALINE GROUNDWATERS									
S. I. (before mineral precipitation)									
T (°C)	Site	Sample ID	pH initial <sup>(1)</sup>	pH final <sup>(2)</sup>	pe final <sup>(2)</sup>	Calcite (CaCO <sub>3</sub> )	Amorphous Fe(OH) <sub>3</sub>	Hematite (Fe <sub>2</sub> O <sub>3</sub> )	Goethite (FeOOH)
15	Forsmark	8016	7.97	7.45	14.05	1.05	3.42	20.07	9.05
		12343	7.26	7.25	14.25	-0.31	2.90	19.04	8.54
		12818	7.04	7.04	14.46	-0.71	2.23	17.69	7.87
	Laxemar	10091	7.99	7.23	14.28	1.53	3.08	19.40	8.72
		15008	7.12	7.10	14.40	-0.19	2.85	18.95	8.49
50	Forsmark	8016	7.66	6.65	-3.38	1.13	-2.96	9.85	3.87
		12343	7.62	7.22	-4.09	0.39	-4.16	7.44	2.66
		12818	7.54	7.41	-4.21	0.11	-4.86	6.06	1.97
	Laxemar	10091	6.90	6.19	-2.39	0.89	-5.68	4.42	1.15
		15008	7.12	6.82	-3.53	0.18	-5.15	5.48	1.68
100	Forsmark	8016	7.19	6.31	-3.73	1.13	-4.69	9.19	3.45
		12343	7.10	6.79	-4.32	0.35	-5.15	8.27	2.99
		12818	7.02	6.95	-4.41	0.06	-5.71	7.15	2.43
	Laxemar	10091	6.74	5.90	-3.16	1.18	-5.87	6.84	2.27
		15008	6.79	6.53	-3.93	0.29	-5.67	7.23	2.47

<sup>(1)</sup> pH before allowing mineral precipitation.

<sup>(2)</sup> pH after mineral precipitation (CaCO<sub>3</sub>+Fe(OH)<sub>3</sub> or FeOOH).

In addition to these simulations, geochemical calculations to evaluate the extent of mineral precipitation reactions linked to the whole range of mixing proportions between the repository depth groundwaters and the corresponding deep saline groundwaters for each site were carried out. The final pH and the precipitated amounts of calcite and ferric oxyhydroxides were estimated for the mixtures at 15°C simulating open repository conditions and at 100°C simulating closed repository conditions. These two scenarios represent two extreme situations in the expected geochemical repository evolution. The results of these calculations are shown in Figure 3-7.

The final pH values at each temperature, after mixing and precipitating the corresponding oversaturated minerals for each mixture, are very similar for the whole range of mixing proportions with deep saline groundwaters. As shown in Figure 3-7, there is some precipitation of calcite and ferric phases even in the pure extreme terms owing to the simple opening to atmospheric conditions (at 15°C) or to the increase of temperature (in the simulations at 100°C). As a general trend, the amounts of precipitated calcite and ferric minerals are similar (same order of magnitude) in the Forsmark and Laxemar groundwaters. Even though the deep saline groundwaters have higher calcium concentrations than the groundwaters at repository depth for both sites (Table 2-1), the highest amounts of precipitated calcite correspond to the lowest proportions of deep saline groundwaters in the mixtures (Figure 3-7). This behaviour can be attributed to the low carbon content of the deep saline groundwater, whose effect on lowering the saturation indexes for calcite exceeds the reverse effect of high calcium concentrations. In fact, the highest amounts of precipitated calcite correspond to the groundwater samples with highest carbonate alkalinity (and thus the highest carbon content) from each site: i.e. samples 8016 and 10091, from Forsmark and Laxemar respectively (Table 2-1).



**Figure 3-7.** Final pH and calculated amounts of precipitated minerals after mixing different proportions of repository groundwater with the corresponding deep saline groundwaters from Forsmark and Laxemar. Open symbols correspond to results at 15°C simulating open repository and solid symbols represent the results at 100°C simulating closed repository conditions.

#### **Geochemical modelling case 4: Mixing with shallow and non-saline groundwaters**

Even with moderate inflows to the open tunnels, large amounts of shallow waters are predicted to percolate throughout the excavation/construction phase. Infiltrating waters will initially be equilibrated with the atmospheric oxygen and carbon dioxide. After the repository closure, it is generally assumed that microbial activity in the overburden and in the first metres of rock will consume the dissolved oxygen in these waters (SKB 2006). However, the existence of open tunnels during the excavation/operation phase may create preferential flow paths for the oxygenated and shallow infiltrating waters.

As for the mixing with saline groundwaters, the most probable scenario of mixing with shallow infiltrating waters in the short and medium terms corresponds to the excavation/construction stage. This scenario has been conceptualized in the calculations by assuming a temperature of 15°C and open repository conditions. However, the potential for mineral precipitation subsequent to mixing with shallow infiltrating groundwaters in a post-closure scenario has also been evaluated at 50°C and 100°C.

As can be observed in Table 3-5, all the groundwaters resulting from mixing are clearly oversaturated with respect to calcite and to the target ferric oxyhydroxides in each temperature case (Fe(OH)<sub>3</sub> at 15°C and FeOOH/Fe<sub>2</sub>O<sub>3</sub> at 50°C and 100°C). Therefore, mineral precipitation reactions are thermodynamically favoured in all the cases.

As also shown in Table 3-5, if these precipitation reactions are allowed to take place they lead to a pH decrease of almost one pH unit. In analogy with the behaviour of the mixtures with deep saline groundwater, the groundwater mixtures with shallow water preserve the reducing character of the original repository groundwaters (pe values between -2.4 and -4) whenever closed repository conditions are assumed, whereas open repository conditions lead to very oxidising groundwaters (Table 3-5).

Similarly the calculations for mixing with deep saline waters, the final pH and precipitated mineral amounts were also evaluated for the whole range of mixing proportions between shallow infiltration groundwaters and repository groundwaters from Forsmark and Laxemar, at 15°C and 100°C and for open and closed repository conditions (respectively). The results are summarised in Figure 3-8.

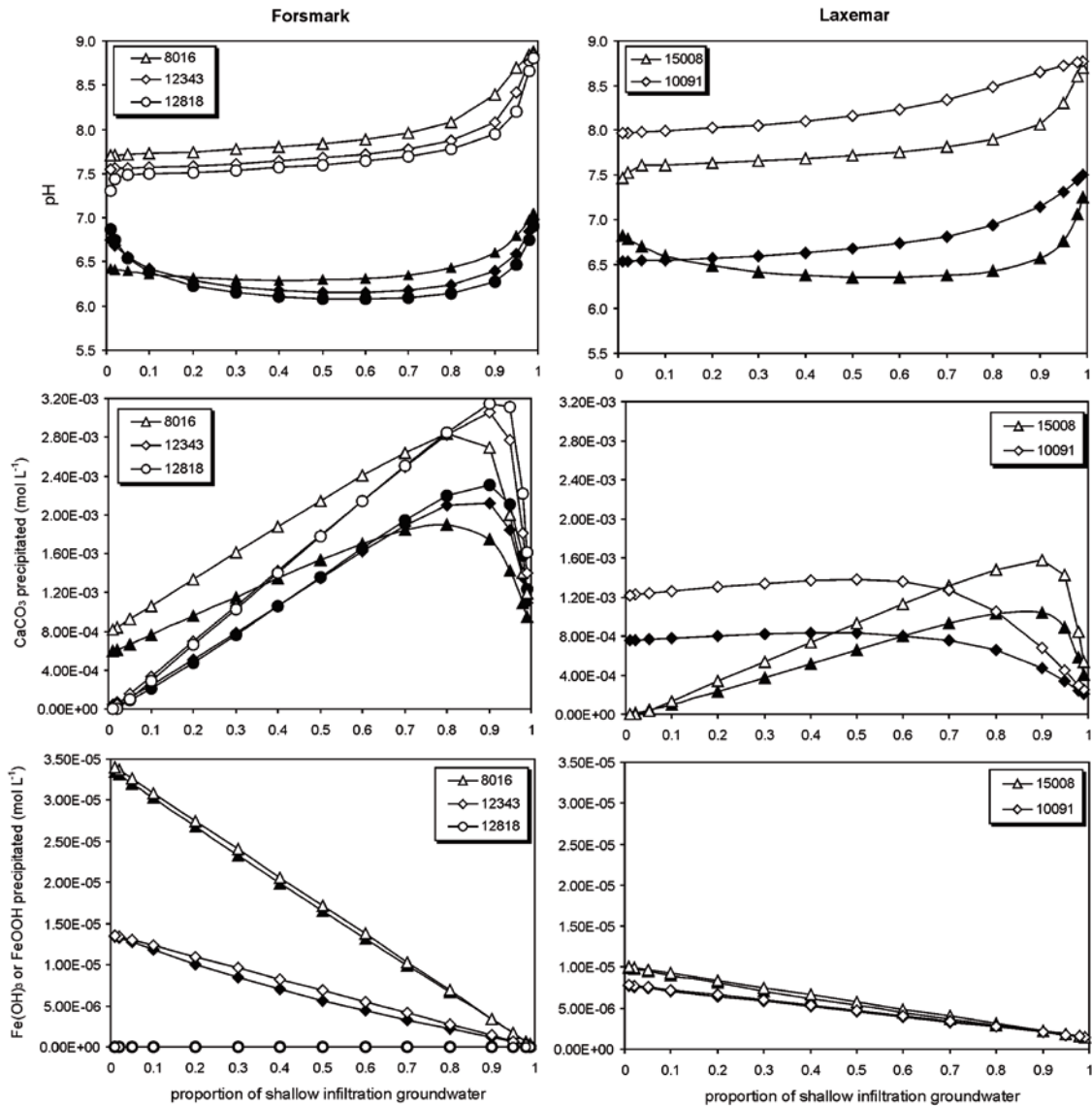
**Table 3-5. Summary of results for the geochemical calculations obtained for the repository groundwaters at Forsmark and Laxemar using three temperatures (15°C, 50°C and 100°C) for modelling case number 4 (mixing of repository groundwaters with equal amounts of shallow infiltration groundwaters).**

MODELLING CASE 4: MIXING 1:1 WITH SHALLOW INFILTRATION GROUNDWATERS									
S. I. (before mineral precipitation)									
T (°C)	Site	Sample ID	pH initial <sup>(1)</sup>	pH final <sup>(2)</sup>	pe final <sup>(2)</sup>	Calcite (CaCO <sub>3</sub> )	Amorphous Fe(OH) <sub>3</sub>	Hematite (Fe <sub>2</sub> O <sub>3</sub> )	Goethite (FeOOH)
15	Forsmark	8016	8.69	7.84	13.66	1.77	3.28	19.80	8.92
		12343	8.59	7.67	13.83	1.85	2.91	19.05	8.54
		12818	8.55	7.60	13.90	1.91	–	–	–
	Laxemar	10091	8.70	8.16	13.34	1.31	2.72	18.67	8.35
		15008	8.40	7.71	13.79	1.38	2.86	18.95	8.49
50	Forsmark	8016	7.56	6.60	-3.27	1.17	-2.95	9.85	3.87
		12343	7.39	6.45	-3.00	1.18	-4.58	6.61	2.24
		12818	7.32	6.37	-2.41	1.21	–	–	–
	Laxemar	10091	7.59	7.01	-3.71	0.71	-0.08	15.60	6.74
		15008	7.45	6.68	-3.29	0.92	-0.08	15.60	6.74
100	Forsmark	8016	7.31	6.29	-3.66	1.43	-4.46	9.63	3.67
		12343	7.19	6.16	-3.53	1.48	-5.05	8.46	3.09
		12818	7.12	6.08	-2.52	1.51	–	–	–
	Laxemar	10091	7.44	6.67	-4.05	1.10	-2.38	13.78	5.75
		15008	7.22	6.35	-3.67	1.20	-2.35	13.86	5.79

<sup>(1)</sup> pH before allowing mineral precipitation.

<sup>(2)</sup> pH after mineral precipitation (CaCO<sub>3</sub>+Fe(OH)<sub>3</sub> or FeOOH).

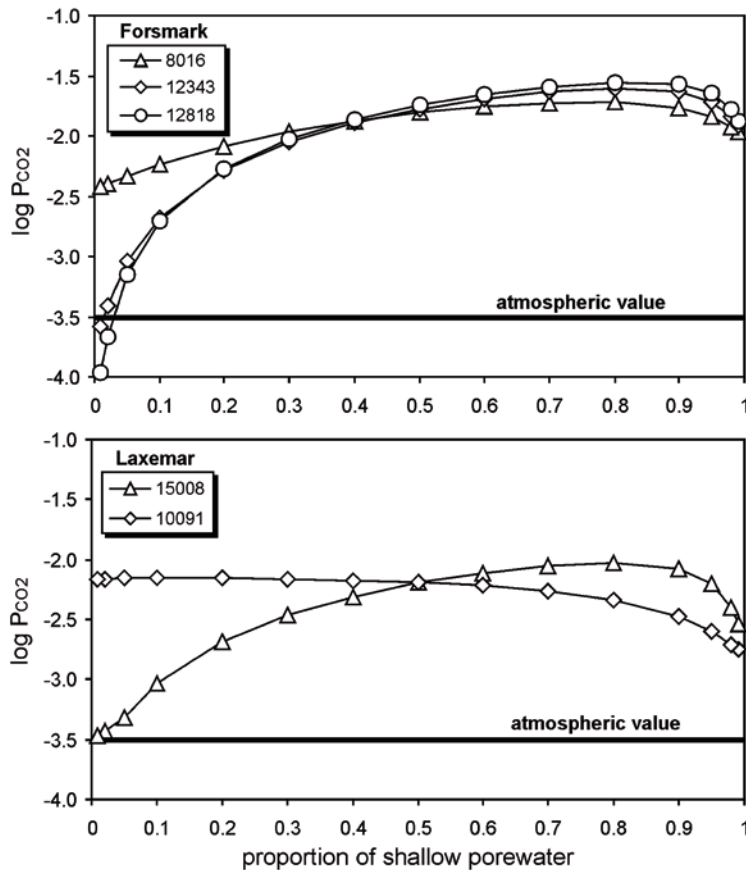




**Figure 3-8.** Final pH and calculated amounts of precipitated minerals after mixing different proportions of repository groundwater and the corresponding shallow infiltration groundwaters for Forsmark and Laxemar. Open symbols correspond to results at 15°C and in open repository and solid symbols represent the results at 100°C and in closed repository conditions.

As already explained for the calculations for mixing with deep saline waters, there is some mineral precipitation even in the pure extreme terms owing to the simple opening to atmospheric conditions or temperature increase (Figure 3-8). As displayed in Figure 3-8, the final pH values at each temperature are very similar for the whole range of mixing proportions used for all the samples. It is noteworthy that the final pH for the waters with the highest proportions of shallow groundwaters at 15°C and under open repository conditions is higher than the pH value for the initial waters. This behaviour can be explained by the loss of dissolved  $\text{CO}_2$  from the mixtures during reequilibration, with the subsequently imposed atmospheric conditions, which imply lower partial pressures of  $\text{CO}_2$ . This explanation is graphically shown in Figure 3-9, which displays the calculated partial pressure of  $\text{CO}_2$  in equilibrium with the whole range of mixing proportions between repository depth groundwaters and shallow infiltration groundwaters from Forsmark and Laxemar, at 15°C and before reequilibrating with atmospheric  $\text{CO}_2$ .

With regard to mineral precipitation reactions, the amounts of precipitated calcite and ferric phases are similar at both sites (Figure 3-8) and in the same order of magnitude than for the mixtures with deep saline groundwaters (Figure 3-7). Since the shallow infiltration waters for both sites are almost iron-free (Table 2-1), the higher the shallow water proportion in the mixtures, the lower the amount of precipitated ferric oxyhydroxides. In contrast, the amounts of precipitated calcite are generally higher for the mixtures with high proportion of shallow infiltration waters, peaking around 90% proportion of shallow waters (Figure 3-8). This behaviour can be attributed to the high carbonate alkalinity in the shallow infiltration groundwater compared with the groundwaters at repository depth (Table 2-1).



**Figure 3-9.**  $\log P_{CO_2}$  after mixing of repository groundwaters and shallow infiltration groundwaters for Forsmark and Laxemar, at 15°C and before equilibrating with atmospheric  $CO_2$  partial pressures.

### **Geochemical modelling case 5: Dissolution of cementitious material used for sealing and grouting**

Grouting and shotcreting are techniques used for mechanically stabilizing the system and to avoid the inflow of water to the tunnels /Luna et al. 2006/. Both techniques are necessary to minimize the meteoric water influx and the corresponding up-coning of saline waters as well as for construction purposes. Limited amounts of grouting will likely be needed at Forsmark, whereas for Laxemar, substantial amounts will probably be required /SKB 2006 and references therein/. The distribution of concrete in the repository will be spatially limited and its potential impact during the excavation and operational phases will be restricted. /SKB 2006/. Most of the leaking porewaters from these materials will be mixed with groundwater infiltrating into the tunnel and will therefore be pumped to the surface.

Cement-based grouts on the other hand have chemical properties quite different from the surrounding rock, and their effects have to be studied. Standard Portland cement paste has been traditionally applied for grouting and sealing when excavating tunnels. One of the main drawbacks



of using Portland-based cements is that porewaters resulting from their dissolution are highly alkaline (pH  $\approx$  12.5) and may have detrimental effects on the rest of the engineering barriers in the near-field (mainly on the bentonite clay). In order to avoid such detrimental effects from porewater diffusing out of the cement matrix, cement recipes with porewaters having pH  $\leq$  11 are being developed. The final recipe for the low-pH grout has not been decided yet, but it will possibly be based on Portland cement and silica fume /Luna et al. 2006 and references therein/.

In order to assess the effects of grouting dissolution on mineral dissolution and precipitation in the EDZ, the mixing of different proportions of porewaters after interaction with cement and the chosen repository groundwaters was simulated. For the calculations, it was assumed that cement and grouting porewater corresponded to the composition of each one of the repository groundwaters from each site (Forsmark and Laxemar) after equilibrium with Jennite ( $\text{Ca}_9\text{H}_2\text{Si}_6\text{O}_{18}(\text{OH})_8 \cdot 6\text{H}_2\text{O}$ ). This mineral is the only CSH cement component leading to a pH of around 11 in equilibrium with the selected Forsmark and Laxemar groundwaters and it has also been used in earlier calculations for the same area /Luna et al. 2006/.

For Jennite, the following reaction and equilibrium constant has been used /after Trotignon et al. 2006/:



The whole range of mixing proportions between representative groundwaters and cement degradation groundwaters has been included in the geochemical calculations. Since thermodynamic data for Jennite at different temperatures are not available, all the simulations have been carried out at 15°C. Both open and closed repository conditions have been taken into account in the calculations. After Jennite has been dissolved to equilibrium, the precipitation of calcite and  $\text{Fe}(\text{OH})_3(\text{a})$  in the cement porewaters has been allowed in all the simulations before mixing with the repository groundwaters (and before exposing the mixtures to open atmospheric conditions in the corresponding simulations) whenever oversaturation with respect to those mineral phases has been reached<sup>1</sup>.

A summary of the results is shown in Table 3-7 and in Figures 3-10 (for open repository conditions) and 3-11 (for closed repository conditions). For most of the mixing proportions, the resulting groundwaters are oversaturated with respect to calcite and calcite precipitation is therefore generally favoured irrespective the assumption of open or closed conditions (Table 3-7). As a general trend, the amount of calcite predicted to precipitate for each groundwater mixture is in the same order of magnitude in Forsmark and Laxemar for both open or closed repository conditions (Figures 3-10 and 3-11).

**Table 3-6: Calculated cement porewater compositions used in the mixing calculations presented in this report (after equilibration with respect to Jennite and precipitation of calcite and  $\text{Fe}(\text{OH})_3$  whenever oversaturation with respect to those phases is reached).**

cement porewater	pH	pe	milimol L <sup>-1</sup>									
			Alkalinity	Na	K	Ca	Mg	Cl	S	Br	F	Fe
F8016	10.63	-7.00	1.79	87.81	0.88	23.30	9.55	153.74	5.25	0.30	-	$3.6 \cdot 10^{-3}$
F12343	10.63	-7.08	0.86	79.07	0.19	45.65	0.46	170.90	0.32	0.58	0.064	$4.5 \cdot 10^{-3}$
F12818	10.55	-6.34	0.78	83.68	0.14	68.54	0.20	214.18	1.05	0.72	0.080	-
L10091	10.86	-7.18	2.44	34.46	0.14	5.43	0.45	39.60	1.36	0.00	0.153	$2.2 \cdot 10^{-3}$
L15008	10.66	-6.95	1.00	92.28	0.36	38.20	2.24	168.11	4.52	0.37	0.090	$3.0 \cdot 10^{-3}$

<sup>1</sup> The possibility of mixing between repository groundwaters and porewaters from cement dissolution *before* reequilibrating with calcite and  $\text{Fe}(\text{OH})_3(\text{a})$  if oversaturation was reached has also been checked without obtaining relevant differences concerning the potential for fracture clogging of the different groundwater mixtures. The same stands for the possibility of mixing *after reequilibrating* with calcite and  $\text{Fe}(\text{OH})_3(\text{a})$  in open atmospheric conditions if oversaturation was reached.

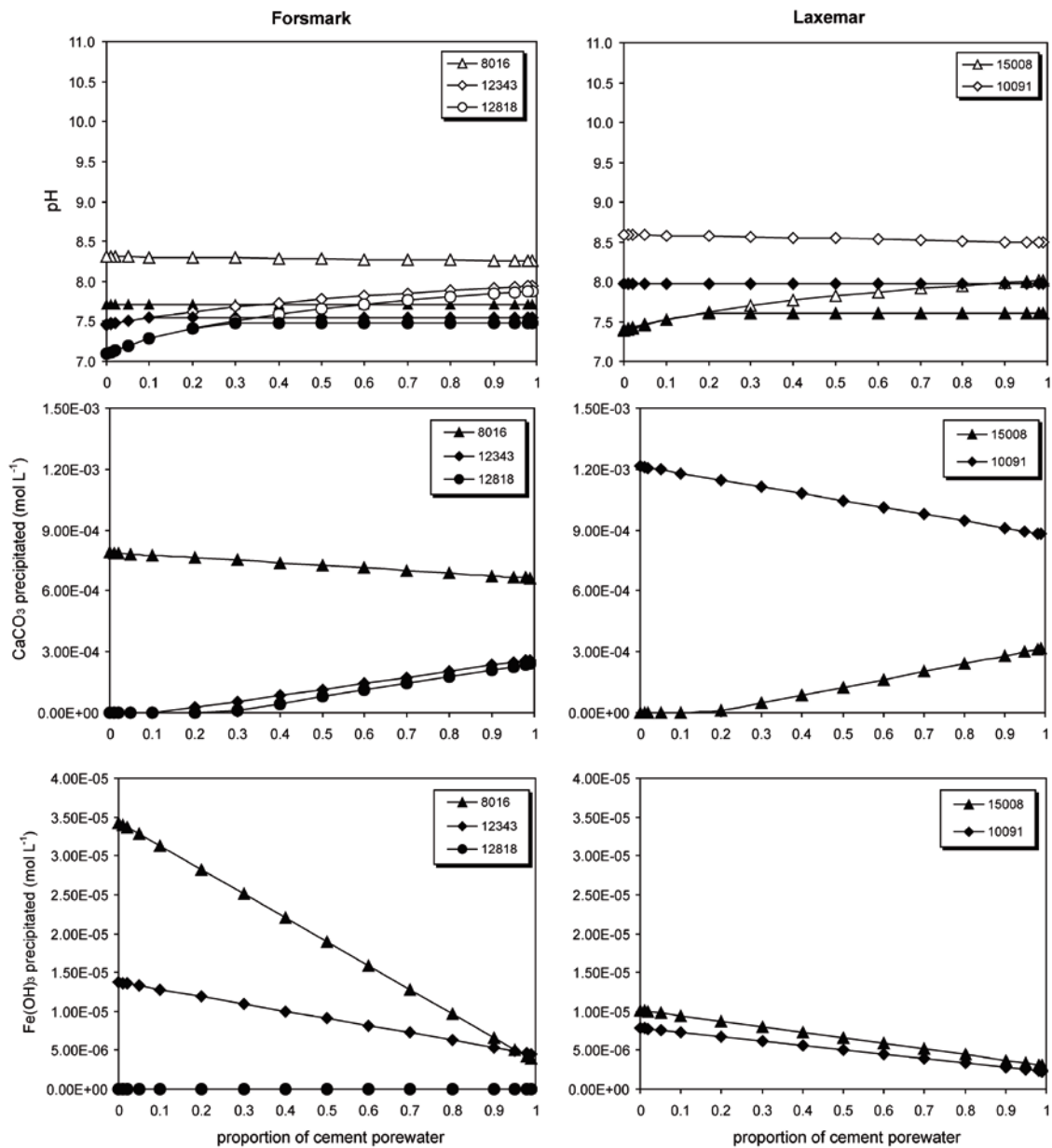
On the other hand, the behavior of the mixtures with regard to amorphous iron hydroxides is notably different depending on the assumption of open or closed repository conditions. In the simulations carried out by assuming open repository conditions, all the groundwater samples except 12818 are oversaturated with respect to amorphous ferric oxyhydroxides (Table 3-7). On the contrary, the same groundwater mixtures are generally subsaturated with respect to amorphous ferric oxyhydroxides in the simulations carried out for closed repository conditions (Table 3-7). In line with these two observations, the amount of precipitated ferric oxyhydroxide is much larger for the simulations assuming open repository conditions. However, the amount of precipitated ferric oxyhydroxides is negligible in most of the simulations if compared with the amount of precipitated calcite. Therefore, the potential of fracture sealing by mineral precipitation reactions under the simulated conditions can be mainly attributed to calcite (Figures 3-10 and 3-11).

**Table 3-7: Saturation indexes with respect to calcite and amorphous iron hydroxides for the whole range of mixing proportions between the repository groundwaters for Forsmark and Laxemar and the cement degraded porewaters (see text for details). The values correspond to the groundwater composition after mixing but before mineral precipitation reactions.**

	SI Calcite (only mixing)						SI Amorphous Fe(OH) <sub>3</sub> (only mixing)					
	Cement porewater proportion	Sample 8016	Sample 12343	Sample 12818	Sample 10091	Sample 15008	Sample 8016	Sample 12343	Sample 12818	Sample 10091	Sample 15008	
CLOSED REPOSITORY	0.99	0.48	0.14	0.07	0.62	0.13	0.02	0.00	–	0.00	0.01	
	0.98	0.71	0.24	0.12	0.87	0.23	0.05	0.01	–	0.01	0.01	
	0.95	1.05	0.46	0.26	1.22	0.43	0.09	0.01	–	0.00	0.02	
	0.9	1.32	0.67	0.42	1.49	0.64	0.12	0.02	–	–0.07	0.03	
	0.8	1.60	0.92	0.62	1.74	0.88	0.05	0.00	–	–0.36	0.02	
	0.7	1.74	1.07	0.76	1.84	1.03	–0.15	–0.06	–	–0.70	–0.03	
	0.6	1.82	1.18	0.86	1.88	1.14	–0.43	–0.16	–	–1.03	–0.14	
	0.5	1.85	1.25	0.93	1.87	1.21	–0.74	–0.32	–	–1.35	–0.32	
	0.4	1.84	1.30	0.98	n.c	1.25	–1.07	–0.57	–	n.c	–0.58	
	0.3	1.79	1.32	1.01	1.72	1.25	–1.40	–0.90	–	–2.01	–0.94	
	0.2	1.70	1.27	1.00	1.54	1.19	–1.75	–1.37	–	–2.45	–1.46	
	0.1	1.56	1.13	0.87	1.15	0.95	–2.14	–2.00	–	–3.23	–2.27	
OPEN REPOSITORY	0.05	1.45	0.98	0.69	0.76	0.65	–2.36	–2.42	–	–3.93	–2.99	
	0.02	1.38	0.83	0.46	0.52	0.19	–2.49	–2.74	–	–4.32	–3.88	
	0.01	1.35	0.77	0.34	0.46	–0.07	–2.51	–2.86	–	–4.41	–4.35	
	0.99	1.11	0.79	0.79	1.10	0.84	2.70	2.77	–	2.45	2.60	
	0.98	1.11	0.78	0.79	1.10	0.83	2.74	2.78	–	2.46	2.61	
	0.95	1.11	0.77	0.77	1.11	0.81	2.82	2.80	–	2.49	2.64	
	0.9	1.12	0.74	0.73	1.12	0.78	2.94	2.84	–	2.54	2.68	
	0.8	1.13	0.68	0.65	1.15	0.71	3.10	2.90	–	2.61	2.76	
	0.7	1.14	0.61	0.57	1.17	0.63	3.22	2.96	–	2.68	2.82	
	0.6	1.15	0.53	0.47	1.20	0.54	3.31	3.00	–	2.74	2.87	
	0.5	1.17	0.45	0.35	1.22	0.45	3.39	3.04	–	2.79	2.91	
	0.4	1.18	0.36	0.22	1.24	0.33	3.46	3.08	–	2.83	2.95	
0.3	1.19	0.25	0.06	1.26	0.20	3.51	3.11	–	2.87	2.97		
0.2	1.20	0.14	–0.13	1.28	0.05	3.56	3.13	–	2.91	2.99		
0.1	1.21	–0.01	–0.39	1.30	–0.15	3.61	3.14	–	2.94	3.00		
0.05	1.21	–0.09	–0.57	1.31	–0.27	3.63	3.14	–	2.96	2.99		
0.02	1.22	–0.14	–0.69	1.32	–0.35	3.64	3.14	–	2.97	2.99		
0.01	1.22	–0.16	–0.73	1.32	–0.38	3.64	3.14	–	2.97	2.99		

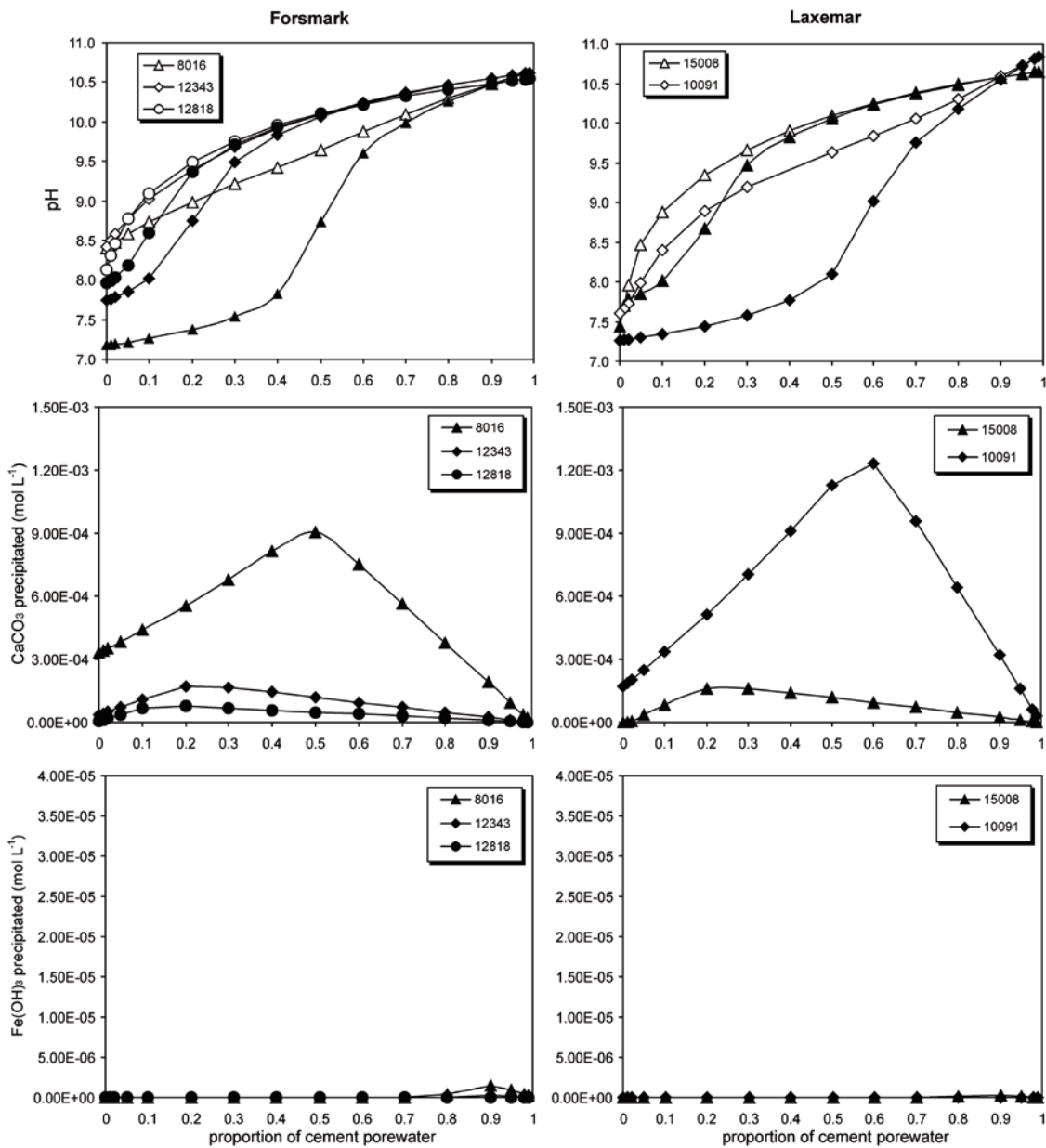
n.c.:no convergence in the calculations is achieved.

Open repository conditions



**Figure 3-10.** Summary of results for different mixing proportions between the selected repository groundwaters in Forsmark and Laxemar and waters after the degradation of cementitious material used for grouting and shotcreting, by assuming open repository conditions (see text for details). Open and solid symbols represent the results obtained before and after mineral precipitation reactions, respectively.

Closed repository conditions



**Figure 3-11.** Summary of results for different mixing proportions between the selected repository groundwaters in Forsmark and Laxemar and waters after the degradation of cementitious material used for grouting and shotcreting, by assuming closed repository conditions (see text for details). Open and solid symbols represent the results obtained before and after mineral precipitation reactions, respectively.

### ***The potential for EDZ fracture sealing by mineral precipitation reactions***

The ability of the precipitating minerals to affect the hydraulic properties of the EDZ by fracture sealing in the short term is preliminary evaluated in this section.

Although more sophisticated calculations would be necessary to clarify the question, a preliminary estimation of the effect of the target mineral precipitation reactions on the hydraulic conductivity of the EDZ can be done. With this aim, the porosity variations caused by mineral precipitation reactions were calculated for each modelling case by taking into account the molar volume of each mineral phase included in the simulations<sup>2</sup>. Subsequently, porosity variations were transformed into hydraulic conductivity variations by means of the Kozeny-Carman equation. Even though this equation is mainly applicable to granular materials, it has been used in these preliminary estimations for simplicity. A similar approach has been adopted in earlier works (Soler and Mäder 2007).

The percent variation of the hydraulic conductivity due to mineral precipitation was estimated in each modelling case for a period of ten years. With regard to flow properties, no clear indication of realistic parameters for the EDZ has been found. A Darcy velocity of  $2.5 \cdot 10^{-3}$  m/y, a kinematic porosity of  $10^{-4}$  and a hydraulic conductivity of  $3 \cdot 10^{-8}$  m/s were assumed for the EDZ (Hartley et al. 2006ab).

The results of the calculations are shown in Tables 3-8 and 3-9. For most of the modelling cases, the estimated decrease of the hydraulic conductivity in ten years is smaller than 2%. The largest variations of the hydraulic conductivity are caused by calcite precipitation. The precipitated volumes for this mineral are generally between one and three orders of magnitude larger than for precipitated ferric phases, as can be deduced from the comparison of their respective potential to decrease the hydraulic conductivity (Tables 3-8 and 3-9).

As shown in previous subsections and deduced from the estimated decreases of the hydraulic conductivity (Tables 3-8 and 3-9), the largest amounts of precipitated ferric phases for any given modelling case are predicted to take place if open repository conditions are assumed (i.e. equilibrium with atmospheric partial pressures of  $O_2(g)$ ). This can be attributed to the setting of oxidising redox conditions in which Fe(II) transforms into Fe(III) and precipitates. Under the reducing conditions present if closed repository conditions are assumed (pe values  $< -2.5$ ) the predicted precipitation of ferric phases is smaller, increasing slightly with the temperature increase, which increases the oversaturation with respect to more crystalline and insoluble ferric phases (mainly goethite or hematite).

As a general trend, the largest hydraulic conductivity variations (largest mineral precipitation amounts) correspond to the mixtures of groundwaters with the shallow infiltration waters. For those mixtures, the estimated decrease of hydraulic conductivity is always larger than 1%.

It is worth noting that most of the target groundwater compositions do not exhibit any capacity to dissolve calcite or ferric oxyhydroxides and, in the scarce cases of subsaturation with respect to those phases, the effect is very small.

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<sup>2</sup>Molar volumes are: 36.934 for calcite ( $CaCO_3$ ), 20.820 for goethite ( $FeOOH$ ) and 34.360 for iron hydroxide ( $Fe(OH)_3$ ). All the values expressed in  $cm^3/mol$  and taken from the thermodynamic database thermo.com.V8.R6.full, generated by GEMBOCHS.V2-Jewel.src.R6 03-dec-1996 (Johnson and Lundeen 1994) and distributed with the software package “The Geochemist’s Workbench” (Bethke 2002).

**Table 3-8: Preliminary estimation of the percent variation of the EDZ hydraulic conductivity due to mineral precipitation for a period of ten years in the modelling cases 1 to 4.**

	Permeability reduction in ten years (%)					
	T (°C)	Site	Sample ID	with CaCO <sub>3</sub>	with Fe(OH) <sub>3</sub>	with FeOOH
<b>CASE 1: TEMPERATURE INCREASE</b>	50	Forsmark	8016	1,00	n.i.m.	0.05
			12343	0.02	n.i.m.	0.02
			12818	0.00	n.i.m.	0.00
		Laxemar	10091	0.89	n.i.m.	0.01
			15008	0.00	n.i.m.	0.01
	100	Forsmark	8016	1.58	n.i.m.	0.05
			12343	0.07	n.i.m.	0.02
			12818	0.00	n.i.m.	0.00
		Laxemar	10091	2.07	n.i.m.	0.01
			15008	0.00	n.i.m.	0.02
<b>CASE 2: OPEN REPOSITORY</b>	15	Forsmark	8016	2.17	0.09	n.i.m.
			12343	0.00	0.04	n.i.m.
			12818	0.00	0.00	n.i.m.
		Laxemar	10091	3.32	0.02	n.i.m.
			15008	0.00	0.03	n.i.m.
<b>CASE 3: MIXING WITH DEEP SALINE GROUNDWATERS</b>	15	Forsmark	8016	1.07	0.05	n.i.m.
			12343	0.00	0.02	n.i.m.
			12818	0.00	0.01	n.i.m.
		Laxemar	10091	1.90	0.02	n.i.m.
			15008	0.00	0.02	n.i.m.
	50	Forsmark	8016	0.54	n.i.m.	0.02
			12343	0.01	n.i.m.	0.01
			12818	0.00	n.i.m.	0.00
		Laxemar	10091	0.83	n.i.m.	0.00
			15008	0.00	n.i.m.	0.01
	100	Forsmark	8016	0.82	n.i.m.	0.03
			12343	0.04	n.i.m.	0.01
			12818	0.00	n.i.m.	0.00
		Laxemar	10091	1.32	n.i.m.	0.01
			15008	0.02	n.i.m.	0.01
<b>CASE 4: MIXING WITH SHALLOW INFILTRATION GROUNDWATERS</b>	15	Forsmark	8016	5.82	0.04	n.i.m.
			12343	4.87	0.02	n.i.m.
			12818	4.83	0.00	n.i.m.
		Laxemar	10091	3.76	0.01	n.i.m.
			15008	2.56	0.01	n.i.m.
	50	Forsmark	8016	2.61	n.i.m.	0.02
			12343	2.46	n.i.m.	0.00
			12818	2.56	n.i.m.	0.00
		Laxemar	10091	1.00	n.i.m.	0.01
			15008	1.04	n.i.m.	0.00
	100	Forsmark	8016	4.18	n.i.m.	0.03
			12343	3.69	n.i.m.	0.01
			12818	3.72	n.i.m.	0.00
		Laxemar	10091	2.28	n.i.m.	0.01
			15008	1.82	n.i.m.	0.01

n.i.m.: mineral not included in the model

**Table 3-9: Preliminary estimation of the percent variation of the EDZ hydraulic conductivity due to mineral precipitation for a period of ten years in the modelling case 5 (mixing with cement dissolution porewaters) for three different mixing proportions.**

	Permeability reduction in ten years (%)				
	Open repository			Closed repository	
	Cement porewater proportion	with CaCO <sub>3</sub>	with Fe(OH) <sub>3</sub>	with CaCO <sub>3</sub>	with Fe(OH) <sub>3</sub>
8,016	0.9	1.86	0.02	0.52	0.00
	0.5	2.00	0.05	2.49	0.00
	0.1	2.13	0.08	1.21	0.00
12,343	0.9	0.65	0.01	0.07	0.00
	0.5	0.32	0.02	0.33	0.00
	0.1	0.00	0.03	0.30	0.00
12,818	0.9	0.58	0.00	0.03	0.00
	0.5	0.22	0.00	0.13	0.00
	0.1	0.00	0.00	0.19	0.00
15,008	0.9	0.77	0.01	0.07	0.00
	0.5	0.35	0.02	0.32	0.00
	0.1	0.00	0.02	0.22	0.00
10,091	0.9	2.50	0.01	0.89	0.00
	0.5	2.87	0.01	3.09	0.00
	0.1	3.23	0.02	0.92	0.00

### 3.4.2 Results of the microbiological modelling

The potential for microbial calcite and iron hydroxide formation during open repository conditions (atmospheric pressure and oxidising conditions) is discussed below for a number of given conditions with input data from the site investigations (Table 3-10). The most important groundwater parameters for microorganisms, are pH and carbonate, ferrous iron, methane and DOC concentrations (see section 3.3). The numerical modelling of how microbial iron oxide and calcite production would influence the hydraulic conditions in fractures close to a tunnel is possible to perform. A bio-precipitation and bio-clogging code can be developed based on the bio-code for microbial processes in deep groundwater from Microbial Analytics Sweden AB. However, since such a code has not yet been developed, the modelling here can only be given in qualitative and relative terms for the different cases given.

The potential for biological iron oxide and calcite production is given in the result tables below in a three level scale, low, intermediate and high. An intermediate or a high potential will result in significant reduction of the hydraulic conductivity in fractures.

It is very difficult to give reliable time frames for the three levels of microbial iron hydroxide and calcite formation in Table 3-10 without proper modelling and test efforts. As rule of the thumb, based on experiences from Äspö, high potential would imply that less than mm sized fractures could seal within a year, while intermediate potential would imply 1 to 10 years and low would mean anything from 10 years to no potential at all.



**Table 3-10. Input data from the site investigations for modelling. Methane was not analysed for several of the water types.**

Water type	site	secmid (m)	IDCODE	pH	HCO <sub>3</sub> <sup>-</sup> (mg/l)	DOC mg/L	Fe <sup>2+</sup> (mg/l)
Brackish marine	Forsmark	512.54	KFM02A	6.9	126	2.1	1.84
Brackish non marine water	Forsmark	571.57	KFM01D	8.4	17.1	11	0.763
Brackish marine	Laxemar	628.75	KLX15A	7.6	14.1	1.5	0.548
Low salinity and a glacial component	Laxemar	411.65	KLX03	8.1	189	13	0.429
Brackish non marine water	Forsmark	673.27	KFM08D	8.3	6.98	0	0.001

***The groundwater composition is unchanged (except for E<sub>h</sub> and pH)***

The potential for microbial iron production will be large in all groundwater with ferrous iron. The production will be significant as soon as the oxygen concentration rises above 0.3 mg L<sup>-1</sup>. This will trigger an increase in the E<sub>h</sub> towards the range where iron oxidation is favourable (> 100 mV).

The potential for microbial calcite formation production will be large in all groundwater with high concentrations of DOC and methane, irrespective of oxygen, E<sub>h</sub> or pH.

Water type	IDCODE	BIOS formation	Calcite formation
Brackish marine	KFM02A	High	High
Brackish non marine water	KFM01D	High	High
Brackish marine	KLX15A	High	Intermediate
Low salinity and a glacial component	KLX03	High	High
Brackish non marine water	KFM08D	Low	Low

***A deep water is 50% mixed***

Deep groundwater generally has less ferrous iron and DOC than intermediate and shallow groundwaters. It can, therefore, be assumed that the rate of microbial iron oxide and calcite formation will decrease, relative to the unchanged situation, except for cases where deep groundwater contains a high concentration of methane that mixes with a sulphate or oxygen rich groundwater.

Water type	IDCODE	BIOS formation	Calcite formation
Brackish marine	KFM02A	Intermediate	Intermediate
Brackish non marine water	KFM01D	Intermediate	Intermediate-low
Brackish marine	KLX15A	Intermediate-low	Low
Low salinity and a glacial component	KLX03	Intermediate-low	Intermediate-low
Brackish non marine water	KFM08D	Low	Low

***A shallow water is 50% mixed***

Shallow groundwater generally has more ferrous iron and DOC (and less methane) than intermediate (unchanged) groundwater. It can, therefore, be assumed that the rate of microbial iron oxide and calcite formation will increase relative to the unchanged situation.



<b>Water type</b>	<b>IDCODE</b>	<b>BIOS formation</b>	<b>Calcite formation</b>
Brackish marine	KFM02A	High	High
Brackish non marine water	KFM01D	High	High
Brackish marine	KLX15A	High	Intermediate
Low salinity and a glacial component	KLX03	High	High
Brackish non marine water	KFM08D	Low	Low

***The groundwater is contaminated by nitrogen compounds (300g/m<sup>3</sup> rock) from explosives***

The contamination by nitrogen compounds will not influence the concentrations of ferrous iron, DOC or methane and the situation will, therefore, not change relative to the unchanged situation.

<b>Water type</b>	<b>IDCODE</b>	<b>BIOS formation</b>	<b>Calcite formation</b>
Brackish marine	KFM02A	High	High
Brackish non marine water	KFM01D	High	High
Brackish marine	KLX15A	High	Intermediate
Low salinity and a glacial component	KLX03	High	High
Brackish non marine water	KFM08D	Low	Low

***The pH is increased by a low-pH cement according to the discussion in SR-Can***

The increase in pH will not have a large effect on the microorganisms, but it will influence the geochemistry as modelled in subsection 3.4.1. However, observations made in tunnels (places other than at the Äspö HRL) where low pH cement has been injected reveal vivid microbial growth and the formation of up to 5 cm thick slime layers on the tunnel walls. These slime microbes most probably grow on additions made to the concrete, in particular different organic plasticizers. The slime locally developed very low pH (1.0) as a result of oxidation of microbial sulphide to sulphuric acid. The slime also clogged water conducting fractures.

<b>Water type</b>	<b>IDCODE</b>	<b>BIOS formation</b>	<b>Calcite formation</b>
Brackish marine	KFM02A	High	High
Brackish non marine water	KFM01D	High	High
Brackish marine	KLX15A	High	Intermediate
Low salinity and a glacial component	KLX03	High	High
Brackish non marine water	KFM08D	Low	Low

***Temperature effect during emplacement and after closure***

There is no information available about the potential for microbial growth and activity at 50°C and 100°C. Many microorganisms have adapted to these high temperatures, so there is no conceptual reason to assume that microbial processes will be absent. More research is needed to develop these cases. The extensive work published on biological iron oxide and calcite forming microorganisms in the Äspö HRL tunnel has been performed at ambient temperature only. If deemed important, experiments can be set up that reproduce high temperature situations. As a rule of thumb, biological processes double for every 10°C increase in temperature. Increasing temperature will then most probably speed up the bio-precipitating processes.

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