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Keywords: geochemical conditions, deep repository, near-field chemistry, concrete, evolution, LILW.

Abstract

The evolution of geochemical conditions in the repository for long-lived low- and intermediate-level waste, SFL 3-5, and in the vicinity of the repository are important when predicting the retention of radionuclides and the long-term stability of engineered barriers. In this study the initial conditions at different repository sites at 300 – 400 m depth, the influence of repository construction and operation, the expected conditions after repository closure and saturation, and the evolution in a long-term perspective are discussed.

Groundwaters that are found at these depths have near-neutral pH and are reducing in character, but the composition can vary from saline to non-saline water. The water chemistry in the near-field will mainly be influenced by the composition of the groundwater and by the large amounts of cementitious material that can be found in the repository. Disturbances caused during construction and operation are not expected to be permanent. Studies of old concrete indicate that leaching of concrete is a slow process. The geochemical conditions in the repository are therefor expected to be stable and prevail for hundreds of thousand years. However, the evolution of the surrounding environment may influence the conditions in long-term perspective.

Sammanfattning

Den geokemiska utvecklingen inuti och i närheten av förvaret för långlivat låg- och medelaktivt avfall, SFL 3-5, är av betydelse. Informationen behövs för att bedöma såväl fördröjningen av radionukliderna som den långsiktiga stabiliteten hos ingenjörs-barriärerna. I den här studien diskuteras de förhållanden som initialt kan råda på ett förvarsdjup av 300 – 400 m, hur bygge och drift påverkar detta, vilka förhållanden som förväntas efter förslutning och vattenmättnad samt, till sist, hur förvarets miljö utvecklas på lång sikt.

Grundvatten på dessa djup har nära neutralt pH och är kemiskt reducerande. Sammansättningen varierar mellan söta och salta grundvatten. Vattenkemin i närzonen bestäms huvudsakligen av grundvattnet och de stora mängder cement och betong som finns i förvaret. Störningar från bygge och drift bedöms inte ge några bestående förändringar. Undersökningar av gamla betongkonstruktioner visar att lakning av betong är en mycket långsam process. De geokemiska förhållandena i förvaret förväntas därför vara stabila och bestå under hundratusentals år. Förändringar i den omgivande miljön skulle dock kunna påverka förhållandena, sett i ett långt tidsperspektiv.

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1 Introduction

1.1 Aim and background

The aim of this report is to describe the chemical conditions inside and in the vicinity of the deep repository for long-lived low- and intermediate-level waste, SFL 3-5. The information is important when predicting the retention of radionuclides and the long-term stability of the engineered barriers. As this repository is largely based on cementitious materials, the water chemistry is very much influenced by the main constituents in cement and concrete.

The near-field water composition, in particular the salinity, affects the water chemistry inside the repository and thereby the sorption, diffusivity and the solubility of the radionuclides in the repository. Furthermore, the aerobic corrosion rates of steel reinforcement are dependent on the salinity. Also dependent on water chemistry is the stability of mineral phases in the bedrock and in the engineered barriers.

1.2 Structure of report

This report gives a description of the expected geochemical conditions in the different repository parts at repository closure, and the normal evolution and possible variations of geochemical conditions in long-term perspective.

The expected initial conditions at the repository site at 300 – 400 m depth are given in Chapter 2. The characteristic properties of the barrier materials used and other materials brought in during construction and operation of the repository are given in Chapter 3. In Appendix C the quantities of stray material potentially remaining in the repository are estimated.

In Chapter 4 the influence of repository construction and operation on groundwater flow and composition, and on near-field rock and engineered barrier properties are discussed. Finally, the expected conditions at repository closure are defined.

After the repository has been closed and sealed, groundwater will infiltrate through the engineered barriers and saturate the repository. In Appendix A the time for resaturation of the repository is estimated based on information on groundwater inflow to underground cavities. The expected geochemical conditions in the different parts of SFL-3-5, after closure and saturation, are given in Chapter 5.

The normal evolution and possible variations of the geochemical conditions in long-term perspective are discussed in Chapter 6 and 7. In Appendix B the leaching of concrete and the influence of it on the near field are discussed.

A pre-study of the SFL 3-5 repository was carried out in 1992 – 1995. Since then the repository design has been revised. For documentation purpose some of the material forming the base for the revision of the design is given in Appendix D.

2 Initial conditions at the repository site

2.1 Location of SFL 3-5

A site for the deep repository for long-lived waste has not been identified yet. One option is to select a site where all parts of the repository can be located, the repository for spent fuel together with the repository for long-lived low- and intermediate-level waste, SFL 3-5. In that case SFL 3-5 will be situated far enough to disregard any interaction between the repositories.

The depth level for SFL 3-5 remains to be selected. A depth of 300 – 400 m will be used in this report. No major discrepancies from the conclusions in this report are expected due to the depth of location, i.e. as long as the repository is not deeper than 700 m or above 100 m (depth). Another important provision is that local conditions are not extreme, for example, fast infiltration of surface water down to deep levels or the occurrence of brines at shallow depths.

2.2 Host rock properties at repository site

The repository will be placed in a crystalline bedrock of granitic composition. A suitable site will be selected in the Fennoscandian Shield in Sweden. The primary role of the rock is to provide stable mechanical and chemical conditions in the repository over a long period of time so that the function of the engineered barriers is not jeopardised. The overlying rock will protect the repository from events at the surface for a length of time where institutional control is no longer feasible. The second role of the host rock is to provide an extra barrier to radionuclide dispersal from the waste. A specific requirement for the repository parts SFL 3, 4 and 5 is that it must be possible to construct large enough caverns at the selected depth and another important issue is hydraulic flow. A low groundwater flow will help to preserve the chemical conditions in the repository, promote the stability of concrete and limit any release of radionuclides from the waste.

Hydraulic pressure at repository depth is about equal to a water column of the same height. This implies that the water pressure in a repository at 300 – 400 m is 3 – 4 MPa. Rock pressure is considerably higher and varies between 10 – 30 MPa at 400 m depth (Stephansson, 1987 and Winberg, 1996).

Hydraulic conductivity generally decreases with depth and most of the reduction of flow occurs in the upper 300 m. Carlsson *et al.* (1983) have calculated the average trends at different study sites and, according to their results, there is a decrease of about two orders of magnitude from 100 m to 300 m depth (roughly 10^{-8} to 10^{-10} m/s). A similar but weaker trend was observed in the boreholes at Äspö (Wikberg (ed.), 1991). Water flow occurs in the fractures of the rock and, on a small scale, there is a large variation. Locations with relatively intact rock will be much less conductive whereas zones with extended fractures or zones of fractured rock can be considerably more conductive than the average at that depth. Galleries and tunnels of SFL 3-5 will cut over relatively large portions of the rock and consequently approach the average. It should also be noted that lower hydraulic conductivity at depth does not exclude the possibility to find highly conductive zones. For example, the study site at Finnsjön has a ca 100 m wide conductive sub-horizontal fractured zone, situated between the levels 100 – 400 m (Ahlbom *et al.*, 1989).

Granitic bedrock consists mainly of quartz, feldspars (alkali feldspar, plagioclase) micas (biotite, muscovite) and amphiboles (hornblende). Accessory minerals are present in minor amounts (calcite, chlorite, clay minerals, pyrite, fluorite, apatite, anhydrite etc.) but they are important due to their influence on groundwater chemistry and the fact that they are common as fracture infill. The importance of rock from a chemical point of view i. e. to control water chemistry and retain radionuclides, will be further treated in this report (water chemistry, see Chapter 7) and elsewhere (sorption, Carbol *et al.*, 1997 and matrix diffusion, Ohlsson and Neretnieks, 1997).

2.3 Temperature at repository depth

The SFL 3-5 repository will, according to the present concept, be situated at about 300 – 400 m depth. Measurements of temperature in bore holes from SKB studied sites, total 11 sites including the Äspö Hard Rock Laboratory, have been evaluated (Ahlbom *et al.*, 1995). The studied sites are geographically spread and represent different rock types. The temperature increases with increasing depth. Temperatures at 500 m depth and gradients at Äspö, and the former study sites Finnsjön and Gideå are, according to Ahlbom *et al.* (1995): 14.6°C, 15.0°C/km; 10.9°C, 15.5°C/km; 14.6°C, 15.0°C/km respectively. From this we estimate a temperature of between 9 – 13°C for the SFL 3-5 repository (the position of 100 – 200 m above the 500 m level makes it 1 – 3°C colder).

2.4 Groundwater composition at repository site

The composition of groundwater under land in Sweden is generally determined by the infiltration of meteoric water. The oxygen in the infiltrating water is largely consumed by biological processes, first in the soil and then further along the flow path in the rock (Pedersen and Karlsson, 1995). Carbon dioxide is generated, mainly in the soil, and carbonates such as calcite are dissolved by the carbonic acid. Other reactions such as weathering and ion exchange will further influence the water chemistry.

Typical deep groundwaters have a low redox potential; measurements indicate Eh in the range -0.4 to -0.1 V (Grenthe *et al.*, 1992). With a pure meteoric origin, near neutral pH is controlled by the carbonate system and sodium, calcium and bicarbonate are the most abundant ions.

Exceptions to this rule are frequently found where saline water is mixed into the meteoric origin water or where the saline water is the largest or only component. Saline, chloride-dominated, groundwater is sometimes found at locations near the seashore, or at great depths. Deep saline water is commonly found where the sea before the land rise has covered land. There are several possible explanations for saline groundwater but the geochemical/hydrological reason behind it is of less relevance to our objectives. The important fact is that deep groundwater can be saline and we need to analyse the consequences of that for deep disposal. This subject has been treated before. The possibility of saline groundwater was discussed in the early performance assessment study for spent fuel disposal KBS-3 (KBS-3, 1983). Saline water was also discussed in the later performance assessment study SKB 91 (SKB 91, 1992). A saline groundwater was in fact used as reference water in the recent performance assessment study SR 95 (SR 95, 1996) where the reference water was selected from results of measurements performed at the Hard Rock Laboratory at Äspö (Smellie *et al.*, 1995). However, saline water is by no means a hindrance to the location of a repository for low and intermediate level waste as is demonstrated by the SFR facility, which is situated under the sea floor in Forsmark, SE Sweden.

Examples of typical saline and non-saline groundwaters are given in Table 2-1. The examples have been taken from investigations (through boreholes) of deep groundwater chemistry in Äspö, prior to the construction of the Hard Rock Laboratory, and from two previous study sites during the 80-ties, Gideå and Finnsjön. These water compositions have been selected as representative for deep groundwaters in the performance assessment study SR 97 on disposal of spent fuel (SKB, 1999).

Table 2-1 Examples of saline and non-saline deep groundwater. The samples are taken from four, near vertical, deep borehole sections in Finnsjön, Gideå and Äspö (Laaksoharju *et al.*, 1998).

Groundwater components	Unit	Äspö saline	Finnsjön saline	Finnsjön non-saline	Gideå non-saline
Bore hole		KAS02	BFI01	KFI07	KGI04
Date of measurement		88-05-04	86-10-27	80-11-19	82-07-04
Depth	m	528	436	508	384
Drilling water content	%	0.19	0.02	–	11.03
Na^+	mg/l	2 100	1 700	275	105
K^+	mg/l	8	13	2	2
Ca^{2+}	mg/l	1 890	1 650	142	21
Mg^{2+}	mg/l	42	110	17	1
Sr^{2+}	mg/l	35	21	–	–
Fe^{2+}	mg/l	0.24	–	1.80	0.05
Mn^{2+}	mg/l	0.29	0.82	0.13	0.01
HCO_3^-	mg/l	10	47	278	18
SO_4^{2-}	mg/l	560	370	49	0.1
Cl^-	mg/l	6 410	5 500	555	178
I^-	mg/l	–	0.12	–	0.14
Br^-	mg/l	40	32	–	–
F^-	mg/l	1.5	1.2	1.5	3.2
HS^-	mg/l	0.15	<0.01 1)	–	<0.01 1)
NH_4^+ calculated as N	mg/l	0.03	0.35	0.09	0.01
NO_3^- calculated as N	mg/l	<0.010 1)	<0.005 1)	<0.002 1)	0.009
NO_2^- calculated as N	mg/l	<0.001 1)	0.005	0.010	<0.001 1)
$PO_{4.tot}$ calculated as P	mg/l	0.005	0.005	0.040	0.008
SiO_2 calculated as Si	mg/l	4.1	5.4	5.6	4.7
DOC (dissolved organic carbon)	mg/l	1	–	6	2
Eh 2)	mV	-308	–	-250	-202
pH 2)		7.7	7.0	7.9	9.3

1) below the detection limit

2) see Laaksoharju et al., 1998

2.5 Summary and concluding remarks

Natural groundwater conditions of importance to the study of SFL 3-5 are as follows:

- Both non-saline and saline groundwater may be encountered depending on the location of the deep repository.
- The composition of groundwater from borehole KAS02 (section 530 – 535 m) or BFI01 (section 439 – 459.1 m) can be taken as examples of deep saline groundwater (see Table 2-1).
- The composition of groundwater from borehole KFI07 (section 511 – 516 m) or KGI04 (section 404 – 406.7 m) can be taken as examples of a non-saline groundwater (see Table 2-1).
- The measured redox potential at 100 m and deeper is generally between -0.4 and -0.1 V. There are no traces of oxygen in deep groundwater as demonstrated by the negative Eh-values.
- The pH is normally in the range 6.5 – 9.5 and mostly controlled by the carbonate system.
- The total concentration of carbonate ions (alkalinity) is in general below 600 mg/l. There is a tendency of lower concentrations at greater depths and values above 300 mg/l at 300 – 400 m are unusual.
- Sulphate concentration is highest in saline water but not necessarily correlated to chloride concentration. The concentration at 300 – 400 m is generally below 600 mg/l.
- Sodium and calcium are the most common cations in groundwater. The concentration of both sodium and calcium is about 2 000 mg/l in saline waters and usually in the range of 10 – 100 mg/l in non-saline waters at 300 – 400 m depth.
- Magnesium and potassium are generally present but their concentrations are kept relatively low by geochemical reactions. Magnesium is generally below 150 mg/l and potassium below 15 mg/l at 300 – 400 m.
- Deep groundwater contains very little nutrients such as P- and N-compounds and the concentrations of dissolved organic matter is low.

Deviations from what is labelled 'normal', 'general' or 'usual' in the points above can of course occur in nature and it is not until a site has been selected and carefully investigated that we are able to give more precise information on the initial groundwater composition at repository level.

3 Engineered barrier properties

The engineered barriers in the SFL 3-5 repository include waste packaging, structures made of concrete, rock reinforcements, tunnel plugs and, finally, backfill in different locations made of porous concrete and gravel (crushed rock). The chemical properties of the introduced materials in the repository are described in the following sections.

3.1 Concrete materials

The most common cement type in Sweden is Portland cement. The most frequently used brand is Degerhamn Standard Portland which is sulphate resistant due to its relatively low content of aluminium (Lagerblad and Trägårdh, 1994). There exist other types of cement such as blast-furnace slag cements etc. Almost all the cement types are based on Portland cement with different added solids. The same hydration products will be found in all kinds of Portland cements, although the proportions may vary.

The cement clinker of Ordinary Portland Cement (OPC) consists mainly of the following solid phases: tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminate ferrite. The typical ranges of concentrations in OPC (Andersson and Allard, 1986) are given in Table 3-1. The Degerhamn Standard Portland Cement (SPC) used as structural cement in SFR has been selected as a reference material in this study. The clinker composition of SPC (Lagerblad and Trägårdh, 1994) is given in Table 3-1.

Table 3-1 Clinker composition of Ordinary Portland Cement (OPC) and Degerhamn Standard Portland Cement (SPC).

Clinker component	OPC[a] weight %	SPC[b] weight %
C_3S	45 - 65	51
C_2S	10 - 30	25
C_3A	5 - 15	1.2
C_4AF	5 - 12	14

Abbreviations: C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3

[a] (*Andersson and Allard, 1986*)

[b] (*Lagerblad and Trägårdh, 1994*)

When the ground cement clinker is mixed with water it hydrates and forms new solid phases. The main hydration reactions for the most important solid clinker phases in OPC are (Czernin, 1969):

C_3S: $2\ C_3S + 6\ H_2O = C_3S_2\ 3H_2O + 3\ Ca(OH)_2$

C_2S: $2\ C_2S + 4\ H_2O = C_3S_2\ 3H_2O + Ca(OH)_2$

C_3A: $C_3A + 6\ H_20 = C_3A\ 6H_2O$

C_4AF: $C_4AF + 2\ Ca(OH)_2 + 10\ H_2O = C_3A\ 6H_2O + C_3F\ 6H_2O$

The hydrated cement forms a rigid gel that also contains some crystalline components. In the solid there is an initially water filled pore system (10 – 15 % of the volume). The gel crystallises slowly, and gel phases are found after very long time (Lea, 1970). The stability and longevity of cement gel is further discussed in Section 7.2.2.

The hydrated cement contains considerable amounts of calcium hydroxide. Calcium silicate, calcium aluminate and calcium ferrite phases are also present.

Various additives are used when cement is mixed with water in order to improve the properties. An addition of a workability aid, e.g. sulfonated melamine-formaldehyde polymer, will presumably be made to all the cements used in a repository. The total amount of additives is usually much less than 3 % of the cement weight (Andersson and Allard, 1986).

Concrete is a mixture of cement and sand. The sand is referred to as the aggregate phase. Various silicate minerals and quartz are generally represented in the aggregate phase and various grain sizes are used from fine sand to crushed rock.

Experimental determinations of pore water composition have been made, mainly for Portland cement (Lagerblad and Trägårdh, 1994). One of these studies compares the compositions of a number of different cements (Andersson 1983, Andersson *et al.,* 1989). Two examples of pore water data for OPC are given in Table 3-2.

The highly soluble alkali hydroxides in fresh concrete will cause a high pH (about 13.5) in the pore water. If the alkali hydroxides are leached out and transported away, the pH will be controlled by the dissolution of portlandite, $Ca(OH)_2$, giving a pH of about 12.5 (see Table 7-5 in Chapter 7). The porosity will be about 0.15.

If the cement phase is depleted of portlandite by leaching, a pH in the range of 12.5 – 10.5 is expected due to the presence of the CSH-phases in the hydrated cement. The reactions controlling the pH are the incongruent dissolution of the CSH-gel and the formation of secondary phases. A successive decrease in pH is expected due to changes in the C/S ratio from 1.7 (giving a pH of 12.5) to 0.85 (giving a pH of 11) (Atkins *et al.,* 1992). This period is then followed by congruent dissolution of the remaining CSH-gel, buffering the pH at a value of about 10. The porosity will be around 0.3 (Höglund and Bengtsson, 1991, Andersson and Allard, 1986).

Table 3-2 Experimental determinations of the composition of cement porewaters. Ion concentrations in mg/l.

	OPC[a]	**OPC**[b]
Age	3 months	10 months
w/c [c]	0.4	0.5
Na	644	1 500
K	3 245	6 300
Ca	36	90
Mg	–	0.2
Al	1.1	<5
Si	22	<6
Fe	–	0.5
Cl	<71	–
I, calc [d]	–	0.23
Eh [e]		139
pH	13.1	13.4

a (Lagerblad and Trägårdh, 1994)
b (Andersson, 1983)
c w/c = water/cement ratio
d ionic strength, calculated according to $I = 1/2\ c_i z_i^2$
e potential measured with platinum electrode, mV

3.2 Gravel

Excavated rock from the construction of tunnels and galleries in SFL 3-5 will be crushed and sifted, and the fraction 4 – 32 mm will be used as backfill. This material will have the same composition as the rock itself (granitic) and the grading of the material will provide for high water conductivity, which is important for the hydraulic shielding of the inner structures (hydraulic cage). The backfill will support the internal structures and the tunnel walls. From a chemical point of view, the surfaces of the grains are available for pH and Eh buffering reactions, for example, consumption of high pH leachates from concrete and residual oxygen that remains after closure and sealing. The backfill will also have a function to retain released radionuclides by sorption and matrix diffusion into the grains, as an additional barrier to the waste packages and concrete structures.

The gravel will of course depend on the type of rock that is excavated at a certain selected site. For example, crushed rock from the Hard Rock Laboratory at Äspö, used in the backfill experiments there, is mainly taken from what is referred to as "Småland granite". The more basic and dense "Äspö diorite" is also abundant in this region. A second example is Finnsjön, which is a study site that was used a lot for investigations by SKB in the 80-ties. Finnsjön is situated in a region with granodiorite, which consists of the minerals, quartz, plagioklas, potassium feldspar and hornblende, with calcite as the dominating fracture filling mineral. Another study site from the same time, Gideå, has a large portion of metamorphic gneissic rock of sedimentary origin. Dolerite is also found in the Gideå area.

However, from a chemical point of view it may not be so terribly important what the rock type is at a particular site, as long as the most important minerals are present. For example, feldspars, quartz and clay-group minerals are present at all three of the above mentioned examples. The chemical elements calcium, magnesium, sodium, and potassium are also present together with iron (II and III) and possibly manganese, see Table 3-3. In Swedish bedrock we should always expect carbonates (fracture fillings) and probably minor amounts of sulphates, phosphates and fluorides.

Table 3-3 Chemical composition of certain volcanic rock types. (Blatt and Tracey, 1996).

	Granite %	Alkaline granites %	Quartz diorites %	Diorites %
SiO_2	72.02	73.86	66.15	51.86
$Ti\ O_2$	0.37	0.20	0.62	1.50
$Al_2\ O_2$	12.86	13.75	15.56	16.40
$Fe_2\ O_3$	0.86	0.78	1.36	2.73
FeO	1.67	1.13	3.42	6.97
MnO	0.06	0.05	0.08	0.18
MgO	0.52	0.26	1.94	6.12
CaO	1.33	0.72	4.65	8.40
Na_2O	3.08	3.51	3.90	3.36
K_2O	5.46	5.13	1.42	1.33
H_2O+	0.53	0.47	0.69	0.8
P_2O_5	0.18	0.14	0.21	0.35

3.3 Other materials

In addition to materials brought into the repository with the waste packages and concrete structures, construction and stray materials are brought in during the construction and operation phases.

Construction material

During the construction of the tunnels, grouting (cement slurry) is injected in bore holes into fracture zones and larger fractures during the excavation. Grouting is an effective method to reduce the water inflow to the tunnels during the operational phase.

The tunnel ceiling and walls will be covered with shotcrete to prevent rock blocks or stones to fall out during the operational phase. The shotcrete is 50 – 100 mm thick in the ceiling and 30 – 50 mm on the walls. In the ceiling 50% of the shotcrete is expected to be reinforced with steel fibres. In addition, rockbolts and steel fabrics, consisting of iron, may be used in order to stabilise the rock and prevent stones to fall out during the operational phase.

When the waste deposition in the tunnels are finalised, these tunnels are isolated from connecting tunnels with concrete plugs.

The concrete materials will influence the pH of the water in the repository, but the buffering capacity in the backfill gravel is expected to buffer and contain the effect of high pH. However, the grouting is in the rock behind the backfill. It may reach some metres into the rock. The grouting can, of course, influence the groundwater and increase the pH in the infiltration groundwater.

Stray materials

Blasting of tunnels introduce gases (nitrogen oxides) and debris from ignition caps (aluminium and plastics). Transports of excavated rock and waste packages will introduce rubber from tyres, diesel fumes (nitrogen oxides), spill of oil (diesel, hydraulic and lubricating oil) and spill of battery acids (sulphuric acid). Organic materials are left in the tunnels due to human activities, construction work (wood) and cleaning operations (degreasing compounds and detergents).

Organic material in the repository may influence its performance. An example is complexing agents in degreasing compounds, detergents and lubricating oils, which may form complexes with radionuclides and influence their transport properties. Organic materials as well as nitrogen may increase the growth of microbes and may therefore indirectly influence e.g. metal corrosion and water chemistry.

An estimate of potential amounts of stray material remaining in the repository after closure is made in Appendix C. The quantities introduced during construction and operation of the repository can be compared with quantities introduced with waste and packagings. In SFL 3 the quantities are relatively small compared to the quantities in the waste, where as in SFL 4 and SFL 5 no material of this kind is brought into the repository with the waste.

4 Construction and operation

The construction and operation of the repository will influence the groundwater inflow, the composition of the inflowing groundwater, the geochemical conditions in the near-field rock and the barrier properties at repository closure.

It will probably take at least a few years to construct the repository. This is followed by the operation phase that is expected to last a further 40 years. The closure and sealing will also take some years. Therefore, in total, the underground facility will be open for about 40 to 50 years. Drainage and ventilation during construction and operation will inevitably upset the natural hydrochemical conditions around the repository. In addition, the excavation of the repository and stray materials left from construction and operation activities may influence the geochemical conditions in the repository.

4.1 Disturbance of groundwater

Salinity variations due to drainage

Drainage during construction and operation will cause a drawdown of water from near the ground surface and an upconing of groundwater from deeper levels, see Figure 4-1. The changes are expected to be larger in the vertical than in the horizontal direction. Groundwater near the surface will have a low content of dissolved solids in contrast to deep groundwater, which is often concentrated in dissolved salts. Drawdown can consequently result in a more dilute composition and upconing can cause the contrary for the water around the repository.

The most abundant ions in deep saline groundwater are Ca^{2+}, Na^{+} and Cl^{-}. There is a general tendency of salinity to increase at very deep levels. For example in Laxemar, close to the Äspö Hard Rock Laboratory, where a 1 700 m deep hole has been core drilled and sampled for groundwater, high salinity was encountered at about 1 000 m (Laaksoharju *et al.*, 1995). The concentration of chloride ions was 10 g/l at 1 000 m and increased to 47 g/l at 1 700 m, see Figure 4-2. Ocean seawater has, for comparison, a Cl^{-} content of 19.4 g/l (salinity 3.5%). Drainage, for 40 – 50 years, of an underground repository at 300 – 400 m depth at a site as, for example, Laxemar will tend to lift the deep saline groundwater towards the facility. However, due to the higher density of saline water, it's far from certain that it will ever reach the repository and, anyway, the bulk of the heavier saline water will tend to sink back after closure (Follin *et al.,* 1995). Only a diffuse mixing transition zone is expected to remain.

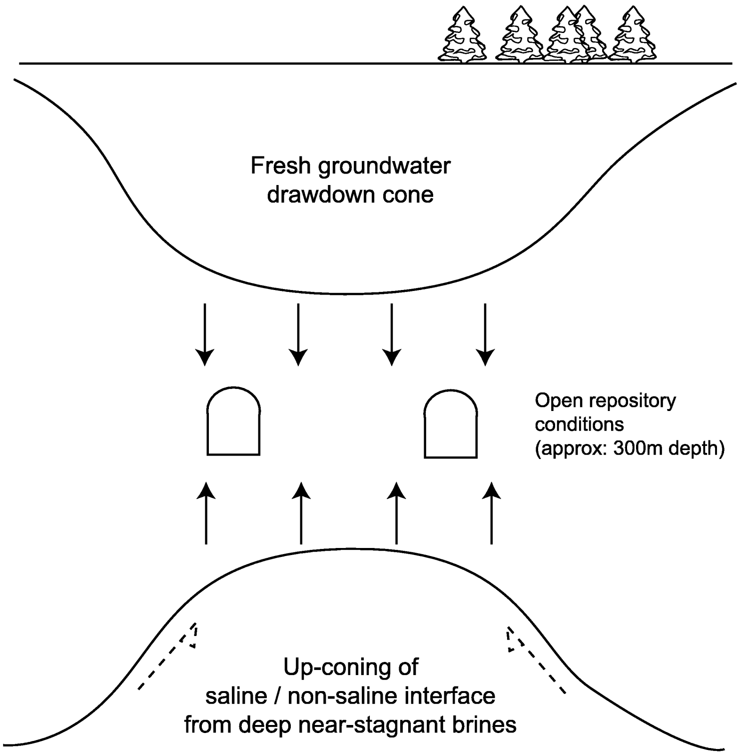

Figure 4-1 Schematic diagram showing potential drainage effects during open repository conditions. In reality the interface will be diffuse, representing a gradual transition from fresh to salt water types.

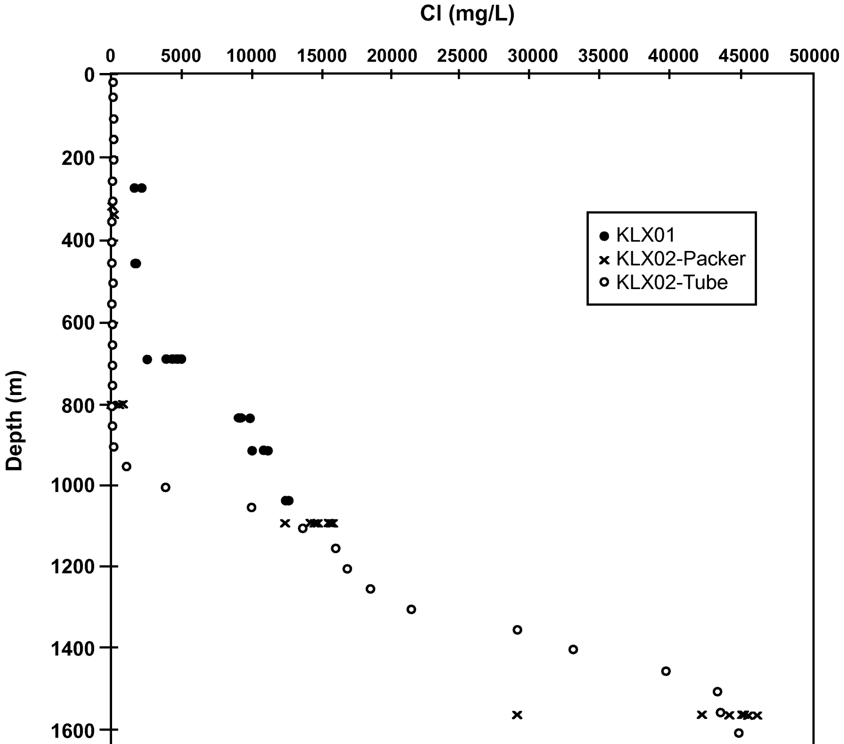

Figure 4-2 Concentration profiles (chloride) from Laxemar, SE Sweden, measured in the drillholes KLX01 and KLX02. After Laaksoharju et al. (1995).

Forced inflow and redox conditions

Surface water contains oxygen in contrast to deep groundwater, which is reducing. At normal recharge conditions much of the oxygen in the infiltrating water is consumed already in the soil cover due to biological processes. This situation will be upset by the drainage during construction. However, no permanent disturbance of deep groundwater Eh is expected despite the increase in infiltration. This has been demonstrated in the in-situ studies performed at the Äspö Hard Rock Laboratory (Banwart *et al.,* 1993). Groundwater that infiltrated through a subvertical fracture zone was sampled by intersecting drill holes from a tunnel at 70 m depth. Oxygen never entered the sampling points despite the forced inflow due to the drainage of the tunnel, see also Chapter 7 for further explanation.

Forced inflow and pH-conditions

Modern surface water can be rather acidic due to atmospheric pollution by for example sulphur dioxide. However, this should not affect the pH at great depth since the rock has a considerable capacity to buffer any attempted lowering of the pH, see Chapter 7. This capacity should be enough even when the inflow of near-surface water is forced due to the drainage of the repository below because this situation will only last for the limited time of construction and operation.

4.2 Disturbance of near-field rock

Influence of ventilation air and engine exhausts

Air will of course enter the repository during construction and operation via the open and ventilated tunnels and shafts. Steel components will be corroded by oxygen in the humid environment. However, the rock itself should be fairly well protected from oxidation in deep underground vaults due to the constant inflow of groundwater with reducing components such as Fe^{2+}.

Excavation effects on near-field rock

The excavation will disturb the rock close to a tunnel. Several experiments aiming to study the magnitude and extension of this disturbance have been carried out. An example is the ZEDEX experiments carried out in Äspö (Emsley *et al.,* 1997). These experiments show that a disturbed zone with increased fracturing and permeability will develop around the tunnel. The extension of this zone around a blasted tunnel is about 0.3 m at the ceiling and at the walls, whereas the extension below the tunnel is about 0.8 m. Furthermore, a stress re-distribution zone will be formed and the extension of this zone is further out, about one tunnel diameter. The stress re-distribution zone shows no new fractures and only small changes in permeability. The reason for this is that there are mainly elastic movements in this zone.

The rock surfaces in the disturbed zone with increased fracturing may to some extent be oxidised during the construction and operation of the repository. However, the depth of oxidation will be limited due to the constant flow of reducing groundwater towards the tunnel, see Section 7.1.4.

4.3 Disturbance of barrier properties

Carbonation of concrete

There will be an addition of carbon dioxide from the engine exhausts (unless electric engines are used) which will cause carbonation in exposed concrete. The reaction produces calcite and the carbonation depth in good concrete is about 5 mm after 50 years (Lagerblad and Trägårdh, 1994).

Steel corrosion

A reaction that will definitely occur is corrosion of steel components due to humid conditions. Aerobic corrosion is expected and it will be enhanced if saline groundwater is seeping into the underground facility, for example, as mine dripping. Steel in concrete will be well protected but exposed or insufficiently covered surfaces will suffer corrosion. Although this can be of some concern during the operation of the facility, it's not important for the long-time safety.

Microbial action

Organic material can be degraded by the action of bacteria and fungi. However, organic material in the waste will be kept away from water in the open and drained phase, and, according to experience, no significant growth of either bacteria or fungi is expected in the waste. The mine walls are different matters. It is well known that the parts of the wall that are wetted by inflow of water are rapidly covered by mats of bacteria (Pedersen and Karlsson, 1995). Some organic material will be generated by this process and left on the mine walls. However, compared to the organic content in the waste itself, all additions by bacterial growth will only be marginal at most.

4.4 Expected conditions at repository closure

Stability of chemical conditions in the repository

No major chemical changes are expected in the waste itself, the concrete structures or in the backfill (gravel and porous concrete) during the 40 – 50 years of construction and operation. Water will be bound as pore water or otherwise absorbed in the materials which will prevent mixing and subsequent reactions that can occur if concrete pore water comes in contact with some of the materials in the waste or backfill. Certain materials can be affected by concrete pore water. For example, aluminium will corrode at high pH and cellulose can become hydrolysed. Other possible reactions are ion exchange in bentonite, if that is used in some parts as backfill or plugging material. However, all the examples mentioned require more saturated conditions so that concrete pore water components can be transported by advection or diffusion to the possible sites of reaction. That is not expected to happen in the open drained and ventilated phase. Possible exceptions would be materials intimately mixed with concrete, for example, spent ion exchange resins or waste sludges conditioned in concrete. However, according to experience, these mixtures of waste and concrete are very stable.

Humidity and pore water in waste and concrete

The repository parts SFL 3, 4 and 5 will, of course, be drained and ventilated during construction and operation. Still they will contain some water, for example, as humidity in the waste and as water left in the pores of the concrete after construction. The water will always be bound in the material because liquid waste will not be accepted for transport and disposal. Waste containing water such as ion exchange resins and sludges will be either dewatered prior to packaging or conditioned in concrete.

The water in the pores of the concrete will have a characteristic chemical signature with high pH and a relatively high content of sodium and potassium ions. Typical concrete pore water composition of Ordinary Portland Cement (Degerhamn anläggningcement) concrete is given in Table 3-2.

4.5 Summary and concluding remarks

The open, ventilated and drained phase of construction and operation is expected to last for about 40 – 50 years. Water chemistry conditions of importance to SFL 3-5 during that phase are as follows:

- The waste, backfill and concrete structures will contain absorbed water. The water left in the pores of the concrete will have a high pH of about 13 with Na^+, K^+ and Ca^{2+} as the main cations to balance OH^-.
- Mass transport of dissolved constituents will be limited. It can be regarded as an unmixed state and no major chemical changes are expected in the waste and backfill despite the high pH in the concrete pore water.
- Bacteria growing on wet rock walls are unimportant compared to the total inventory of organic material in the repository.
- Drawdown of surface water due to drainage can dilute the groundwater, but no permanent changes in redox or pH conditions are expected as a result of the forced inflow.
- Upconing of saline groundwater from deeper levels can increase the concentration of ions in the near field of the repository. However, upconing of very saline water from levels more than 500 m below the repository is not expected.
- Oxygen in the ventilation air will corrode exposed steel in the humid environment. Concrete covered steel will be better protected.
- Carbon dioxide in the air will cause some carbonisation of the concrete.
- Bacteria and fungi are not expected to cause any significant decomposition of organic material in the waste.

5 Saturation and mixing after closure

5.1 General conditions in SFL 3-5

Restoration of groundwater head and infiltration into the repository

After the drainage pumps have stopped and the repository is closed and sealed, groundwater will slowly fill the voids and its level and heads will be restored to former conditions. The time needed for restoration depends on the inflow rate, which can vary as much as 0.3 – 300 m^3/m of tunnel and year according to experience from the SFR facility, Stripa Mine and Äspö Hard Rock Laboratory. Consequently the restoration time can vary as much as tens to a few hundred years depending on the hydraulic qualities of the host rock, see Appendix A.

The inflow of surface water will slow down when the groundwater level is restored and any upconing of heavier saline water will tend to sink back as soon as the drainage stops. This does not necessarily mean a complete return to the composition the groundwater had before construction of the repository; a large portion of modern water from near surface localities will probably remain. If saline water has been pumped up to the facility it might leave a diffuse mixing transition zone after it has reverted to its former depth. However, large deviations in the concentration of main components are not expected compared to what was analysed prior to excavation. A safe assumption is to expect a composition anywhere between saline and non-saline water. Natural redox conditions are expected to be restored as indicated by observations made at the Äspö Hard Rock Laboratory (Banwart *et al.*, 1993).

Post closure groundwater conditions in the near field

It is difficult to say what unsaturated conditions would cause if the drainage pumping would lower the groundwater level down to repository depth. However, the reducing capacity in the bedrock is considerable and the time of construction and operation is limited. So, apart from mixing, a composition similar to that before excavation would be expected in the near-field groundwater, at least as far as pH, redox and major components are concerned, see Chapter 7.

Groundwater infiltrating the repository will pass the engineered barriers and finally reach the waste, see Figure 5-1. A water phase will be established in the porosities and voids of the barriers and the waste. Air left in the voids will be compressed and start to dissolve in the water. Components from the different materials will be dissolved in the infiltrating water and chemical reactions can occur, for example precipitation, corrosion, hydrolysis, ion exchange etc. Water will have different compositions in different parts of the repository, for example, close to ambient deep groundwater in the backfill and close to concrete pore water inside the structures. Flow and diffusion will tend to even out the different compositions with time but this will take considerably longer than to reach the hydraulic equilibrium and some chemical characteristics, for example the high pH of concrete, can remain for hundreds of thousand years. The intention of this section is to describe the chemical changes and conditions that develop during the time of hydraulic saturation which is expected to take less than a few hundred years.

Air trapped in the repository

Air will be left in the porosities and voids of the sealed repository. When water enters the air will become compressed according to Boyle's law. For example a hydraulic pressure of 40 bar at 400 m depth will decrease the air volume by a factor of 40. Air will start to dissolve in the water (Henry's law) and a relatively inert component, such as nitrogen, will slowly diffuse through the water filled pores. Oxygen, however, will react and eventually be consumed by, for example, steel corrosion, oxidation of ferrous iron and sulphides, and decomposition of organic materials. The redox reactions will be unevenly distributed through the repository depending, among other things, on the materials present in different parts. Microbes can possibly assist and speed up the oxygen consumption.

Influence of the concrete on water composition

Concrete walls, reinforced with steel, will be built in SFL 3 and SFL 5, and high porosity concrete will presumably be used as backfill between the waste packages in SFL 3 and SFL 5. Some of the waste containers are made of steel reinforced concrete and concrete will be used for conditioning of spent ion exchangers and sludges. Some of the waste packages are backfilled with concrete. The composition of the cement will be identical or similar to Degerhamn Standard Portland Cement. The chemical composition of the pore water in the cement at the time of closure and sealing will be similar to that given in Table 3-2.

The concrete will influence groundwater, entering the repository after the drainage has stopped. Fresh concrete can create a pH of more than 13 due to its content of highly soluble sodium and potassium hydroxide, see Table 3-2. Leaching of concrete can exhaust the alkali hydroxides and the pH will then be controlled by portlandite at a value of about 12.5. This has been convincingly demonstrated by cement leaching experiments (Engkvist *et al.*, 1996). The chemical composition of water that fill up the voids of the repository during the time of hydraulic saturation, will depend on a series of conditions such as geometry, time of saturation, mass transport by advection and diffusion, cement to water ratio, and other materials present.

5.1.1 Summary and concluding remarks

The time after closure will start with a period of hydraulic saturation that will last less than a few hundred years. The infiltrating water is expected to induce the following chemical changes and conditions:

- Air trapped in the repository will be compressed and start to dissolve in the water entering the repository after closure and sealing.
- Oxygen from the air will be consumed by reactions such as steel corrosion, oxidation of ferrous iron and sulphides, and decomposition of organic material.
- The hydrogeochemical parameters such as pH and Eh will be restored in the host rock.
- The concentration of main components in the near-field groundwater will start to normalise after the drainage pumping has stopped. However, an upconing of saline water can possibly leave a diffuse zone of mixing behind.

- Alkali hydroxides and portlandite in cement will increase the pH of water in contact with concrete. The pH can range from 12 to more than 13 depending on the leaching conditions. Total silica content in the water can increase as a result of the pH increase.
- Concrete (Degerhamn Standard Portland Cement) can add Na^+, K^+ and Ca^{2+} to the water by dissolution and consume SO_4^{2-}, Mg^{2+} and CO_3^{2-} by precipitation in the cement (ettringite, brucite and calcite).

5.2 Conditions in SFL 3

5.2.1 Infiltration and development of water composition

SFL 3 is designed as a cavern with concrete caissons where waste from Studsvik and operational waste from CLAB and the encapsulation plant will be emplaced (Forsgren *et al.,* 1996). The cavern walls will presumably be lined with shotcrete and the floor drained by a bed of gravel covered by a layer of concrete. The interior of the concrete caissons is foreseen to be backfilled with porous concrete and the empty void between the concrete structure and the near-field rock is foreseen to be backfilled with gravel.

After closure and sealing, water will start to infiltrate the SFL 3 cavern, seep through the shotcrete lining and through the gravel bed. Water reaching the backfill will penetrate it and eventually find its way into the concrete caissons. There is no means to prevent intrusion of water, due to the hydraulic pressure that will build up outside the repository when the drainage stops (maximum of about 40 bar at 400 m depth).

Water coming into the caisson, through cracks or joints in the concrete structure, will be distributed through the porous concrete backfill there and finally find its way into the waste packages. Again, the build-up of hydraulic pressure will eventually be high enough for the water to penetrate the concrete lids and walls of the packages.

The chemistry of water will change along the flow path. The infiltrating groundwater may pick up some cement components from either shotcrete or floor paving. Still, the chemistry of the water entering the backfill should not be much different from groundwater. However, inside the SFL 3 caissons the porous concrete backfill and all other concrete components should have a profound influence on the water chemistry.

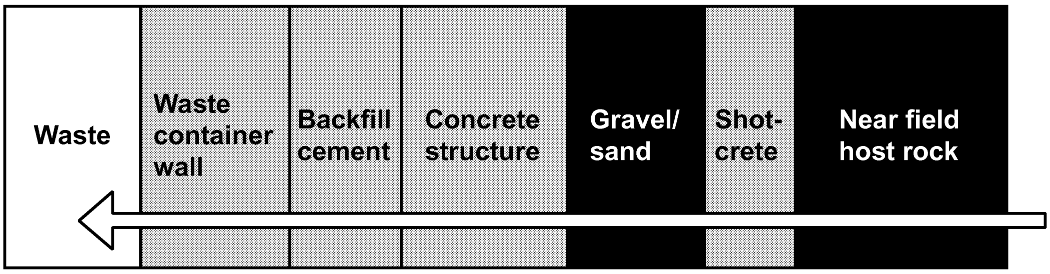

Figure 5-1 Schematic illustration of water infiltrating SFL 3 after closure and sealing of the repository.

5.2.2 Reactions induced by infiltrating water

Steel corrosion and redox conditions

Oxic corrosion of steel components will continue for some time after closure of the repository. This will help to consume the oxygen left in the trapped air and create reducing conditions, which are generally beneficial. However, after all oxygen has been consumed the corrosion will continue as an anaerobic process although at a lower rate (Neall, 1994) and hydrogen will be generated.

Anaerobic steel corrosion could in principle generate hydrogen at a rate high enough to exceed the solubility of hydrogen in water and create a separate gas phase. This is important for the performance of the repository barriers (gas release, displacement of water etc.), but not so much from a chemical viewpoint. It is unclear whether hydrogen gas will be reactive or relatively inert under repository conditions. It can act as a reductant if used by bacteria (as electron donor). However, none of these reactions are important for performance assessment.

Anaerobic corrosion will produce ferrous iron compounds, and Fe^{2+} ions will be released to the water. Ferrous iron will keep the redox potential down even when all the steel has been corroded away and the redox pair Fe^{2+}/Fe(III) is expected to define a redox potential in the repository (Sharland *et al.*, 1986).

Aluminium corrosion

Aluminium is relatively stable in groundwater but it will start to corrode if the pH increases by the influence of concrete. Corrosion of aluminium will also generate hydrogen and the rate is relatively high. A potentially high rate of gas formation is important to consider for the performance assessment of the repository barriers.

Influence on organic materials

A high ionic strength, due to concrete leaching and saline groundwater, can at least in principle influence the ion exchange resins, which is also of importance for performance assessment (sorption of radionuclides on ion exchange resins).

A high pH and calcium concentration due to concrete has been demonstrated to influence some of the organic compounds present, by hydrolysis. Most of the organic materials in the repository are not seriously affected but cellulose is of some concern because compounds are generated which form strong complexes with some of the radionuclides at high pH (Allard *et al.*, 1995).

Microbial actions

Microbes trapped in the repository will experience a gradual loss of oxygen during the phase of saturation. Oxygen will be consumed by steel corrosion, sulphides in the bentonite, infiltrating reducing groundwater (Fe^{2+}) etc. Bacteria can in fact speed up the process by, for example, metabolic oxidation of organic material. Some bacteria can be active without oxygen, and anaerobic biodegradation of organic materials such as cellulose is a possible source of methane and carbon dioxide in a closed repository (Wiborgh (ed.), 1995). Carbon dioxide will be consumed by reactions in concrete (carbonation of cement) but methane could possibly form a separate gas phase. This has been evaluated (Wiborgh (ed.), 1995) and it was concluded that the rate will be relatively low compared to, for example, hydrogen generation by steel corrosion.

An increase in the content of dissolved organic matter in the repository SFL 3 and its near-field water has to be anticipated. Bacterial decomposition is one possible source; hydrolysis of cellulose has been mentioned above. Part of the dissolved organic matter is believed to be similar in character to the natural dissolved organic substances in groundwater.

Summary of processes induced by infiltrating water

The infiltrating water will change the conditions in the SFL 3 repository and set the stage for the long-time performance. The following chemical reactions are of importance:

- Steel corrosion will help to consume the oxygen left by aerobic corrosion. Slow anaerobic corrosion will take over when oxygen has disappeared and generate hydrogen. This will continue for at least 1 000 years.
- Aluminium is relatively stable in groundwater but it will start to corrode (and generate hydrogen) if the pH is increased by the cement.
- High pH water can affect (hydrolyse) organic material, in particular cellulose. This is important because complexing agents can be generated that way.
- Microbes can assist in the reduction of oxygen and anaerobic bacteria can possibly decompose cellulose, which would generate methane and carbon dioxide.

5.2.3 Expected water composition in SFL 3 at saturation

The composition of water inside the walls of the concrete structure will be similar to that obtained in experiments with cement leaching or pressing of concrete pore water. Initially the pH could reach as high as 13.5 and gradually leaching of alkali hydroxides and portlandite leads to a reduction of the pH to about 12.5. This has been demonstrated by experiments (Engkvist *et al.,* 1996). However, it cannot be excluded that isolated pockets or voids in the waste may retain a low pH, but any migrating species to or from the waste will have to pass concrete walls and porous concrete backfill with high pH.

The composition of water in the backfill gravel outside the SFL 3 caissons is less certain. Groundwater flow conditions, concrete leach rates and geochemical reactions will be the governing factors. A safe assumption would be a composition interval between that of pure groundwater and water inside the structure.

Two examples of the development of the water composition inside the concrete structures are illustrated in Table 5-1. In Case 1 non-saline groundwater is assumed to intrude SFL 3 and in Case 2 saline water intrusion is illustrated. Cement pore water from fresh concrete will have a pH of 13 to 13.5 as has been demonstrated by pore water sampling, see Table 3-2. With time the pH of the intruding groundwater will increase too, but not reaching as high as the cement pore water in all parts of the repository. However, any mass transport occurring to or from the waste will have to pass zones of high pH (around 13) in concrete walls and concrete backfill containing pore water, at least until the bulk of alkali hydroxides (NaOH and KOH) have been leached out or lost due to reactions.

The sodium content in the intruding groundwater can either decrease or increase depending if the water is rich (saline) or poor (non-saline) compared to the cement pore water. Potassium, on the other hand, is always limited in groundwater in contrast to concrete pore water, which is rich in K^+, so potassium concentration will increase. Calcium will become controlled by the solubility of portlandite ($Ca(OH)_2$) when pH starts to increase. Magnesium will precipitate (as brucite) and carbonate ions will precipitate due to increase in pH, which shifts the bicarbonate ions over to carbonate (forming calcite). Sulphate and, to some extent, chloride can be taken up by the cement but leaching experiments indicate that they may remain relatively high.

Table 5-1 Examples of water composition development inside the SFL 3 (and SFL 5) structures after the repository has been saturated with groundwater.

	Case 1. Non-saline groundwater[a]			Case 2. Saline groundwater[b]		
Element and pH	Intruding groundwater mmoles/l	Direction of change in the groundwater	Cement pore water[c] mmoles/l	Intruding groundwater mmoles/l	Direction of change in the groundwater	Cement pore water[c] mmoles/l
pH	9.3	increase	13.1	7.7	increase	13.1
Na^+	5	increase	28	91	decrease	28
K^+	0.05	increase	83	0.2	increase	83
Mg^+	0.04	precipitate	<0.02	2	precipitate	<0.02
Ca^{2+}	0.5	–	0.9	47	precipitate	0.9
$CO_3{}^{2-}{}_{tot}$	0.3	precipitate	0.1	0.2	precipitate	0.1
$SO_4{}^{2-}$	0.001	–	0.04	6	decrease	0.04
Cl^-	5	–	<2	181	decrease	<2

[a] The non-saline water from section 404 – 406.7 m in KGI04, Gideå, is taken as an example (see Table 2-1).

[b] The saline water from section 530 – 535 m in KAS02, Äspö is taken as an example (see Table 2-1).

[c] The cement pore water obtained from a 3 month old sample of Degerhamn standard Portland cement is taken as an example (see Table 3-2).

The expected ranges of water composition inside the walls of the SFL 3 (and SFL 5) concrete structures, at saturation, can be summarised as follows:

- pH in the range 12.5 – 13.5 with values above 13 mainly in the concrete pores.
- Sodium concentration mostly dependent on the original groundwater (5 – 100 mmoles/l).
- Potassium concentrations well above ambient groundwater (0.05 – 100 mmoles/l).
- Calcium concentrations controlled by pH and portlandite (1 – 20 mmoles/l).
- Magnesium and carbonate are held at low concentrations by precipitation.
- Sulphate and chloride possibly modified by the concrete but relatively close to that of the ambient groundwater (0 – 6 mmoles/l for sulphate and 5 – 200 mmoles/l for chloride).

The expected ranges of water composition in the gravel backfill at saturation can be summarised as:

- pH in the range 7.7 – 12.5.
- Sodium, chloride and sulphate close to that of ambient groundwater (5 – 100 mmoles/l for sodium, 5 – 200 mmoles/l for chloride and 0 – 6 mmoles/l for sulphate).
- Potassium slightly enriched and the ions calcium, bicarbonate and magnesium possibly depleted due to the influence of concrete (if the pH is affected).

5.3 Conditions in SFL 4

5.3.1 Infiltration and development of water composition

SFL 4 consists of tunnels which will be used for deep disposal of the fuel storage canisters from CLAB, the decommissioning waste from CLAB and the encapsulation plant, the transport casks and transport containers. This waste will arise very late in the program. A layer of gravel, with concrete paving will cover the tunnel floor. The walls will presumably be lined with shotcrete. Steel containers will be used and the containers will presumably be backfilled with concrete or a more inert material (sand). The waste will consist of scrap metal, concrete debris etc. Not much organic material will be included in this kind of waste. Gravel will be used to backfill SFL 4.

The concrete components in SFL 4 could influence the groundwater infiltrating after closure and sealing. However, this is not certain, considering the large amount of water and the limited amount of concrete components. Therefore, a better assumption is a range of compositions between pure groundwater and the concrete affected groundwater, similar to the situation in the gravel backfill of SFL 3 (see Section 5.2.3).

5.3.2 Steel corrosion and redox conditions

The mild steel components will corrode and consume much of the oxygen left in SFL 4. Anaerobic corrosion will continue after all oxygen has been consumed and that will generate hydrogen. It should be noted that anaerobic corrosion would also include stainless steel.

Redox conditions will stabilise after oxygen has been consumed. Iron, iron corrosion products and groundwater components will be important, and the redox pair Fe^{2+}/Fe(III) is expected to define a redox potential in the repository (Sharland *et al.*, 1986).

5.3.3 Expected water composition in SFL 4 at saturation

The expected water composition in SFL 4 at saturation depends on the backfill in the containers. There are two possibilities presented here, one with concrete as backfill and a second with a more inert backfill (e.g. sand).

The expected ranges of water composition in SFL 4 when saturated by intruding groundwater will be similar to that described for the gravel backfill in SFL 3 if the containers are backfilled with inert (sand), which can be summarised as:

- pH in the range 8 – 12.5.
- Sodium, chloride and sulphate close to that of ambient groundwater (5 – 100 mmoles/l for sodium, 5 – 200 mmoles/l for chloride and 0 – 6 mmoles/l for sulphate).
- Potassium slightly enriched and the ions calcium, bicarbonate and magnesium possibly depleted due to the influence of concrete (if the pH is affected).

If the containers are backfilled with concrete the expected ranges of water composition in SFL 5 at saturation is the same as for SFL 3 (see Section 5.2.3). The expected ranges of water composition inside the SFL 4 containers is the same as the composition inside the walls of the SFL 3 (and SFL 5) concrete structures. The water composition in the SFL 4 gravel backfill is within the same ranges as for the backfill gravel in SFL 3 (and SFL 5).

5.4 Conditions in SFL 5

5.4.1 Infiltration and development of water composition

SFL 5 is a cavern for disposal of core components and internal parts from the nuclear power reactors. The waste will be placed in concrete containers. The design of the concrete structures is the same as in SFL 3 and shotcrete will presumably be used to line the rock walls. The voids in the caissons will be backfilled with porous concrete, after emplacement of the waste containers. The concrete structure will rest on a bed of gravel. After SFL 5 has been filled, a lid of concrete elements is placed on top of the compartments and gravel is used to backfill all voids between the concrete structures and the rock walls

Infiltrating water, after closure and sealing, will find ways through the shotcrete, gravel bed, gravel backfill and concrete structure, and finally reach the waste containers. The process will be similar to that described for SFL 3 (see Section 5.2.1).

5.4.2 Steel corrosion and redox conditions

Aerobic corrosion of mild steel components will help to consume the oxygen trapped in the voids and porosities after closure, and aerobic corrosion will be followed by a slow anaerobic corrosion after oxygen has disappeared. SFL 5 contains considerable quantities of stainless steel, which will also corrode in an oxygen free environment but at a slow rate.

As for SFL 3, anaerobic corrosion could in principle generate hydrogen in SFL 5 at a rate high enough to exceed the solubility of hydrogen in water and thereby generate a separate gas phase. Again, this is important for the performance of the repository barriers but not for the chemical composition of water because hydrogen gas is relatively inert under repository conditions. The corrosion products can, on the other hand, be important as a source of ferrous iron and the redox pair Fe^{2+}/Fe(III) is expected to define the redox potential in the repository (Sharland *et al.*, 1986).

5.4.3 Expected water composition in SFL 5 at saturation

The expected ranges of water composition in SFL 5 at saturation are the same as for SFL 3, see Section 5.2.3.

6 Normal evolution in long-term perspective

The evolution of the geochemical conditions in the repository and the vicinity of the repository in long-term perspective, without considering any external changes or disturbances, is often the definition of a normal evolution scenario ”Reference Scenario”. Here the focus is on the geochemical conditions in the near field of the repository. Therefore, the boundary conditions at the interface between the far-field rock and the near-field rock are assumed to be constant with time.

In this chapter the normal evolution of the geochemical conditions in the different repository parts of SFL 3-5 is discussed.

6.1 Normal evolution of SFL 3

6.1.1 The concrete structure

Concrete can be damaged by excessive leaching but studies of old concrete and natural analogues to concrete support the conclusion that Standard Portland cement will retain its binding capacity for at least as long as pH is controlled by portlandite. Therefore, in the absence of excessive leaching, the normal evolution in a long-term perspective is that concrete will essentially retain its structural strength (Wiborgh (ed.), 1995). At least, there is no reason to believe that it would start to crumble until it lost its portlandite component. Calculations show that for a fully hydrated structural concrete the porosity after leaching of alkali hydroxides and all portlandite may increase from about 15% to about 16% (Höglund and Bengtsson, 1991; Höglund, 1993). The time it takes to leach the portlandite to a depth of 1 m in a concrete barrier has been estimated to be of the order of a hundred thousand years and possibly longer, see Appendix B. After leaching of all calcium silicate hydrate (CSH), the porosity of a structural concrete has roughly doubled, i.e. increased from about 15 to 30% (Höglund and Bengtsson, 1991, and Andersson and Allard, 1986).

Corrosion of steel reinforcement, on the other hand, is inevitable and it cannot be expected to last as long as concrete itself. The loss of strength due to loss of reinforcement can be neglected because the underground structures are static as they are supported on the inside by the backfill of porous cement. However, the volume increase around the reinforcement due to the formation of corrosion products, with a lower density than steel, will eventually cause cracking and fragmentation of concrete. This is not too serious because reinforcement nets are close to the outer surface of the structure so the effect will essentially be limited to spallation of an outer layer of concrete.

Another possible mode of damage is if the rock pressure is transferred to the inner structure. A certain amount of rock creep is expected. The backfill gravel can take up part of that displacement but, if the movement continues, there will eventually be an increase of stress on the underground structure. As a normal scenario we assume that the displacement is small and that the structure can take the additional stress without any damage in the long-term perspective. However, we will also analyse the consequences of additional fracturing of the structure by this or any other cause (e. g. earthquake).

6.1.2 Water composition

Carbonate and magnesium transported to the repository by hydraulic flow and diffusion will precipitate as calcite and brucite respectively. There may also be some uptake of sulphate and chloride in the concrete. Soluble components can be lost from the concrete by leaching, for example, the alkali hydroxides. Apart from being very mobile the alkali hydroxides have also a tendency to react with, for example, silicate and alumina-silicate minerals. Such minerals are abundantly present in the concrete aggregates and in the backfill of crushed rock. There will evidently be a gradual loss of alkali hydroxides due to leaching or reactions or both and, with time, portlandite will stabilise the pH at about 12.5. The time it takes to leach the portlandite to a depth of 1 meter in a concrete structure has been estimated to be of the order of a hundred thousand years and possibly longer, see Appendix B. This means that the pH inside the concrete enclosure in SFL 3 and will not fall below about 12.5 during this time.

Since water is expected to eventually enter all voids of the repository we expect pH to be consistently high throughout the repository. It may be argued that, for example, some waste packages will remain tight enough to allow a local water composition to establish itself. However, these pockets of different water composition must have very little connection with its surrounding in order to remain unperturbed, considering the high mobility of hydroxide ions or, alternatively, be dynamic enough to consume these as they arrive. In any case, different chemical environments inside the SFL 3 structure will, figuratively speaking, represent ”isolated islands in the concrete environment”.

Any release of high pH components is expected to be neutralised by reactions in the backfill of crushed rock, see Appendix B.

6.1.3 Metals, organic materials and redox conditions

Metals such as steel, zinc and aluminium will corrode and hydrogen will be generated for as long as there are any of these metals left.

Groundwater at repository depth is reducing and these conditions will be further promoted by some components in the repository, for example, iron and corrosion products of iron, and organic materials.

Anaerobic processes are the only options for microbes in the repository. Microbes must also be extremely alkalofilic in order to remain active under chemical conditions dominated by concrete, unless they are able to find isolated locations, for example, in waste drums where concrete pore water leachates have not reached, or that the organisms themselves can lower the pH in these places. Organic material will be present and some production of carbon dioxide and methane is feasible.

6.1.4 Expected water composition in SFL 3 in a long-term perspective

In summary, the composition inside the SFL 3 structure is expected to be as follows:

- A homogenous water composition is expected to be established with pH in the range 12.5 – 13.5. With time the alkali hydroxides will cease to dominate and pH become controlled at about 12.5 by the influence of portlandite.
- The dominating cations are Na^+, K^+ and Ca^{2+}, where the latter ion is controlled by portlandite solubility.
- The dominating anions are OH^- from cement (controlling pH), Cl^- from groundwater (if saline) and SO_4^{2-} from either cement or groundwater.
- The concentration of DOC (dissolved organic carbon) can be increased by the presence of organic materials in the waste.
- It is likely that hydrogen will be generated by anaerobic corrosion. Another possible gas is methane from fermentation reactions, but carbon dioxide is expected to be precipitated as calcite by concrete pore water.

The water composition in the backfill will continue to be influenced by the mass of concrete. So even in the long-term perspective we expect the ranges of composition presented for the gravel backfill at saturation (see Section 5.2.3):

- pH in the range 7.7 – 12.5.
- Na^+, Cl^- and SO_4^{2-} close to that of ambient groundwater.
- The ions Ca^{2+}, Mg^{2+} and HCO_3^- possibly depleted due to high pH reactions in the concrete or backfill (gravel).
- It is likely that hydrogen will be generated by anaerobic corrosion.

6.2 Normal evolution of SFL 4

The expected groundwater composition in SFL 4 in a long-term perspective is dependent on the amount of concrete in the tunnels. The amount of concrete in SFL 4 is limited compared to SFL 3 and 5 if the containers will be backfilled with sand. Another possibility is to backfill the containers with concrete and in this case there will be considerable amounts of concrete in the SFL 4 tunnels.

The amount of concrete in SFL 4 is limited compared to SFL 3 and 5, if the containers are backfilled with sand. However, even the limited amount of concrete could influence the groundwater composition. The extent of this influence is difficult to predict so therefore a range of compositions between pure groundwater and concrete affected groundwater is assumed for the long-term perspective too (see Section 5.3.3):

- pH in the range 8 – 12.5.
- Na^+, Cl^- and SO_4^{2-} close to that of ambient groundwater.
- The ions Ca^{2+}, Mg^{2+} and HCO_3^- possibly depleted due to high pH reactions in the concrete or backfill (gravel).

On the other hand, if the containers are backfilled with concrete the expected ranges of water composition in SFL 4 for the long-term perspective is assumed to be the same as for SFL 3 (see Section 5.2.3). The expected ranges of water composition inside the

SFL 4 containers is the same as the composition inside the walls of the SFL 3 (and SFL 5) concrete structures. The water composition in the SFL 4 gravel backfill is within the same ranges as for the backfill gravel in SFL 3 (and SFL 5).

Not much organic material will be present in SFL 4 waste so the influence on the dissolved organic content, DOC, is disregarded.

6.3 Normal evolution of SFL 5

SFL 5 has basically the same design and structure as SFL 3, but the waste is simpler from a chemical point of view, i. e. the waste is metallic (e. g. stainless steel and zircaloy) and no organic materials. Therefore, the same development is expected for SFL 5 as for SFL 3 (see Section 6.1). However, considering chemical conditions, it is important to note that there is no contribution to DOC from organic components in the waste (see Section 6.1.4). In addition to that, inhomogenities in water composition are even more unlikely in SFL 5 as compared to SFL 3 due to the more homogeneous composition of SFL 5 waste.

7 Possible variations in long-term perspective

7.1 Geochemical stability of groundwater composition

7.1.1 Introduction – Development of groundwater composition

Meteoric water, i. e. rainwater and snowmelt, is almost pure water with air dissolved in it. Most of the groundwater found under land has a meteoric origin but a composition that is much different. Compared to rain water there is an increase in total dissolved solids, there is always some organic matter in groundwater and, most important, deep groundwater is devoid of oxygen. A widespread conception is that the typical groundwater composition is generated by the equilibration of rock minerals with meteoric water (unless, of course, seawater has infiltrated):

Meteoric water + Rock minerals → Groundwater

This is misleading because the biologically driven processes, during the early part of the recharge through soil layers and upper part of the rock, are very important. Organic matter, constantly added to the soil, is being consumed by biological oxidation and carbon dioxide is generated. The partial pressure of carbon dioxide in air is $3 \cdot 10^{-4}$ atm, but the composition of soil gas in the unsaturated soil zone will have a few hundred times higher CO_2-concentration than in the atmosphere (Stumm and Morgan, 1981). Carbon dioxide will form carbonic acid in the water and, for example, dissolve calcite minerals:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

The water in the unsaturated zone can take up oxygen, which is an open system to the atmosphere. The maximum concentration of oxygen is limited by the solubility of oxygen in water, at atmospheric pressure (about 10 mg/l). Deeper, where the soil (or rock) is saturated with water and isolated from direct contact with air, groundwater will start to lose oxygen as a result of biological and geochemical reactions. Recharge water entering the system of open fractures in the underlying rock may still contain oxygen though, especially if the soil layer is very thin or most of the rock surface in the area is devoid of soil cover. However, some organic matter is always dissolved in the infiltrating water and even in an area with little humic input there may be at least more than 10 mg/l of dissolved organic carbon (DOC) in the water. That is more than enough to consume any oxygen in the groundwater. For example, for a stochiometric composition CH_2O of the organic matter, less than 4 mg/l DOC is needed to consume 10 mg/l of oxygen. If the organic matter has the composition of methane, CH_4, less than 2 mg/l DOC is enough. It is uncertain and even unlikely that most of the organic constituents will react spontaneously with oxygen in groundwater, but microbes will mediate the reactions and they are proven to be very efficient (Pedersen and Karlsson, 1995).

This is a simplified description but it accounts for most of the typical groundwater constituents and, therefore, a much better ”groundwater formula” than the first one presented would be:

Water + Air + Organic matter + Minerals in soil and rock → Groundwater

Granitic groundwater composition at depth is relatively stable and insensitive to outer disturbances. Measured composition, pH and redox properties are generally repeated at different sites and typical values are obtained throughout the Fennoscandian Shield. Saline groundwater, which is found at very deep levels or at coastal sites, is of course a notable exception, but apart from that there is very little variation. The processes during recharge through the soil layers are part of the explanation. Other processes involving the rock minerals add to the overall capacity of the geochemical environment to buffer the groundwater composition. An important aspect of all such reactions is the kinetics involved. For example, a slow reaction might be fast enough in closed or near stagnant systems, but insufficient to control the properties in flowing groundwater. We can make general statements of the geochemical stability, but it is a considerable advantage to know the nature of any disturbance in order to make quantitative assessments of the geochemical reactions that neutralise it. An important task is therefore to find and analyse the different scenarios that influence the groundwater chemistry at repository depth. In the following, different groundwater properties and their sensitivities to chemical disturbances are summarised as a first step in the assessment of geochemical stability.

7.1.2 Acid/base reactions

Acids and calcite

Reactions between acids and calcite are fast and efficient. The products are carbonate species (HCO_3^- , H_2CO_3 and CO_2) and there is no protective layer formed which could hinder or slow down the reaction. Calcite is generally abundant in granite and there may be as much as a 1 – 2 %, concentrated to the fractures, which is where the water flows. Therefore, calcite will protect groundwater against acidification and it has not become depleted in the Swedish bedrock despite the constant addition of carbonic acids to the recharge water, at least not at great depths. For example, in the study of drill cores from the site Klipperås in SE Sweden, it was observed that calcite had been lost in the rock fissures of the upper part of the bedrock, but not below 100 m. It is remarkable that the front has not moved deeper despite the geologic scale of time (Tullborg, 1986). The main reason is probably the fact that only a fraction of the meteoric water is recharged into the rock and from that only a small fraction continues beyond 100 m. The mass-transport by advection down into the rock is very small compared to the conditions at the surface. At the surface acid input, for example by atmospheric pollution with sulphur dioxide, rapidly becomes a problem. We can illustrate the importance of depth and flow with a simple example. A reasonable average flow rate at 100 m depth at a typical site in Sweden would be 10 l/m^2a (Neretnieks, 1986 and Carlsson *et al.,* 1983). Let us assume a calcite content of 1 % and, further, that all the rock above 100 m is depleted of its pH-buffering capacity, and the water entering the 100 m level has pH = 4. The average speed of the pH-front would then be 2 µm/a and it would take 1 000 years for the front to move 2 mm and 1 million years to move 2 m. The rate will slow down even more at greater depth. This is due to the reduction of flow as a result of smaller lateral differences in the hydraulic pressure (and generally lower hydraulic conductivity) at deeper levels. Down at the 500 m level flow is generally below 0.1 l/m^2a.

Acids and aluminosilicate minerals

Calcite is by no means the only mineral that will react with acids. It has been argued that feldspars, which are part of the granitic minerals, and clay minerals, are in fact equally important. A natural case, which illustrates this, was found in a uranium mine in Poços de Caldas, Brazil. This site was carefully studied by an international team as an analogue to spent fuel disposal (Chapman *et al.*, 1993). Near surface water in the area is very acidic due to oxidation of pyrite, which generates sulphuric acid in the water. There is very little carbonate in the ground, but acidic infiltrating water is neutralised by reactions with potassium feldspars in the phonolitic rock and, as a result of that, the groundwater is dominated by potassium and sulphate ions. The pH at shallow depth is around 3 and typical groundwater below 20 m is in the range of 6 – 7 (Nordstrom *et al.,* 1992). The alkalinity of groundwater ranged from 2 to 20 mg/l. A second example is the groundwater at the uranium mine Cigar Lake, Canada. This was also used as a natural analogue study site similar to Poços de Caldas. Water was carefully sampled in boreholes from the surface and down to a depth of about 500 m. It was concluded that infiltrating groundwater was acidified by passage through the organic zone of the soils in the area. The overburden sand and the underlying sandstone is poor in carbonate and H^+ was apparently consumed by the dissolution of the clay minerals kaolinite and illite, which are abundant in the overburden (Cramer and Smellie, 1994). Possibly there was also some dissolution of feldspars and quartz. The pH in Cigar Lake groundwater samples ranged from 5.6 to 7.8 and the alkalinity from 10 to 100 mg/l. The two examples from Poços de Caldas and Cigar Lake demonstrates that if carbonate is not there to react with acids then aluminosilicate minerals will serve as well. The reaction is apparently relatively fast, at least compared to the rate of recharge at the depth of a few ten meters.

Bases reacting with silicate and aluminosilicate minerals

Silicate minerals in granitic rock will react with high pH-solutions, for example, in the form of leached pore fluid from cement which has a pH in the range 12 – 13 due to dissolution of alkali hydroxide and/or portlandite (calcium hydroxide) in the cement. The silicate minerals will dissolve as a result of hydrolysis reactions and, in return, secondary products will precipitate, for example CSH-phases, CASH-phases and zeolites. Valuable insight in the path of reactions between high pH groundwater and rock have been obtained by natural analogue studies, for example, the investigations of hyperalcaline springs in Maqarin, Jordan (Alexander, 1995). It was observed that CSH-phases where preferably generated at high pH and high calcium concentration, and CASH and zeolites at lower pH and calcium (but higher silica and alumina content in the water). A plume of dissolved portlandite from concrete underground is therefore expected to develop CSH near the source and, presumably, CASH and zeolites further out (Savage, 1996). The formation of zeolites would generally require pH 7 – 10.

The rate of dissolution at different pH-values has been measured for quartz (Knauss and Wollery, 1988) and albite (sodium feldspar) (Knauss and Wollery, 1986) at 70°C. This was further tested by experiments with synthetic cement pore fluids and rock forming silicate minerals (Savage *et al.*, 1992), where the rates determined by Knauss and Wollery were confirmed at pH 11 – 13. The rate of dissolution of quartz at pH=12 and 70°C was roughly 0.8 mol/m^2a and log(rate) was proportional to pH/2. The corresponding rate at 25°C is about 2 orders of magnitude lower with the same dependency on pH (Knauss and Wollery, 1988). There was no diffusion-limitation observed in the experiments despite the growth of secondary solids on primary silicates. However, we cannot rule out that the reaction will have a tendency to slow down with time and integrated progress. The fact that concrete can exist for 50 – 70 years in saturated conditions with pore water pH well above 12 and the ballast relatively intact indicate that the reaction is not all that efficient. A safe assumption is therefore to consider only a layer of the exposed rock as accessible to reaction and pH buffering at the rates given by Knauss and Wollery. Solubility and reaction rates of silica decrease with pH but, given enough time and contact surface, the geochemical reactions should be sufficiently effective to bring down pH to about 10 – 11 if a strong base intrudes the groundwater. This is an area that need to be further investigated and such work is in progress (e.g. the HPF experiments in Grimsel, Switzerland).

Groundwater alkalinity and pH-buffering

In Sweden carbonic acid from additions of carbon dioxide will generate bicarbonate ions by reactions with calcite or feldspars. The groundwater will have a pH in the range of 6.5 – 9.5, the carbonate system will be in equilibrium and the carbonate ions will give the water a pH-buffering capacity (Stumm and Morgan, 1981). The total carbonate concentration in groundwater is generally below 600 mg/l. There is a tendency for alkalinity to decrease with depth and values above 300 mg/l (total carbonate concentration) are unusual at 500 m depth. Very low values were, for example, measured in groundwater sampled from deep drillholes in the Stripa mine in mid Sweden (Nordstrom *et al.,* 1989). The alkalinity was of the order 10 – 20 mg/l and pH-values in the range of 9 – 10 at a depth of about 0.8 – 1 km in granitic rock. The high pH was explained to be the result of aluminosilicate hydrolysis, i. e. weathering of feldspars. An input of Ca^{2+}, due to the weathering reaction (or some other source), would cause calcite precipitation, which explains the low alkalinity. So the alkalinity can vary considerably but even low values will stabilise the pH of groundwater and give it a buffering capacity. For example, $2 \cdot 10^{-3}$ moles of H^+ or OH^- will be needed to push pH under 6 (acid addition) or above 10 (base addition) in one litre of groundwater with a pH of 7 and an alkalinity of 120 mg/l ($2 \cdot 10^{-3}$ moles/l, in this case bicarbonate). This is a normal value, frequently used in the laboratory to simulate groundwater at 300 – 400 m depth.

7.1.3 Main components and geochemical reactions

Calcium and sodium

The dominating cations in Swedish groundwater are Ca^{2+} and Na^+. Calcium is being generated by the dissolution of calcite by carbonic acid, as described above, and calcium and sodium can both be added by weathering of feldspars. Sodium has in some cases been introduced by the recharge of seawater, for example, at the coast or areas, which have been covered by the sea. There is evidently a balance between Ca^{2+} and Na^+ in granitic groundwater. Meteoric origin water with initially only calcium develops a sodium concentration at deeper levels and infiltrating sea water experiences a loss of sodium in exchange for calcium. The reason for this balance is probably either ion exchange in clay minerals or weathering/precipitation-reactions or both. The fact is that there exists such a balance, which will guarantee a certain concentration of calcium if sodium is present and vice versa. Very dilute groundwater is unusual at depth and the concentration of calcium (and sodium) is usually above 10 mg/l ($0.25 \cdot 10^{-3}$ moles/l) at 300 – 400 m depth. This is important because Ca^{2+} serves to destabilise colloidal particles and a minimum concentration of about 4 mg/l ($0.1 \cdot 10^{-3}$ moles/l) is needed for that.

Magnesium and potassium

The cations Mg^{2+} and K^+ are generally present but their concentrations are kept down by geochemical reactions. This is clearly seen in areas where seawater, originally rich in magnesium and potassium, has infiltrated. Magnesium is generally below 150 mg/l ($6 \cdot 10^{-3}$ moles/l) and potassium below 15 mg/l ($4 \cdot 10^{-4}$ moles/l) at 300 – 400 m depth. Probable explanations for that are ion-uptake in clay minerals (e. g. potassium in smectite) or precipitation reactions.

Carbonate, chloride and sulphate

The dominating anions in Swedish groundwater are HCO_3^- (CO_3^{2-} at high pH), Cl^- and SO_4^{2-}. The carbonate system has already been described in Section 7.1.3 and chloride is a conservative ion, not influenced by geochemical reactions. Chloride concentration can vary considerably with location and depth. It is therefore practical to distinguish between ”normal granitic groundwater” with HCO_3^- as the dominating anion and ”saline groundwater” with Cl^- as the most abundant negative ion. The chloride concentration in saline water is generally below 7 g/l (0.2 moles/l) at 300 – 400 m depth, but considerably higher concentrations can be found deeper (Smellie *et al.,* 1995). Sulphate concentration is highest in saline water. Sulphate is not necessarily correlated to chloride. Gypsum solubility is normally not a limiting factor but sulphate can be reduced by bacteria and that is a feasible explanation for the sometimes apparent loss of sulphate where seawater has infiltrated. Sulphate concentrations at 300 – 400 m is generally below 600 mg/l ($6 \cdot 10^{-3}$ moles/l), even in saline water.

Fluoride

The concentration of fluoride is low and controlled by the solubility of calcium fluoride ($pK_s = 10.3$) in combination with the concentration of calcium. In fact, fluoride is one of few groundwater components that are controlled by a relatively simple solubility relation.

7.1.4 Redox reactions

Bacterial reduction of oxygen, ferric iron and sulphate by organic matter

The consumption of atmospheric oxygen during recharge of groundwater through soil layers and the upper part of the bedrock has been described above in Section 7.1.1. Organic matter is the main reductant and microorganisms are playing a key role as catalysts of the redox reactions (Pedersen and Karlsson, 1995). At deeper levels, where oxygen has been depleted, there is an increase of dissolved iron, Fe^{2+}. The ferrous ions are generated by the reduction of ferric iron from minerals by iron reducing bacteria, IRB, which use organic matter as a reductant (Chapelle and Lovley, 1992). There is typically a maximum in the Fe^{2+}-concentration (about 0.1 – 1 mg/l) at a depth of roughly 100 m, but the concentration generally decreases down to a few µg/l at deeper levels, for example at 300 – 400 m. The reason for this is a competition between IRB and sulphate reducing bacteria, SRB (Chapelle and Lovley, 1992). The SRB also uses organic material and are more successful than IRB at deeper levels. The concentration of dissolved organic matter is lower at deeper levels and this seems to promote SRB. A possible explanation is that SRB are more efficient at low concentrations of nutrients compared to IRB. Reduction of sulphate, SO_4^{2-}, generates sulphide, SH^-, which precipitates Fe^{2+} as iron sulphide or pyrite. This explains the decrease in dissolved iron, which is generally found at deeper levels. Sulphide is common below 100 m but the concentration is generally in the µg/l-range. Concentration of organic matter decreases with depth as a result of these processes. The content of dissolved organic carbon, DOC, near the surface can be 10 – 20 mg/l and drop down to 1 – 2 mg/l at depth. Part of the organic matter consists of humic and fulvic acids. Low molecular fulvic acids dominate over humic acids at depth. A large part (sometimes the major part) of DOC is hydrophilic carboxylic acids.

In-situ experiments, performed at the Äspö Hard Rock Laboratory in SE Sweden, have demonstrated the efficiency of bacteria to reduce the infiltrating water and control the redox conditions (Banwart (ed.), 1995). Groundwater infiltrating through a vertical fracture zone was monitored from a tunnel at a depth of 70 m. By further excavation the tunnel intersected the zone and increased the inflow. After three weeks there was an arrival of shallow surface water but it remained anoxic despite the short distance to the ground surface. Microbial activity in the fracture zone was indicated. The soil is very thin in the recharge area, but there is apparently enough there to supply the infiltrating water with the organic matter needed for the reduction processes.

As shown by the Äspö experiments, organic matter at the ground surface infiltrates along with oxygen and this explains why the deep groundwater is shielded off from the atmospheric oxidation. However, the situation is different if oxygen is introduced directly into the near-stagnant water at, for example, 300 – 400 m depth. The concentration of organic matter at that depth is roughly 1 mg/l DOC, which implies that the capacity left to reduce the intruding oxygen would be very limited. It also remains to be demonstrated that the organic matter left is indeed useful. At worst the fact that it still remain could indicate that it is ”hard to digest” by the microbes. So we conclude that dissolved natural organic matter is an effective scavenger of oxygen in recharge water but its capacity to counter redox disturbances at depth is low and not yet fully proven.

Inorganic reduction by sulphide minerals

Pyrite reacts with oxygen in groundwater and the kinetics of this reaction has been investigated (Nicholson *et al.*, 1988 and 1990). The fact that the reaction occurs and is relatively fast is also demonstrated by the observations of a redox front in pyrite-containing rock. A good example was found in the uranium mine in Poços de Caldas, Brazil (Chapman *et al.,* 1993). Oxidising water had been infiltrating the rock containing pyrite and uranium, and a sharp front was clearly visible between red oxidised (ferric iron) and grey pyrite-containing rock. The sharp front indicated that pyrite oxidation was fast compared to diffusion. There were no signs of bacteria that could have mediated the reaction. Precipitated uranium was found a few centimetres behind the front, on the reducing side, which indicated that not only molecular oxygen was reduced but also uranyl ions (U(VI) to U(IV)). Pyrite is commonly present as an accessory mineral in low concentration in granitic rock. It is more frequent at depth (e. g. below 100 m) and part of the total pyrite content is concentrated in the fracture fillings where it can be easily attacked by oxidants. We assume 1% of the rock to consist of fracture minerals and at least 0.1% of that to be pyrite (Tullborg, 1996). This amounts to a total reducing capacity from pyrite in deep granitic rock of 1 µmoles/kg (µmoles electrons).

Inorganic reduction by iron(II) minerals

Ferrous iron, Fe(II), is relatively abundant in the granitic rock minerals. There may be more than 1% iron in Swedish bedrock and most of it is divalent iron. Laboratory experiments with bedrock samples indicate that at least part of the iron(II) in the minerals is available for oxidation at a rate that is observable in the laboratory system (days and weeks) (Wikberg, 1987). Detailed studies of redox kinetics and iron(II) dissolution from iron containing silicates have also been reported (White and Yee, 1985, Malmström *et al.,* 1995, and Malmström and Banwart, 1997). Two possible reaction paths have been suggested: a) dissolution of Fe^{2+} and subsequent reaction with dissolved oxygen, and b) direct uptake of O_2 by Fe(II)-sites at the mineral surfaces. The latter alternative is supported by Cui who studied the reduction of pertechnetate ions, TcO_4^-, and concluded that sorption of the ion was needed prior to reduction by iron(II) (Cui, 1996). Either way, the redox reaction with Fe(II)-minerals is expected to occur and consume oxygen with a time constant in the range tens to hundreds of years.

Laboratory experiments have been carried out to measure the capacity of rock samples to consume oxygen (Pirhonen and Pitkänen, 1991). A high pressure of O_2 was used (autoclave, 100 bar and 25 °C) and the decrease of Fe(II) in the sample was measured. The redox capacity, according to this method, varied between 7 and 220 µmoles/kg. A sample of granite had the capacity 10 µmoles/kg. To reach Fe(II) in the matrix of the samples requires oxygen transport by diffusion, which is a slow process (Neretnieks, 1986). This will have an influence on the total rate and it is necessary to take this into account when calculating oxygen consumption by reactions with iron(II) in rock.

Observations of in-situ consumption of oxygen in granitic rock have been reported by Gascoyne (1997). The experiment was performed at the 420 m level in the Underground Rock Laboratory (URL) at Lac du Bonnet in Manitoba, Canada. The URL is situated in a granitic batholith, which is part of the Canadian Shield. Three boreholes in the unfractured grey granite were filled with air saturated de-ionised water and a total of 6 zones in these boreholes were isolated by water filled packers. The primary aim was to observe the rate of influx of dissolved ions from the rock matrix but it also gave the opportunity to estimate the rate of oxygen consumption by the rock. A minimum oxygen consumption rate of $1.5 \cdot 10^{-10}$ mol/m^2/s (4.7 mmol/m^2/a) was obtained.

In-situ redox experiments are being carried out at the Äspö Hard Rock Laboratory. This is called the REX-project and the goal is to assess and demonstrate the capacity of the rock to buffer against oxidising disturbance, and determine the kinetics of oxygen consumption (SKB*,* 1997).

Groundwater redox capacity and Eh

Deep groundwater is strictly oxygen free and the only oxidising components are sulphate ions (generally below 500 mg/l at depth) and traces of, for example, nitrate ions. Reducing components are only present at trace levels (a few mg/l to µg/l) at depth, for example Fe^{2+}, HS^-, Mn^{2+} and DOC. A platinum electrode or some other inert electrode (e. g. gold or glassy carbon) can measure an Eh-value. It has to be done on site and preferably in-situ (Wikberg, 1987).

It should be noted that there is a marked contrast between acid/base-conditions and redox conditions in groundwater. The H^+-ions are solvatised, the acid/base reactions in solution are fast and there is, in general, enough bicarbonate ions to stabilise and buffer the pH. It is therefore relatively simple to measure a stable pH, which applies to all acid/base-pairs in solution. The only exception is where solid phases are involved, for example silica and aluminosilicate minerals. However, the redox active electron, e^-, is not solvatised in water but only carried inside a reductant. Kinetics becomes important and redox reactions are frequently slow or inhibited. There is no well defined pe (i. e. $-\log\{e^-\}$) that applies to all redox pairs in groundwater. For example, Fe^{2+}/Fe^{3+} and SO_4^{2-}/HS^- are generally not in equilibrium with each other and a reason for that is the inhibited reduction of SO_4^{2-} [S(VIII+] protected by the shell of 4 O[II-]).

It is still meaningful though to measure a pe, or Eh, by using electrodes in groundwater. Firstly, because Eh-measurements are extremely sensitive to oxygen. Traces of oxygen, which cannot be measured by e g an oxygen electrode, will have a strong influence on a platinum electrode for Eh. Secondly, it has been demonstrated that the redox couple Fe^{2+}/Fe^{3+} is generally effective in deep groundwater and defines an electron activity (chemical activity) that is also measured by the electrodes (Grenthe *et al.*, 1992). Dissolved divalent iron can be obtained by analyses and the activity of Fe^{3+} is given by the solubility of hydrous ferric oxide, which depends on pH. The Eh-value calculated by these parameters fits well the measurements with Eh-electrodes (Brandberg *et* al., 1993). The redox potential at 100 m depth and below is in general between -400 and -100 mV, which suggests two important conclusions for performance assessment: firstly the deep environment is completely anoxic, and secondly redox sensitive elements like U, Np and Tc will appear in their tetravalent, low soluble and less mobile, oxidation state. However, the effective redox capacity of groundwater is very low and there is only Fe^{2+} and/or HS^- ions at trace levels. This makes the water reducing in all cases, except when bacteria can catalyse reactions with sulphate, which can be relatively abundant in groundwater. Sulphate is used by strains of sulphate reducing bacteria, SRB, as electron acceptor (oxidant) for biochemical reactions with organic material or hydrogen electron donors (reductants).

7.2 Old concrete and natural analogues

7.2.1 Concrete properties

Cement

Portland cement is made by the heating of an intimate mixture of clay and limestone (roughly 1/5 clay and 4/5 limestone) in a rotary kiln up to a final temperature of about

1 450 °C. Phases of lime, belite (a calcium silicate), aluminate and ferrite are beginning to form at about 800 °C. At temperatures above 1 300 °C, alite (another calcium silicate) is being formed at the expense of lime and belite (Taylor, 1990). The phases in the cooled cement clinker product are crystalline and most important are alite and belite which are referred to in cement chemistry nomenclature as C_3S (tricalcium silicate) for alite and C_2S (dicalcium silicate) for belite, see Table 7-1. The clinker is crushed and mixed with various additives, for example gypsum, to give the product the desired properties.

Table 7-1 The phase composition of Degerhamn Std Portland cement (Lagerblad and Trägårdh, 1994).

Idealised formula	Cement nomenclature	Wt. %
Ca_3SiO_5	C_3S	51
Ca_2SiO_4	C_2S	25
$Ca_3Al_2O_6$	C_3A	1.2
$Ca_2(Al,Fe)_2O_5$	C_4AF	14

Cement paste

Concrete is a mixture of cement, sand, gravel (or crushed rock) and water. More precisely, the mixture is termed *mortar* if only sand is used and *concrete* when it contains coarse aggregates such as gravel or crushed rock. Cement and water forms *cement paste*, which sets and hardens due to the hydration reactions of the cement grains. Cement paste with a water to cement ratio (w/c) of about 0.38 should, in principle, be fully hydrated (Taylor, 1990). However, unhydrated cement minerals can be found even in concretes with a higher w/c (Lagerblad and Trägårdh, 1994). The hydration products start to grow from the surface of the clinker grains and fill the space between the aggregate grains. The main hydration products are poorly crystalline calcium silicate hydrates and calcium hydroxide (portlandite). The calcium silicate hydrates form a gel in the cement paste and is referred to as C-S-H in concrete chemistry nomenclature (Calcium-Silicate-Hydrogel). The wet density of the gel phase C-S-H is 1.85 – 1.9 g/cm^3 and that of saturated cement paste is 1.9 – 2.1 g/cm^3 (Taylor, 1990, p 141). In hardened concrete C-S-H is the principal binding phase, which holds the solid grains of cement, sand and gravel together.

The calcium silicate hydrogel, C-S-H, is semicrystalline and X-ray diffraction gives a diffuse pattern with only general indications of its structure. The Ca/Si ratio can vary from 0.8 to 3 with variable amounts of water. The reference concrete, made by Degerhamn Std Portland cement has the Ca/Si ratio in C-S-H of about 1.7 (Lagerblad and Trägårdh, 1994). Calcium silicate hydrates are known as minerals and closest in composition to C-S-H in cement are tobermorite ($C_5S_6H_9$ approx.) and jennite ($C_9S_6H_{11}$ approx.). Semicrystalline calcium silicate hydrates exists which are intermediate in structure between these two compounds and C-S-H gel, for example C-S-H(I) and C-S-H(II). They are relatively well defined and close to tobermorite and jennite in composition and structure (Taylor, 1990, p 143). In cement paste there will also be some substitution of Si for Al and Fe(III).

Investigations of the C-S-H structure in hardened cement paste indicate a layer structure which, together with a pore solution, forms a rigid gel with pores ranging in size from macroscopic (>50 nm) to enlarged interlayer spaces of nanometer dimensions. The C-S-H layers are expected to form subparallel groups, a few layers thick, which enclose pores of dimensions from interlayer spaces and upwards (Feldman-Sereda model, presented in Taylor, 1990, p 252).

Water in cement paste

Water in hardened paste is present in different thermodynamic states depending on if, and how, the water molecules interact with the cement phases:

- **Free water** where the water molecules are not directly affected by the forces from the mineral surfaces.
- **Absorbed water** which consists of about two layers of water molecules influenced by the mineral surfaces.
- **Structural water** in the minerals such as crystal water and hydroxyl groups (e. g. portlandite).

Several methods have been used to study how water occurs in the cement paste and how it is bound, for example, TG (TermoGravimetry) and DTA (Differential Thermal Analysis). A fully hydrated and saturated Portland cement with w/c ratio 0.5 is described by Taylor (Taylor, 1990, p 251) to consist of 21 % (weight % of total water) capillary water, 38 % gel water and 41 % of non-evaporable water (Powers-Brownyard description). Free water, according to the definition above, will be found in the capillary fraction and in parts of the gel (pore spaces). Absorbed water will mainly be in the gel, where it is expected to be the dominating form. Possibly there is also some absorbed water in the non-evaporable part. Structural water is essentially found in the fraction of non-evapourable water.

The water in the gel phase is finely dispersed; most of it is sorbed or remains in narrow, possibly isolated, pore spaces. Consequently, it has a very low permeability, which is typical for a gel phase, and the hydraulic conductivity of a cement paste is restricted to the fraction of capillary water. The amount of capillary water will, of course, depend very much on the w/c ratio.

Cement pore water is a definition, which refers in general to water present in concrete. It can also be seen as an operational definition referring to the water obtained by pressing samples of cement paste or concrete. Dissolved constituents in concrete will be present in the free water but also, to some extent, affected by sorption. However, the influence of sorption is not expected to be strong enough to influence the results of sampling by pressing so the analysis of pore water samples should be relevant for the conditions in the cement paste.

Cement pore water composition

Alkali hydroxides (NaOH and KOH) in the fresh cement paste will generate a high pH of about 13 and more, see Table 3-2. If the alkali hydroxides are leached out or consumed by chemical reactions, there is enough portlandite ($Ca(OH)_2$) to keep the pH of cement pore water at about 12.5. The capacity to control the pH at a high level can be estimated from the composition of cement (see Table 7-2) or measured in leaching experiments.

Table 7-2 The analytical composition of Degerhamn Std Portland cement (Lagerblad and Trägårdh, 1994).

Oxide	% of weight	Oxide	% of weight
CaO	64.5	K_2O	0.6
SiO_2	22.2	Na_2O	0.1
Al_2O_3	3.5	Total alkali (as % Na_2O)	0.5
Fe_2O_3	4.7	Free lime[a]	0.8

[a] *Free lime is CaO from unreacted rests of burnt lime.*

It is reasonable to expect that a major portion of the alkali metals Na and K can be released as NaOH and KOH by leaching. Degerhamn std Portland cement with a composition according to Table 7-1 has a total alkali oxide content of 0.5 % (weight % as Na_2O), see Table 7-2. For simplicity, we assume that all of it can be released as hydroxides. Concrete contains roughly 350 kg of cement per m^3, which could then release a total of 56 moles of alkali hydroxides per m^3 of concrete.

The same way of reasoning can hardly be applied to calcium hydroxide because the calcium, originating from calcium silicates (alite and belite) and free lime, will appear both in C-S-H and portlandite in the hydrated cement paste; most of it will be in C-S-H. There will also be some unhydrated clinker left with Ca bound in it. Therefore, it would be exaggerated to assume that all of the CaO in Table 7-2 is available as portlandite. Engkvist *et al.* (*1996*) leached samples of crushed cement paste until pH was below 12 and found a weight loss of 20 % (Albinsson, 1996). Most of this is $Ca(OH)_2$. Concrete contains about 350 kg of cement (ca 420 kg as hydrated cement paste) per m^3 concrete which, combined with Engkvist's results, implies that 1 m^3 of concrete can release 2 300 moles of hydroxide ions from $Ca(OH)_2$. According to Taylor (Taylor, 1990, p 129) 1.15 moles of portlandite is obtained by the hydration of C_3S in cement. Using Taylor's data and the content 51 % of C_3S according to Table 7-1 a portlandite content of 900 moles is obtained. The free lime (see Table 7-2) would add another 100 moles to that so the total would be 1 000 moles of $Ca(OH)_2$ (2 000 moles of hydroxide ions) in 1 m^3 of concrete which is in reasonable agreement with the previous value. In summary, we conclude that between 2 000 – 2 300 moles of hydroxide ions can be dissolved from $Ca(OH)_2$ in 1 m^3 of concrete.

Leaching of C-S-H will start when there is no portlandite left. The dissolution of C-S-H is incongruent with a higher Ca/Si-ratio in solution than in the solid. The Ca/Si ratio of remaining C-S-H will go down to 0.85, where dissolution becomes congruent (Atkins *et al.*, 1992). The pH will successively drop to 11 and remain there during the congruent phase. A model for the dissolution of C-S-H has been developed by Berner (1987). For stoichiometric reasons it is not possible to release more hydroxides from C-S-H dissolution than what remains of calcium after the leaching of portlandite. The total analytical content of CaO is 65.3% (including free lime) according to Table 7-2. Subtracting the portlandite part, we find that less than 6 000 moles of hydroxide ions can be released from C-S-H in 1 m^3 of concrete.

Table 7-3 Release of hydroxides from 1 m^3 of concrete due to leaching.

Leached material/compound	pH	Moles OH^-
1 m^3 of concrete (350 kg of cement)		
NaOH and KOH	13.5 – 12.5	<56
$Ca(OH)_2$	12.5 – 12	2 000 – 2 300
C-S-H	12 – 11	<6 000

7.2.2 Old concrete

Modern cement of the Portland type has existed for about 90 years. That is not very old but it is still worthwhile to study samples from early concrete structures and look for trends of changes because signs of recrystallisation and products from later reactions can be analysed. Old concrete in contact with air generally shows signs of carbonation to a certain depth due to intrusion of carbon dioxide. This is less relevant for underground structures and concrete samples from water saturated environments are therefore preferred.

Structure of old cement paste

The cement paste in samples of old concrete from the wall of a water tunnel at the Porjus dam were investigated by Grudemo (1982) with X-ray diffraction. The tunnel was built in 1914 but, according to the analysis, no significant change in crystallinity had occurred after 65 years in a water filled inflow tunnel. It was concluded that the C-S-H phases would remain stable for a long time. Rayment (1986) made an electron micro-probe analysis of C-S-H in 136-year-old cement paste and found no major difference compared to modern Portland cement. The C-S-H had remained stable and still unreacted cement clinker grains were observed. Rayment and Pettifer (1987) examined samples of mortar from the Hadrian’s Wall, built by the Romans 1 700 years ago. The ancient Roman concrete is different from modern concrete made by Portland cement. The Roman concrete is based on the reactions between slaked lime and pozzolanic materials like volcanic ash. It is not quite certain if the Romans were consciously attempting to use hydraulic cement for the structure of the wall or merely lime mortar which, by chance, happened to include a silica component. However, despite the differences, products typical of hydraulic cement were formed in Hadrian’s Wall, for example C-S-H phases, and the investigation found that the poorly crystalline phases had remained in the Roman mortar.

Lagerblad (1996) made a comprehensive study of samples from old concrete structures throughout Sweden. The aim was to find and investigate cases relevant to the deep repository situation and preference was given to samples from water saturated environments. Thin section microscopy, SEM and X-ray diffraction were used. An overview of the study is given in Table 7-4.

Table 7-4 Summary of observations made by Lagerblad (1996).

Name	Age	Environment	Clinker	w/c[a]	New phases and crystals
Sillre/Oxsjön hydropower dam	59 y	Humid	Relic grains	>0.65	Calcite and ettringite
School building in Gävle	100 y	Dry	Relic grains	>0.7	Calcite and/or ettringite
Midskogsforsen hydro power plant	52 y	Saturated	Hydrated	0.5	Ettringite
Rocksta mill	96 y	Wet	Hydrated	>0.7	Ettringite and portlandite
Älvkarleby hydropower plant - inspection tunnel	79 y	Dry	Relic grains	<0.3	N. D.
Älvkarleby hydropower plant - discharge chamber	79 y	Saturated	Some relic grains	0.4 – 0.6	Ettringite and portlandite
Uppsala castle water tank	90 y	Saturated	Relic grains	0.4	Calcite, ettringite and portlandite

[a] *Estimate of w/c by comparison to modern concrete.*

The investigators found relic grains of unhydrated cement clinker, up to a particle diameter of 0.3 mm, in most of the samples. Cases were also found where the grain had left a hollow shell of hydration products behind. Leaching could possibly explain that phenomenon. Calcite precipitations were found, and crystals of ettringite and portlandite, which tend to grow into voids left in the cement paste. The C-S-H in the good quality old concretes (e. g. the water tank) has a composition similar to modern cement paste and it was concluded that C-S-H is very stable if the leaching is kept down by, for example, a low hydraulic conductivity. Concrete with a relatively low w/c ratio (e. g. the inspection tunnel and the water tank) showed a positive maturity development where slowly hydrating clinker grains fill the pore spaces and the concrete gains additional strength by these reactions. The water tank in Uppsala has a quality today that would be difficult to reproduce in young concrete, at least without using superplasticisers.

Reactions at cement/rock interfaces

Hodgkinson and Hughes (1996) investigated cores taken from the Hadrian's Wall (1 700-year-old Roman structure). The core intersected the contact between the old mortar and a quartz dolerite block. The methods SEM (Scanning Electron Microscopy) and microprobe was used for the analysis and an increased porosity, mainly due to feldspar dissolution, was found 1 – 2 mm into the dolerite. Phases of C-A-S-H had replaced feldspar and pyroxene to a depth of 0.5 mm into the dolerite. It was concluded that feldspar is the most reactive of the dolerite minerals followed by quartz, pyroxene etc. This is in good agreement with the laboratory experiments, which demonstrates that feldspar, and quartz reacts with high pH solutions from cement, see Section 7.1.2. The high pH source in Roman cement is slaked lime ($Ca(OH)_2$) and it would be interesting to know whether portlandite is still present in the samples.

Pore water leaching

Samples from the water tunnel at the Porjus dam were also used for analysis of pore water composition, see Table 7-5. The pore water was obtained by pressing (Gjörv, 1982 and Gjörv and Havdal, 1982).

Table 7-5 Pore water from samples of the 65-year-old Porjus hydropower plant (from the inflow tunnel) compared to pore water from samples of fresh standard Portland cement.

	Fresh std Portland[a]	Old Porjus cement[b]
pH	13.2 – 13.4	12.4 – 13
	mmoles/l	mmoles/l
Na^+	60 – 80	4 – 150
K^+	140 – 120	3 – 130
Ca^{2+}	0.5 – 2	0.8 – 10
SO_4^{2-}	1 – 8	1 – 7

[a] *Andersson et al., 1989*
[b] *Gjörv and Havdal and Gjörv, 1982.*

The samples in Porjus were taken from the walls of the inflow tunnel. There is obviously portlandite left in the Porjus concrete, and probably alkali hydroxides too, despite the 65 years of lake water rushing through the tunnel. The concrete must have remained very dense and only allowed a slight loss of dissolved pore water constituents by diffusion.

Another example of concrete in contact with fresh water for a long time is the 90 year old water tank in Uppsala (Trägårdh and Lagerblad, 1998). The expected depletion of portlandite by leaching has been estimated in Appendix B. The value obtained is about 5 cm but the mortar has a thickness of about 2 cm so, according to the calculations, portlandite should have been completely leached out by now. This is in contrary to the observations that portlandite still exists in the cement and only the first cm is leached. It can be concluded that either the diffusion or the dissolution, or both, are slower than expected.

The observations from the studies of old concrete can be summarised as follows:

- Rests of unhydrated clinker grains can remain for at least 100 years and possibly much longer in a dense concrete.
- The strength tends to increase with time and the hydraulic conductivity decreases in a good quality concrete stored under saturated conditions, provided there is no strong hydraulic gradient driving water through the structure.
- Concrete with a high w/c ratio leave hollow spaces and shells, which can later be filled with recrystallisation and hydration products.

- Calcite is found as precipitates in the structure (due to infiltration of carbon dioxide or dissolved carbonates).
- Recrystallisation has been observed for ettringite and portlandite. The crystals are formed in void spaces in the structure.
- No recrystallisation of C-S-H is observed and this phase remains stable, at least as long as the pore water composition is controlled by portlandite (high pH and calcium concentration).
- Portlandite depletion of concrete due to leaching is at least a factor of 10 less than previously assumed in our performance assessments of repository structures.

7.2.3 Natural analogues

Background

Some of the mineral phases in cement paste and also the cement pore water composition are unusual in nature. However, the examples that exist are of great interest in so far as they can give us an insight into the long-term stability of concrete and its influence on the near-field environment. The last issue, concerning the high pH of pore water in Portland cement, has been the reason behind studies of so called hyperalkaline wells. Many of these are associated with ophiolite formations and, typically, can have a pH of up to about 11. Such wells are found, for example, in Cyprus and Oman. The water-mineral reactions, which give the high pH, are part of the alteration of highly reactive ultramafitic (rich in Mg and Fe) rock to serpentinite ($Mg_3Si_2O_5(OH)_4$). The water produced by the wells is generally rich in sodium, potassium, and calcium and saturated in magnesium (low concentration due to the high pH). Anions, in addition to hydroxide, are chloride and sulphate. Sulphide is common which tends to make the water reducing (Eh down to about -0.4 V).

Hyperalkaline wells in Oman have been studied as a natural analogue to the influence of cement on radioactive waste (Bath *et al.*, 1987). The well water pH was in the range 11 – 12. Trace concentrations of the elements Se, Pd, Sn, Zr, Ni, U and Th were analysed and compared to calculated values. This was a valuable test of the models and data, and our general ability to calculate the solubility of radionuclides at high pH in a repository. Bacteria and colloids were also analysed in the well water. Alkalophilic bacteria were found who could survive the high pH and some indications of colloids were also found, too uncertain for definitive conclusions but interesting enough to warrant further studies at other sites.

The Maqarin analogue

The hyperalkaline wells in Maqarin in Jordan have a different origin (Alexander (ed.), 1992). Bituminous marl (limestone and clay minerals), with an organic content of 15 – 20% has been burnt in situ to a cement-like material after spontaneous ignition, possibly caused by pyrite oxidation. The metamorphic zone of cement-like material lies within the original bituminous marl. The zone extends through the area with strongly varying thickness, of about 2 – 3 m to a maximum of 60 m. Groundwater, in contact with the metamorphic zone, develops a composition close to that of cement pore water. The pH is in the range 12 – 13 and the dominating cations are calcium, sodium and potassium.

Sulphate is a common anion in addition to hydroxide. A full description of the mineralogy etc. of cement-like material in Maqarin and its alteration products are given by Milodowski *et al.* (1992).

Maqarin is not unique in the area. There are similar zones of metamorphic cement-like rock, for example, in Central Jordan. According to Kolodny (1979) they are part of the so-called Mottled Zone complex and cement-like materials have been identified on other sites in the Mottled Zone.

Cement like material in Maqarin

The ^{230}Th ingrowth method was used to measure a maximum age of about 0.5 – 2 Ma for the metamorphism which produced the cement zone in Maqarin (Alexander *et al.,* 1996). Spontaneous combustion does still occur in the bituminous marl due to, for example, exposure following mechanical excavation. Temperatures of about 450 °C have been indicated at such events. Higher temperatures, in the range 800 – 1 000 °C, have been indicated by mineral analysis of the old metamorphic zones. The absence of C_3A phases is an indication that the temperatures were always lower than ambient in a cement kiln (1 450 °C). Therefore, according to Taylor (1990), we should expect belite (C_2S) and lime (CaO) but not much alite (C_3S). A calcium silica mineral C_2S (larnite) has been found and also CS (wollastonite) but the closest we come to alite in Maqarin is spurrite (C_5S_2-carbonate). However, tricalcium silicate, hatrurite (C_3S), has been identified in those parts of Mottled Zone, which are situated in the Negev desert. A reason for hatrurite to occur in Negev and not in Maqarin might be differences in maximum temperatures but more likely is the explanation that dry conditions in Negev have preserved tricalcium silicate from hydration. Some of the cement-like minerals identified in Maqarin and other parts the Mottled Zone are given in Table 7-6.

Table 7-6 Identified cement-like minerals from the metamorphic zone in Maqarin and in other locations of the Mottled Zone complex.

Mineral	Ideal formula	Cement nomenclature	Reference
wollastonite[a]	$CaSiO_3$	CS[a]	d,e
rankinite	Ca_3Si_2O	C_3S_2	d
larnite[b]	Ca_2SiO_4	C_2S	d,e
spurrite	$Ca_5(SiO_4)_2CO_3$	C_5S_2-carbonat	d,e
hatrurite[c]	Ca_3SiO_5	C_3S	d
brownmillerite	$Ca_2(Al,Fe)_2O_5$	C_4AF	d,e
mervinite	$Ca_3Mg(SiO_4)_2$	C_3MS_2	d
lime	CaO	C	d,e

[a] *Calcium monosilicate (CS) is not really a component of cement which is burnt at normal high temperature (1 450 °C).*
[b] *Larnite is similar to belite in cement (C_2S).*
[c] *Hatrurite is similar to alite in cement (C_3S).*
[d] *Kolodny (1979).*
[e] *Milodowski et al. (1992).*

Hydration of cement like phases

The formation of a hydrous gel phase (plombierite) from the natural dicalcium silicate mineral (CS_2) larnite has been described by McConnell (1954). The gels were collected at dolerite-chalk contacts at Ballycraigy and Scawt Hill near Larne in Northern Ireland. Pure larnite nodules were found, surrounded by sheets of gel up to 5 cm in thickness. The gel is transparent to translucent and brittle (hardness ca 4). An X-ray investigation showed that the silica hydrogel is essentially amorphous. According to McConnell the study suggested that the corresponding gel in hydrated cement would be stable for an indefinite period of time, at least in the presence of unhydrated clinker particles, and ”that, at high density, the gel would be competent to act as a rigid bonding medium in set cement”.

Carbon dioxide would eventually have destroyed the calcium silica gel, but a dense layer of carbonates, formed by initial carbonation, apparently protected the underlying gel.

The low-temperature reactions with the cement clinker-like phases in the metamorphic rock in Maqarin, such as hydration, carbonation and sulphatisation, have created a so-called retrograde assemblage of alteration minerals. This includes calcite, apatite, ettringite, thaumasite and portlandite, see Table 7-7. Locally and in some veins and dissolution cavities it was found that gypsum, afwallite apophyllite, vaterite, birunite and various tobermorites were the major minerals. The veins could be monomineralic. Many of the minerals in the retrograde assemblage in Maqarin are common to cement paste, including portlandite, ettringite and calcium silicate hydrates. Much of the alteration is very fine-grained and the different phases are often intimately intergrown and very hydrous. Larnite (C_2S) and spurrite (C_5S_2-carbonate) are the most readily altered, followed by ellestadite, then brownmillerite, with primary calcite and fluorapatite being the least reactive. Alteration along fractures has caused some degree of expansion and microfracturing. Some primary calcite appears to have been removed.

The earliest hydration product in Maqarin appears to have been calcium silicate hydrate with a gel-like morphology which have lined or infilled fractures and other cavities. The Ca/Si-ratio is between 0.8 – 0.85, which is similar to tobermorite ($C_5S_6H_9$). Ettringite (AFt) is very abundant and may dominate altered lithologies. In most fractures, ettringite is accompanied by thaumasite. Afwillite ($C_3S_2H_3$) seems to have replaced ettringite in some veins (preceded by precipitation of thaumasite).

Table 7-7 Identified cement-paste-like minerals in the retrograde metamorphic assemblage at Maqarin (Milodowski *et al.*, 1992).

Mineral	Ideal formula	Cement nomenclature
calcite[a]	$CaCO_3$	–
gibbsite [b]	$Al(OH)_3$	AH
brucite[c]	$Mg(OH)_2$	MH
portlandite	$Ca(OH)_2$	CH
quartz[d]	SiO_2	S
gypsum	$CaSO_4$	–
ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}\ 25H_2O$	AFt
thaumasite	$Ca_6Si_2(SO_4)_2(CO_3)_2(OH)_{12}\ 24H_2O$	AFt
afwillite[e]	$Ca_3Si_2O_4(OH)_6$	CSH
tobermorites[e]	$Ca_5Si_6O_{16}(OH)_2\quad 2\text{-}8H_2O$	CSH
jennite[e]	$Ca_9H_2Si_6O_{18}(OH)_8\ 6H_2O$	CSH
C-S-H gel	amorphous	C-S-H

[a] *As carbonation product in cement paste.*
[b] *Not a normal component of Portland cement (occurs in aluminate cement paste).*
[c] *Present if there is dolomite in the ballast or due to seawater intrusion.*
[d] *Silica present in the ballast and sometimes used as additive (e g silica fume).*
[e] *Calcium silica hydrates present as gel phases, with varying Ca/Si-ratios, in cement paste (see Section 7.2.1).*

High pH water in Maqarin

The hyperalkaline groundwater in Maqarin was sampled at several points (Alexander (ed.), 1992). Two are presented here as examples of their compositions, see Table 7-8.

Table 7-8 The MQ-2 samples are taken from a vertical tunnel, Adit 6, which cuts into the metamorphic zone. Water was collected dripping from a series of stalactites on the wall of the adit. Site MQ-5 is an artesian well on the bank of the Yarmouk river, about 10 cm above river level (Alexander (ed.), 1992).

Components	MQ-2 water	MQ-5 water
pH	12.34	12.52
Eh	308 mV	127 mV
	mmol/l	**mmol/l**
Ca^{2+}	14.7	26.2
Na^+	2.13	5.74
K^+	0.3	15.7
Sr^{2+}	0.08	0.18
SO_4^{2-}	2.90	15.4
Cl^-	1.59	1.44
F^-	0.021	0.049
NO_3^-	0.08	0.62
Ionic strenght	41.4	85.9

It is interesting to compare the composition of the hyperalkaline groundwater from Maqarin with the pore water pressed from fresh and old (Porjus) Portland concrete as presented in Table 7-5. The ions Na^+ and K^+ are within the range of that obtained from the concrete samples but concentrations of Ca^{2+} and SO_4^{2-} are slightly higher in Maqarin. The pH of Maqarin water is within the range of pore water from old concrete but lower than fresh concrete. The comparison implies that the Maqarin waters, in terms of concrete pore water composition, are slightly more developed than the old concrete water, i. e. pH is closer to 12.5 and Ca^{2+} starts to dominate over the alkali ions Na^+ and K^+. Another difference, less significant from this point of view, is the higher sulphate content, which is probably due to the local abundance of pyrite in Maqarin.

Hyperalkaline plume

An important task in the Maqarin project is the evaluation of the hyperalkaline groundwater influence on minerals in the surrounding rock (Savage, 1996 and Alexander *et al.*, 1996). It has been suggested that alkaline leachates from cement could influence the host rock in the near field of the repository and thereby change its radionuclide retention properties. This was evaluated from a theoretical point of view. Geochemical calculations were made with the code EQ 3 (Savage, 1996). Important parameters were pH, Ca^{2+}, dissolved silica and alumina in the plume water. A sequence of minerals was predicted where zeolites are formed first, when pH start to increase, followed by calcium alumina silicates (CASH) and calcium silicates (CSH), see Figure 7-1. The same sequence of minerals was identified in Maqarin and it was observed that fractures tend to seal as a result of the secondary minerals formed. Although the open fractures tend to clog, the pore spaces in the rock behind the fractures are still accessible to diffusion so the porosity in the adjacent rock has, apparently, remained open.

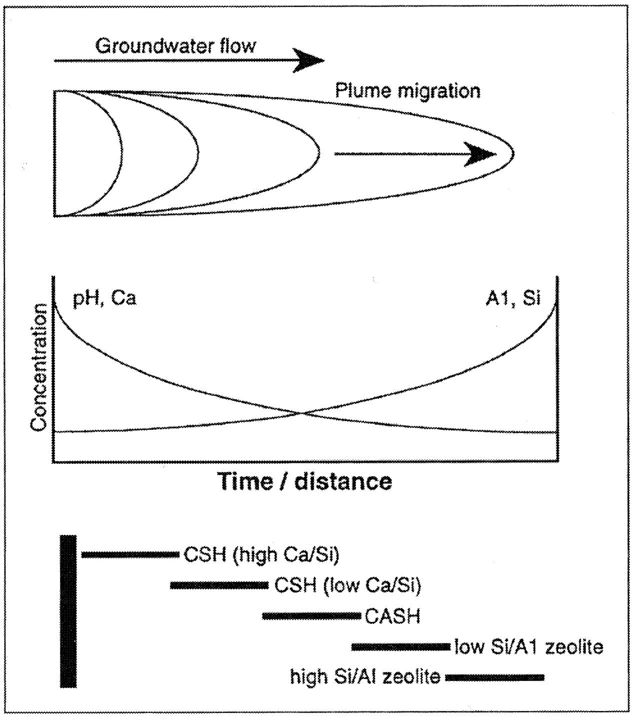

Figure 7-1 Schematic diagram of hyperalkaline plume migration from a cementitious source, showing hypothesed variations in fluid composition and alteration mineralogy in space and time (Savage, 1996).

Colloids and bacteria

Colloids, dissolved organic material and bacteria are also being studied in Maqarin. Colloid concentration is very low in the highly mineralised groundwater, in agreement with independent observations of low colloid concentrations in concrete pore water. Therefore, the Maqarin results support the conclusion from laboratory studies that colloids are not formed by cement paste. However, it has been argued that colloids could possibly be formed when pH drops at the front of the pH-plume, for example, due to silica supersaturation. This latter phenomenon has not been specifically investigated but, on the other hand, there is no other evidence of colloid formation in Maqarin either.

Dissolved organic matter in Maqarin groundwater is different from humic substances normally found in groundwater. Possible origins are infiltrated dissolved organics from the soil which have been transformed by the high alkalinity or, alternatively, soluble organic compounds from high pH leaching of the organic rich marl. These options are being further analysed.

It is possible that the organic matter has an influence on the solubility and sorption on the trace metals present in the Maqarin groundwater but no effect has been observed, despite the thorough trace element analyses and numerous calculations of their solubilities. This implies that any increase in solubility due to complex formation with the organics is relatively small. Some trace metals, which have been investigated in Maqarin, are: Al, V, Mn, Fe, Ni, Cu, Zn, Cr, Mo, Pb, La, Th and U (see below).

Investigations of the alkaline wells in Oman indicated the existence of bacteria which could survive at high pH (Bath *et al.*, 1987). Small populations of heterotrophs and sulphate reducing bacteria were found. These bacteria were also indicated by on-site tests of the hyperalkaline wells in Maqarin, Jordan, but it proved impossible to isolate them and they seemed to be inactive (Alexander (ed.), 1992). Later investigations of the Maqarin wells confirmed this result. Microorganisms were found in all of the Maqarin groundwaters but it could not be demonstrated that they were viable and growing there. The DNA (16S r RNA) gene sequencing technique was used for the analysis but no sequence found was typical for alkalophilic organisms. Therefore, it was suggested as a hypothesis that most of the Maqarin springs may be a bit too extreme for active life (Pedersen *et al.*, 1997).

Test of thermodynamic databases

The Maqarin water contains the trace elements: B, Li, Ba, Si, F, Br, P, Al, V, Mn, Fe, Ni, Cu, Zn, Cr, Mo, Pb, As, Se, La, Ra, Th and U. A selection of these trace elements: Se, Sn, Pb, Ni, Ra, Th and U (Alexander (ed.), 1992) were used in an exercise of predictive modelling where several groups independently calculated the concentration, speciation and solubility limiting phases of the trace elements in Maqarin groundwater. The trace elements had been carefully analysed and attempts made to identify the source minerals and phases, which control the solubility. The data were compared to the outcome of the calculations. The results were in general conservative in the sense that solubilities were overestimated in most cases. A reason for lower than predicted observations of solubilities can be found in the occurrence of solid solutions of trace elements in major mineral phases. The chemical activity of a trace element, contained as solid solution in another solid phase, is less than unity (in proportion to its concentration in the other phase) and its solubility in the water is lowered by that.

Compared to similar exercises with data from other sites, where groundwater pH is closer to neutral, there seems to be more discrepancies and more spread in the calculated values of Maqarin which implies that the thermodynamic database is more uncertain in the high pH-region. This is not unreasonable considering the difficulties to measure the chemical parameters at a very high pH and it supports the conclusion that directly measured solubilities are good complements to calculated values in cement environments.

The conclusions from the Maqarin analogue study can be summarised as follows:

- For more than 100 000 years cement minerals can remain and, to some extent, escape hydration under unsaturated conditions.
- Cement paste minerals, including CSH phases, remain for more than 100 000 years, at least if the hyperalkaline conditions prevail.
- C-H-S gels are found in the mineral assemblage and there is some tendency to a more ordered structure with time.
- The hyperalkaline water has a composition that is similar to solutions leached from old concrete (a later stage of leaching than, for example, the Porjus concrete).
- The hyperalkaline water reacts with the rock minerals (alumina silicates and silicates) and secondary minerals are formed which tend to clog the fractures and prevent water flow.
- The fracture surfaces are affected but the porosity of the adjacent rock is still open and accessible to diffusion of ions.
- Colloid concentration is very low in the strongly mineralised water and there is no colloid production observed.
- Dissolved organic matter is different from that in normal groundwater and possibly generated by hydrolysis of organic material in the marl. The dissolved organic compounds can, in principle, have an effect on metal solubility due to complex formation but there are no dramatic influences according to the trace element analysis.
- Bacteria are present in hyperalkaline water, but they may not be viable and growing at pH >12.5.
- Chemical thermodynamic data can be used, with care, to calculate element solubilities in hyperalkaline groundwater. The results are in general conservative due to the formation of solid solutions in major mineral phases. Thermodynamic data are more uncertain at a very high pH and comparisons to directly measured laboratory data are recommended.

7.3 Climate scenario

The spans of time considered in the assessment of the environmental impact of a deep repository with waste containing long-lived radionuclides are so long that changes in climate can be expected to occur. In Scandinavia, long-term changes in climate have led to not only changes in the biosphere, but also the formation of permafrost and continental ice sheets. Changes similar to those we have seen in the past are expected to occur in the future as well.

The description of the Scandinavian climatic conditions in SR 97 (SKB, 1999) is based on three climate-driven process domains, which are:

- Temperate/boreal domain
- Permafrost domain
- Glacial domain

The climate-driven process domains are supposed to provide a general picture of climate-driven conditions of importance for the evolution, performance and safety of the repository.

During the Quaternary period, the past 2 million years, the earth's climate has had several global cold periods when continental ice sheets and glaciers have formed. The cold periods have been followed by briefer warm periods with a climate similar to that of today. The cold periods are termed glacials and the warm periods are termed interglacials. During the past 900,000 years or so, a pattern is repeated with approximately 100,000-year-long glacials, ending abruptly in a transition to a warm interglacial climate.

The long cold periods, the glacials, contain colder and warmer stages called stadials and interstadials, respectively. During glacial periods, continental ice sheets and permafrost have extended over Scandinavia. During the warmer interstadials, the extent of the ice sheet may have been limited to the Caledonian mountains. Southeast of the ice, conditions may have gradually changed from permafrost to a temperate/boreal domain. During the cold stages, or stadials, the ice may have covered large parts of Norway, Sweden and Finland, extending during the most extreme cold periods in over Russia in the east and down to Germany and Poland in the south.

SR 97's climate scenario is based on a number of relatively simple calculations of the climatic evolution during the next glacial and interglacial period. It describes climate change during the coming 130,000 years. Conditions vary considerably during a glacial. The fluctuations can be seen as a variation of the extent of the climate-driven process domains in time and space. The evolution on a given site can be described as a temporal series of climate-driven process domains (SKB, 1999).

Temperate/boreal domain

The change within the temperate/boreal domain that is of the greatest importance for a repository is shoreline displacement. When the climate becomes colder, the sea level falls as water is bound in inland ice sheets all over the world. At the same time, the growing ice sheets cause downwarping of the earth's crust. In Sweden, crustal downwarping is generally greater than sea-level lowering. The sea level relative to a fixed point on the earth's crust – the relative coastline – rises during a glaciation.

The relative coastline rises as the ice sheet grows and the crust is depressed. Lowering of the relative coastline occurs during interglacial periods, when the previously ice-loaded and downwarped crust rebounds. The fastest lowering of the relative coastline occurs when the ice has just retreated from an area. Lowering of the relative coastline also occurs during the transition towards a colder climate due to the fact that the sea level falls.

When the relative coastline falls, the seabed becomes land. Groundwater flow gradients increase. Fresh precipitation water infiltrates the new land areas. When the relative coastline rises, land becomes sea once again. In the sea-covered areas, differences in water density can drive the groundwater flow. Salt water has a higher density than fresh water, and seawater can therefore infiltrate the bedrock.

Permafrost domain

Permafrost exists in areas where the ground temperature is below 0ºC for at least two consecutive years. Permafrost may be discontinuous or continuous. In areas with continuous permafrost, the ground is frozen everywhere, with the exception of major lakes and watercourses. In areas with discontinuous permafrost, sections with frozen ground are interspersed with unfrozen parts. In the transition towards temperate (boreal) conditions, the occurrence of permafrost becomes increasingly sporadic.

The climate is cold and relatively dry, with perhaps 50% of today's precipitation levels. Reduced precipitation and frozen ground result in very little groundwater recharge. The groundwater flow is limited to unfrozen sections of ground. The closely-spaced sections of frozen ground drive the groundwater flow to greater depths. Sections without permafrost are also frozen at the surface for most of the year. Most of the precipitation is cycled at the surface, so there is little water flow in the bedrock compared with present-day conditions. When the water in the rock fractures freezes, it expands and widens the fractures. Since the deformation is not fully elastic, the widening is partially permanent. The low temperatures lower reaction and dissolution rates. At the same time, the solubility of carbon dioxide increases, which means that the solubility of calcite increases. Water is frozen out, which means that salinity will increase.

Glacial domain

A glacial domain prevails in the presence of a continental ice sheet. Under the central portions of the ice sheet – the ice divide zone – the ground is frozen. The permafrost depth may be up around 400 m. Nearer the front of the ice sheet the pressure melting point is reached and a zone is formed where melting occurs in the interface between ground and ice, the melting zone.

In an analysis of the groundwater flow under glaciers, Boulton *et al*. (1999) suggest that the meltwater is mainly transported towards the ice marginal through ice tunnels in the ice/bedrock interface. The meltwater is transported in to the ice tunnels by groundwater flow. Water pressure and flow when the ice marginal lies in the sea are shown in Figure 7-2. The gradients for groundwater flows are high at the ice marginal and in towards the ice tunnels. Groundwater flow takes place both in towards the ice tunnels and out towards the ice marginal. The glacial meltwater is oxygen-rich. In the ice divide zone the ground is frozen and no groundwater flows occur.

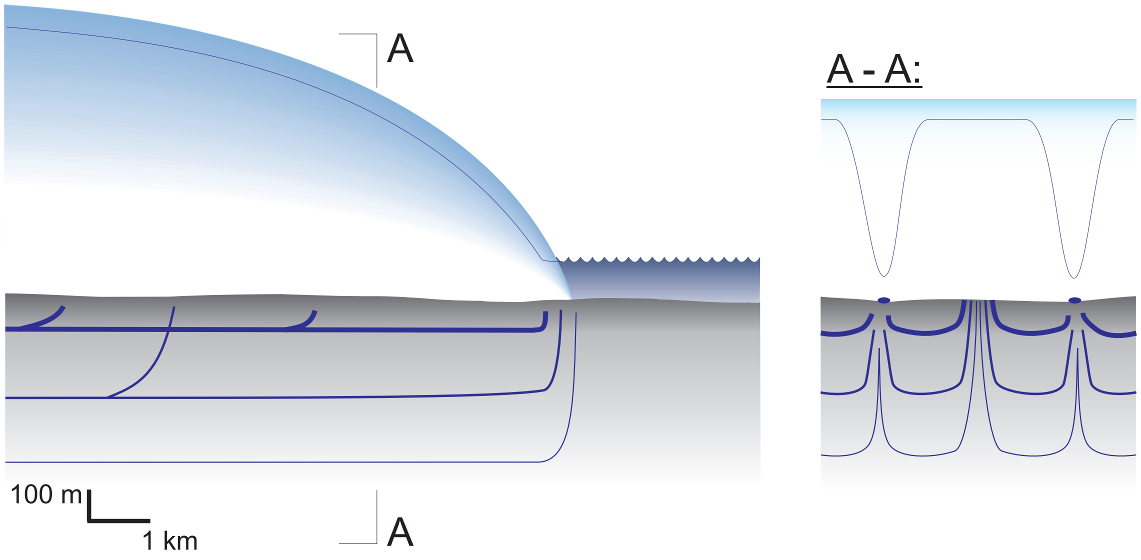

Figure 7-2 Groundwater flow in the melting zone. The ice marginal is in the sea.

When a continental ice sheet moves over an area, the prevailing rock stresses are affected. In the ice divide zone where the ice cover is thickest, the stresses are great. The bedrock is compressed and fractures are squeezed together. The ice in the melting zone is less thick and the water pressure is locally high. The high water pressures can lead to widening of fractures, resulting in increased water permeability.

7.3.1 Influence on SFL 3-5 repository performance

A qualitative discussion of how the characteristic conditions within each climate-driven process domain may influence SFL 3–5 follows below.

Temperate/ boreal domain

Changes in the size and direction of the groundwater flow during this period will have an impact on the groundwater flow to and through the repository. In addition, the altered environmental conditions may lead to that new recipients may have to be considered for the release from the repository.

Furthermore, the salinity of the groundwater may be affected and thereby the retention of some radionuclides in the rock and the near field. However, the buffering capacity of the rock will limit the impact of changes in surface-water composition on groundwater composition at deeper depths, see Section 7.1

Permafrost domain

Permafrost entails that the water in the ground is frozen all year long. This prevents migration and helps sealing the repository. If, on the other hand, the frost should go so deep that the water freezes in the repository itself, this could at worst lead to damage to the barriers in the near field caused by bursting. This means that the water flow through the repository barriers could increase in a later phase.

If glaciation accompanied by deep frost down to depths of more than hundred meters, it can possibly affect the groundwater composition. Recharge will stop and the salinity may increase as a result of stagnant conditions (leaching) and due to the freezing out of ice leaving the dissolved salts behind in the remaining water phase. This has in fact been given as one of several explanations to why saline groundwater is found at depth. Changes in the salinity of the water may influence the radionuclide release from the repository by affecting the retention of radionuclides in near-field barriers and surrounding rock.

Glacial domain

A continental ice sheet on the surface exerts a significant impact on the landscape, but this is of less importance for the repository, which is located 300 m or deeper down in the rock. If the ice cover grows very thick, however, the rock stresses at repository depth increase and this can affect and possibly damage the rock caverns and tunnels in the repository.

After an ice age, as the ice melts at the margin of the ice sheet, a situation might arise where the flow of groundwater increases (Ahlbom *et al.*, 1991). In addition, the groundwater composition, e.g. oxygen content alkalinity, will change. The meltwater has a low concentration of dissolved salts and has a greater chance of preserving its dissolved atmospheric oxygen during the infiltration due to the ice and the cold climate. The total concentration of oxygen in water saturated with air at atmospheric conditions is roughly 10 mg/l. It has been argued that the melt situation might involve trapped air bubbles, which would dissolve in the melt water at increased hydraulic pressure and possibly generate a higher concentration (up to about 30 mg/l).

There will possibly be a lack of an organic soil layer and of bacterial activity during the glacial domain. The content of carbon dioxide can therefore be low compared to present day recharge that have been in equilibrium with a carbon dioxide rich soil atmosphere. Less carbon dioxide means less carbonic acid and therefore lower alkalinity, which is generated by carbonic acid dissolution of calcite in the soil and rock. Furthermore, a lack of organic soil and low biological activity will leave removal of oxygen to the inorganic geochemical reactions with iron(II) and sulphide minerals.

It is not likely that any of the processes described for the glacial domain will appreciably affect the repository in any way. The melting period at any given place is limited, and the repository has a great inherent capacity to absorb and react with oxygen due to its content of metals and organic substances. Furthermore, relatively few radionuclides are adversely affected by oxidation.

7.4 Acid rain scenario

Surface water today in Sweden can be rather acidic due to fallout of sulphuric acid by atmospheric pollution from burning of oil, coal etc. However, this should not affect the pH at depth (not even under the forced groundwater inflow conditions when the repository is open and drained because of the limited duration of that period). The rock has, as we have seen, a considerable capacity to buffer any attempted lowering of pH due to the abundance of calcite and feldspars. It has been rightly stated that any phase of acidification that would consume all the pH-reactive minerals in bedrock down to repository depth, would probably make life for Man impossible on this planet (Nebot and Bruno, 1991, and Wersin *et al.*, 1994).

7.4.1 Influence on SFL 3-5 repository performance

Penetration of low pH water to repository depth due to acid rain is highly unlikely in itself, and, in addition to that, there are very large amounts of concrete in SFL 3-5, which further adds to an already enormous capacity to buffer acidic water in the rock.

8 Discussion and conclusions

8.1 Chemistry of deep groundwater

The repository SFL 3-5 will, according to present plans, be constructed at a depth of 300 m or below. The chemical composition of groundwater at that depth is generally different from shallow potable groundwater, normally encountered in wells used for drinking, irrigation etc. Deep groundwater is devoid of oxygen and reducing in character due to its content of ferrous iron or sulphide. Reactions with the minerals will limit the variation in chemical properties, such as redox and pH. However, frequently there is an increase in salinity with depth and relatively high concentrations of sodium and calcium chloride can sometimes be encountered. Very deep groundwater at 1 km and deeper can even reach brine concentrations (TDS 100 g/l).

Good examples of groundwater composition at repository depth are given by the performance assessment study SR 97 (SKB, 1999). Representative samples from bore hole sections at the sites Äspö, Finnsjön and Gideå have been analysed and selected. The three sites together offers a suite of compositions from non-saline Na-Ca-HCO_3 to saline Na-Ca-Cl dominated deep groundwater, all reducing and with near neutral pH.

8.2 Chemical influence of construction work and concrete

The construction of the repository will disturb the ambient geochemical conditions at depth. Drainage by pumping and ventilation will introduce air, and cause drawdown as well as uplift of groundwater from other levels. Much of the change will not be permanent. Groundwater levels will be restored after closure and entrapped oxygen will be consumed by reactions with the minerals and repository materials (e g steel). However, one notable change will remain; the emplacement of large amounts (about 30 000 m^3) of concrete will dominate the near-field chemistry of the repository for the future. The Portland type cement in concrete contains alkali hydroxides and large amounts of portlandite, which will keep the pH at 12,5 (portlandite) or above (alkali hydroxides).

The development of water and pore water chemistry in the underground structures made of concrete in SFL 3-5 is summarised in Table 8-1.

Table 8-1 Expected water composition in the near-field barriers in SFL 3–5 for a saline versus a non-saline intruding groundwater.

	Concrete enclosure, SFL 3 and 5 and waste packages, SFL 4		Gravel fill, SFL 3, 4 and 5	
	Saline water	**Non-saline water**	**Saline water**	**Non-saline water**
Redox	Reducing conditions		Reducing conditions	
pH	$13.1 \rightarrow 12.5^{a}$	$13.1 \rightarrow 12.5^{a}$	$7.7 - 12.5^{b}$	$9.3 - 12.5^{b}$
Important cations				
Na^{+} (mmol/l)	91	$28 \rightarrow 5$	91	5
K^{+} (mmol/l)	$83 \rightarrow 0.2$	$83 \rightarrow 0.05$	0.2	0.05
Ca^{2+} (mmol/l)	$1 \rightarrow 20^{a}$	$1 \rightarrow 20^{a}$	≤ 47	≤ 0.5
Mg^{2+} (mmol/l)	≤ 0.02	≤ 0.02	≤ 2	≤ 0.04
Important anions				
Cl^{-} (mmol/l)	181	5	181	5
$CO_3^{2-}{}_{tot}$ (mmol/l)	0.1	0.1	≤ 0.2	≤ 0.3
SO_4^{2-} (mmol/l)	6	0.001	6	0.001

[a] *The arrow → shows how the water will change with time*

[b] *Possible range of pH in the water in the gravel fill*

The effect of pH-values in the range 12 – 13 on an underground environment has been studied in the hyperalkaline wells of Maqarin in Jordan (Nagra 1992, Nirex 1998 and Smellie (ed.), 1999). From a chemical point of view, this is a dynamic state because rock-forming minerals, such as quartz and feldspars, will start to dissolve when pH rises above 10 – 11. The dissolution rate will depend on pH, temperature, silica concentration, reactive surfaces and precipitation of secondary minerals. The backfill barrier of crushed rock has a large active surface that should be enough to contain the increase of pH to the near field, despite any leaching of concrete. However, it is necessary that the backfill particles have an active surface area greater than 1 000 m^2/m^3.to be able to contain all the alkali that can be leached without exceeding a penetration depth of 50μm, see Appendix B.

8.3 Stability of concrete

Studies of old concrete, stored under water saturated conditions indicate that the cement paste will retain its binding properties for at least as long as the pore water pH is controlled by portlandite dissolution. Leaching of portlandite is slow according to analysis of the surface of the old concrete samples. The obtained rates indicate that portlandite will be present and pH kept up in the repository for hundreds of thousands of years, see Appendix B. The stiff C-S-H gel is an important component of the cement paste. At lower pH-values C-S-H becomes unstable and starts to dissolve. A loss of C-S-H is detrimental because it may decrease the mechanical stability of concrete.

Groundwater components, such as magnesium, sulphate and carbonate ions, can precipitate in contact with concrete pore water. However, the concentrations in groundwater are low and the mass transport to the repository is a slow process.

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Appendix A: Resaturation of SFL 3-5

Contents

1 Introduction

On repository closure, pumping of the rock caverns will be terminated and the repository vaults and tunnels will be filled by water entering from the surrounding rock. Due to drawdown effects (atmospheric pressure prevails initially in the rock caverns) the time taken to resaturate the repository and re-establish the original hydraulic conditions is short compared to the time of interest in repository performance. Despite this, there are some aspects of the resaturation phase that may be important. Unsaturated conditions during the resaturation phase may delay the initiation of barrier and waste alteration/degradation processes, such as the corrosion of steel packaging and metal waste and the dissolution of other waste types. This time delay may consequently affect the release of short-lived nuclides from the repository. Another aspect concerns the water chemistry during the resaturation phase. Due to dissolution of entrapped air and other potential processes initiated when intruding groundwater comes in contact with the materials in the repository the chemistry will be different during the resaturation phase compared to the chemistry in the long-term.

To give a first indication of the duration of the resaturation phase, some simple calculations have been made of the required inflow of water to the SFL 3-5 repository vaults for different assumed resaturation phase durations. The results of these calculations are compared with reported measurements of water inflow to underground openings and other estimates of resaturation times reported in the literature.

2 Required water inflow to SFL 3-5 for various resaturation times

The inflow of water required to resaturate the SFL 3-5 repository vaults within periods of 10, 50, 150 and 250 years has been calculated. In order to compare the results with measurements of inflow to various underground openings (see Chapter 3), the results are expressed both as inflow per m^2 wall of the tunnels/vaults and as inflow per m tunnel/vault length.

The total volume accessible to water in the different repository parts has been estimated based on design data (Skagius *et al.*, 1999) and on volumes and porosities of the waste packages from waste characterisation studies (Lindgren *et al.*, 1998). The volumes as well as the inflow area and length of the tunnels are given in Table 1.

Table 1 Void volumes, inflow areas and lengths of the tunnel/vaults in SFL 3-5.

	SFL 3	SFL 4	SFL 5
Void volume, m^3	9 500	16 750	9 700
Inflow area, m^2	9 300	26 200	9 300
Tunnel/vault length, m	133	900	133

The required inflow of water was calculated for different assumptions regarding the duration of the resaturation phase and assuming that the total inflow of water during the resaturation phase equals the void volume in the repository. The results are given in Table 2.

Table 2 Water inflow to SFL 3-5 for different assumed resaturation phase durations.

	Resaturation time, [years]			
Water inflow	**10**	**50**	**150**	**250**
SFL 3				
m^3/year	950	190	63	38
m^3/year, m^2	0.10	0.02	0.007	0.004
m^3/year, m	7.1	1.4	0.5	0.3
SFL 4				
m^3/year	1 675	335	112	67
m^3/year, m^2	0.06	0.01	0.004	0.003
m^3/year, m	1.9	0.4	0.1	0.07
SFL 5				
m^3/year	970	194	65	39
m^3/year, m^2	0.10	0.02	0.007	0.004
m^3/year, m	7.3	1.5	0.5	0.3

The groundwater flow rates into the different parts of the repository given in Table 2 are based on the assumptions that no water uptake in the repository barriers occurs prior to repository closure and that the inflow of water is constant during the resaturation phase. These assumptions are probably not correct since the barrier materials in the repository parts most likely will take up some water already during the operational phase. In addition, the inflow of water will probably decrease with time during the resaturation phase due to the decrease in pressure gradient. Therefore, the values given should be considered only as a first indication of the magnitude of groundwater inflow rates required for the assumed resaturation times.

3 Measured water inflow to underground openings

To be able to make an assessment of the expected inflow of water to SFL 3-5 during the resaturation phase and thereby the duration of the resaturation phase, information from measurements of water inflow in different underground openings have been used.

SFR

Results from inflow measurements to the SFR facility, located at about 60 m depth in the rock below the Baltic Sea outside Forsmark, are reported in (Larsson, 1994). The groundwater inflow to different parts of the facility was estimated from inflow measurements and the reported values are:

Silo 1:	0.3 l/min,1 000 m^2 rock surface 3.6 l/min,100 m tunnel
BMA:	1.1 l/min,1 000 m^2 rock surface 9.4 l/min,100 m tunnel
BLA+BTF+cavern and central tunnels	2.6 l/min,1 000 m^2 rock surface 11 l/min,100 m tunnel

The location of the SFR-facility is much shallower than the planned location of SFL 3-5. However, results from inflow measurements to more deeply located mines are also reported in (Larsson, 1994). For the mines, the inflow rates are reported as inflow rate per 1 000 m^2 surrounding rock surface at a distance of 25 m from the rock surfaces in the mine, and as inflow rate per m depth of the mine.

Kristineberg

The Kristineberg underground mine is located in the district of Lycksele, at a depth of about 700 to 1 000 m. The inflow to the mine is reported to be (Larsson, 1994):

~1 900 l/min, corresponding to
~0.4 l/min,1 000 m^2 surrounding rock surface, and
~1.9 l/min,m depth of the mine.
About 45% of the inflow emerges from the rock above the 250 m level, about 33% from the rock between 250 and 490 m depth, and about 22% from the rock between 490 and 1 000 m depth.

Grängesberg

The Grängesberg mine in Bergslagen is an open pit/underground mine with a depth of 650 - 730 m. The inflow to the mine is reported to be (Larsson, 1994):

~4 500 l/min, corresponding to
~1 l/min,1 000 m^2 surrounding rock surface, and
~6 l/min,m depth of the mine.

Stripa

In the Stripa mine in Bergslagen, inflow of water to the experimental drift was monitored for more than two years during the 3-D tracer test experiment. The drift is located at about 360 m depth and has a length of about 100 m and the rock surface in the drift is about 1 400 m^2. The inflow to the drift is reported to be (Abelin *et al.*, 1987):

3 l/hour, corresponding to
0.04 l/min,1 000 m^2 rock surface, and
$5 \cdot 10^{-4}$ l/min,m tunnel.

Äspö

In Äspö the inflow of water to the tunnel is monitored in sections along the tunnel. Estimated monthly averages of the flow into the different sections from May 1991 to September 1994 are reported in (Rhén *et al.*, 1994, Appendix 4, Table 2-3). For most measurement sections the estimated values do not differ much during the later part of the measurement period. The reported average for September 1994 in the different measurement sections between 1 584 m and 3 599 m (tunnel face) are given in Table 3. This part of the tunnel is located between about 200 and 450 m depth in the rock.

Table 3 Average measured inflow into the Äspö tunnel during September 1994 (Rhén *et al.*, 1994, Appendix 4, Table 2-3).

Measurement section		Water flow	
identification	length, [m]	[l/min]	[l/min, m tunnel]
1584-1745	161	19.3	0.12
1745-1883	138	29.7	0.22
1883-2028	145	27.9	0.19
2028-2178	150	47.4	0.32
2178-2357	179	73.5	0.41
2357-2496	139	4.1	0.03
2496-2699	203	55.8	0.28
2699-2840	141	27.4	0.19
2840-2994	154	76.2	0.50
2994-3599 (tunnel face)	605	324	0.54

It should be pointed out that the measured inflow to the tunnel is largely dependent on the extent of grouting. Normally grouting of the rock is done only to such extent that the environment becomes tolerable for the personnel working in the underground openings, and not with the purpose of limiting the inflow as much as possible (Rhén I, 1995).

4 Resaturation times, SFL 3-5

To get a first indication of the resaturation times for SFL 3-5, the calculated required inflow rates to SFL 3-5 are compared with the reported inflow rates from measurements in underground openings. To facilitate the comparison, these latter values are given in

Table 4 in the same units as those calculated for SFL 3-5, i.e. as m^3 water per year and m^2 rock surface, and m^3 water per year and m tunnel. Concerning the inflow in the Äspö tunnel, the lowest and the highest flow rates are chosen.

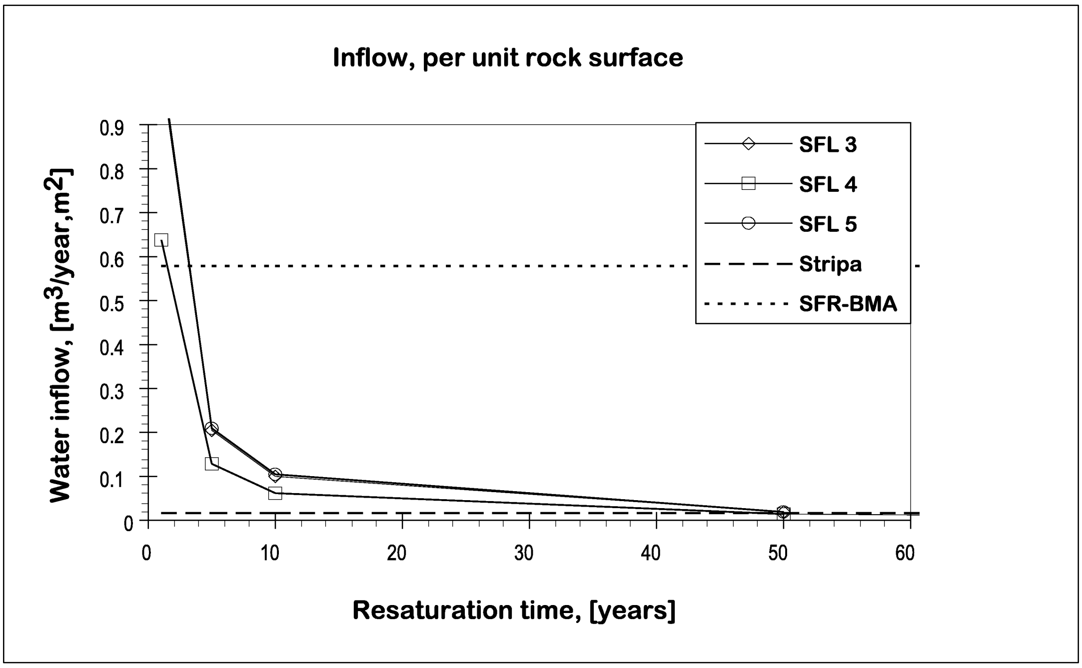
Table 4 Compilation of measured water inflow to underground openings.

Underground opening Name	Depth [m]	Water inflow [m^3/year, m^2]	 [m^3/year, m]
SFR			
Silo 1	60	0.16	19
BMA	60	0.58	49
BTF+BLA+tunnels	60	1.4	58
Mines			
Stripa, 3-D drift	360	$1.9 \cdot 10^{-2}$	0.26
Grängesberg	650-730	0.52*	
Kristineberg	690-1 000	0.21*	
Äspö			
2357-2496 (min)	~300		15
2994-3599 (max)	~450		280

* *based on rock surface at 25 m distance from the mine*

The compilation in Table 4 shows that the Stripa 3-D drift has the lowest estimated inflow of water. Comparing this low inflow with the calculated inflow values to SFL 3-5 in Table 2 indicates a resaturation time of the order of 50 to a few hundreds of years for the repository parts in SFL 3-5, see Figure 1. All the remaining estimated inflows to underground openings suggest resaturation times of less than 10 years for all three repository parts.

It should be noted that the inflow measurements are carried out in open tunnels/drifts where atmospheric pressure prevails. SFL 3-5 contains barrier materials that may have lower hydraulic conductivity than the surrounding rock, and as resaturation proceeds, the driving force for inflow of water will decrease as the pressure in the repository increases. Under such circumstances the inflow rates may be lower than those measured in unsealed and drained openings.



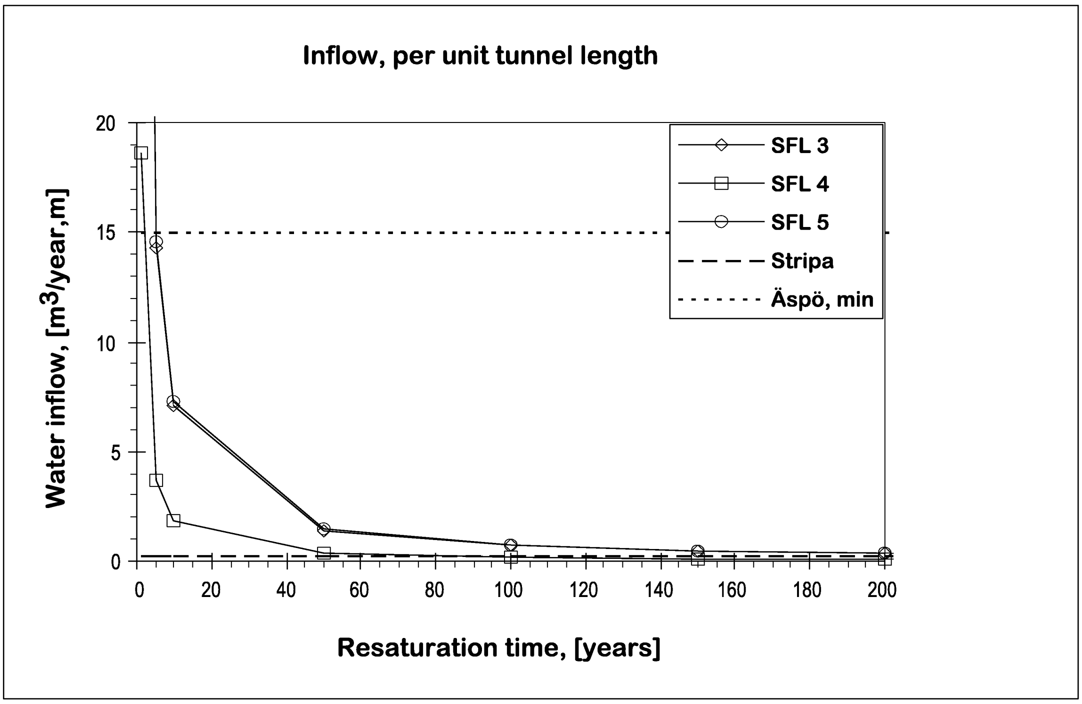


Figure 1 *Calculated water inflow versus resaturation time for SFL 3-5, and some measured water inflow to underground openings.*

Sand/bentonite has been discussed as an alternative to the sand/gravel backfill outside the concrete compartments in SFL 3. In the WP-Cave concept the internal part of the cave where the fuel is stored is surrounded by a 5 m thick sand/bentonite barrier, and the time to resaturate a repository according to the WP-Cave concept has been calculated (Svemar, 1985). The inflow of water to the cave and the filling time were calculated assuming a hydraulic conductivity in the sand/bentonite of $1 \cdot 10^{-10}$ m/s and for different values of the conductivity in the rock. For a hydraulic conductivity in the rock of $1 \cdot 10^{-9}$ m/s the inflow was estimated to about 0.9 l/s and the filling time to about 10 years. A ten times lower conductivity in the rock increased the filling time to about 80 years. It was further concluded that to substantially increase the filling time, the hydraulic conductivity in the sand/bentonite barrier must be reduced to at least 10^{-12} m/s. Despite the difference in size and free volume between a WP-Cave and the SFL 3 repository, these results suggest that it would be difficult to significantly prolong the resaturation phase by the presence of a bentonite barrier in SFL 3.

5 Conclusions

This first estimate of the resaturation times for SFL 3-5 indicates that they are relatively short. In a ”dry” rock similar to the rock surrounding the Stripa 3-D test drift, resaturation times of the order of 50 to a few hundred years could possibly be expected. In a more water conductive rock, the resaturation times would probably be less than 10 years.

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Appendix B: Possible buffering of pH-plume by silicate in the sand/gravel backfill

Contents

1 Introduction

A plume with increased pH is formed due to the leaching of hydroxide from concrete. The extent of this high-pH plume is of interest especially with regard to the stability of the bentonite in the deep repository for spent fuel. Leaching of concrete starts with leaching of the alkali hydroxides NaOH and KOH and continues with leaching of portlandite, $CaOH_2$.

Silicate minerals dissolved in the ground water, for example quartz, SiO_2, in the granitic sand/gravel backfill and in the rock will precipitate as CSH-phases at high pH. These reactions consume hydroxide ions and therefore buffer the high-pH plume.

2 Massbalances

A first estimate of the extent of the high pH-plume can be made from a massbalance. Massbalance is assumed between the total amount of leachable hydroxide ions in concrete on one hand and the available amount of quartz, SiO_2, in the granitic sand/gravel backfill, on the other hand. It is further assumed that every mole of SiO_2 reacts with 2 moles of OH^-. Tables 1 – 3 give the data used to calculate the volumes of concrete and sand/gravel backfill in the different repository parts. Additional data, for example concentrations of alkalihydroxides and portlandite in concrete, needed to calculate the massbalances are given in Table 4. The massbalance calculations for all the three repository parts, SFL 3, SFL 4 and SFL 5, show that the amount of SiO_2 in the backfill is large enough to consume the hydroxide ions leached from the concrete.
SFL 5 is the repository with most concrete in comparison with sand/gravel backfill and even for this repository part the massbalance show that only 6% of the available SiO_2 is needed to complete the buffering reaction.

Table 1 **Data used to estimate the volumes of concrete and sand/gravel backfill in SFL 3.**

SFL 3	
Concrete structure	
Length	114.6 m
Width	10.8 m
Height	10.7 m
Length, long walls	113.8 m
Width, short walls	10.8 m
Height, outer walls	10.2 m
Thickness, outer walls	0.4 m
Thickness, internal walls	0.4 m
Thickness, bottom	0.5 m
Thickness, lid	0.6 m
Number of internal walls	22
Width, internal walls	10 m
Height, internal walls	9.9 m
Volume, bottom	619 m^3
Volume, long walls	929 m^3
Volume, short walls	88 m^3
Volume, lid	683 m^3
Volume internal walls	871 m^3
Volume concrete structure	3 190 m^3
Concrete packaging and backfill	
Length, inside compartment	5 m
Height, inside compartment	9.6 m
Width, inside compartment	10 m
Number of compartments	21
Volume inside one compartment	480 m^3
Outer volume of one concrete container ILW	1.7 m^3
Concrete volume of one concrete container ILW	1.2 m^3
Number of concrete containers/compartment	256
Volume of all concrete containers	9 290 m^3
Volume of porous concrete inside all compartments	790 m^3
Concrete volume of all concrete container ILW	6 467 m^3
Sand/gravel backfill	
Excavated volume	34 000 m^3
Outer volume of concrete structure	13 243 m^3
Volume of sand/gravel backfill	20 757 m^3
Total volume of concrete and porous concrete	**10 447 m^3**
Total volume of sand/gravel	**20 757 m^3**

Table 2 **Data used to estimate the volumes of concrete and sand/gravel backfill in SFL 4.**

SFL 4	
Concrete structure (bottom plate)	
Length	900 m
Width	8 m
Height	0.2 m
Volume concrete structure	1 440 m^3
Concrete packaging and backfill	
Number of unit vessels	725
Outer volume of one unit vessel	13.8 m^3
Average volume of concrete waste in one unit vessel	0.61 m^3
Void possible to backfill inside one unit vessel	11.8 m^3
Volume of concrete waste	441 m^3
Volume of porous concrete in all unit vessels	8 559 m^3
Sand/gravel backfill	
Excavated volume	40 000 m^3
Outer volume of concrete structure	1 440 m^3
Outer volume of all unit vessels	10 005 m^3
Volume of sand/gravel backfill	28 555 m^3
Total volume of concrete excl. porous concrete	**1 881 m^3**
Total volume of concrete incl. porous concrete	**10 439 m^3**
Total volume of sand/gravel	**28 555 m^3**

Table 3 **Data used to estimate the volumes of concrete and sand/gravel backfill in SFL 5.**

SFL 5	
Concrete structure	
same as SFL 3	
Concrete packaging and backfill	
data on compartments see SFL 3	
Number of concrete containers/compartment	64
Outer volume of one concrete container	6.9 m^3
Concrete volume of one concrete container	2.3 m^3
Volume of all concrete containers	9 290 m^3
Volume of porous concrete inside one container [a)]	3.15 m^3
Volume of porous concrete inside all compartments	790 m^3
Concrete volume of all concrete container	3 107 m^3
Volume of porous concrete inside all containers	4 234 m^3
Sand/gravel backfill	
Excavated volume	34 000 m^3
Outer volume of concrete structure	13 243 m^3
Volume of sand/gravel backfill	20 757 m^3
Total volume of concrete and porous concrete	**11 321 m^3**
Total volume of sand/gravel	**20 757 m^3**

a) Assumed that the whole volume between cassette and container and half of the volume inside the cassette is backfilled.

Table 4 **Data used to estimate the amount of OH^- in concrete and SiO_2 in sand/gravel backfill.**

Initial concentration of alkali	56 mol XOH/m^3 concrete
Initial concentration of portlandite	1 000 mol $Ca(OH)_2/m^3$ concrete
SiO_2 in granite	30 weight %
Density granite	2 700 kg/m^3
Moleweight SiO_2	60 g/mol
Initial concentration SiO_2 in granite	13 500 mol/m^3 granite
Porosity sand/gravel	0.3
Initial concentration SiO_2 in sand/gravel	9 450 mol/m^3 sand

Table 5 **Comparison of massbalances between leachable amount of OH^- in concrete (alkali and portlandite) and amount of SiO_2 in the sand/gravel backfill for SFL 3, SFL 4 and SFL 5.**

	Amount OH^- as alkali (mol)	Amount OH^- as portlandite (mol)	Total amount OH^- (mol)	Amount SiO_2 (mol)	Mole SiO_2 needed/ mole available
SFL 3	$5.85 \cdot 10^5$	$2.09 \cdot 10^7$	$2.15 \cdot 10^7$	$1.96 \cdot 10^8$	5%
SFL 4	$1.05 \cdot 10^5$	$3.76 \cdot 10^6$	$3.87 \cdot 10^6$	$2.70 \cdot 10^8$	1%
SFL 4[a)]	$5.85 \cdot 10^5$	$2.09 \cdot 10^7$	$2.15 \cdot 10^7$	$2.70 \cdot 10^8$	4%
SFL 5	$6.34 \cdot 10^5$	$2.26 \cdot 10^7$	$2.33 \cdot 10^7$	$1.96 \cdot 10^8$	6%
Total	$1.91 \cdot 10^6$	$6.82 \cdot 10^7$	$4.86 \cdot 10^7$	$6.62 \cdot 10^8$	4%

a) Includes porous concrete inside unit vessel, the total for SFL 3, SFL4 and SFL 5 in this case is 5%.

3 Reaction depth in the sand/gravel particles

The reaction depth in the sand/gravel particles in the backfill determines the buffering capacity. Although the massbalance calculations show that 6% or less of the available SiO_2 is needed for buffering of all the hydroxide ions leached from concrete in the different repository parts, limited accessibility for the reaction inside the sand/gravel particles may decrease the buffering. In the calculations below, total buffering is assumed, i.e. all the leached OH^- ion will react with dissolved SiO_2.

If the sand/gravel particles are assumed to be spheres, the reaction depth can then be calculated as: $s = r - (r^3 - r^3 \cdot X)^{1/3}$, where r is the initial radii and X is the part of SiO_2 that is reacted (i.e. the right column in Table 5). The reaction depth as a function of the particle diameter is given in Figure 1. The penetration depth is linearly dependent on the particle diameter, for example a particle diameter of 10 mm leads to a penetration depth of about 0.1 mm if all the OH^- is consumed. The particle size of the proposed sand/gravel backfill is 4 – 32 mm in diameter. The average diameter for the backfill material, calculated from the average volume, assuming spherical particles, is:

$$d_{av} = \left(\frac{\left(d_{\min}^3 + d_{\max}^3 \right)}{2} \right)^{1/3} = \left(\frac{\left(4^3 + 32^3 \right)}{2} \right)^{1/3} = 25\ mm$$

When considering non-spherical particles or particles with a porous surface in the sand/gravel backfill, an appropriate assumption is that the reaction depth is related to the area-volume ratio for the particles. It is assumed that the change in volume is negligible due to the small reaction depth. The reaction depth can then be calculated according to: $s = X \cdot 1/(A/V)$, where X is the part of SiO_2 that is reacted (i.e. the right column in Table 5) and A/V is the ratio between the surface area and the volume. The reaction depth as a function of the area-volume ratio is given in Figure 2 for all three repository parts, including the tunnel system filled with sand/gravel.

Rock pieces, which were stored in concrete pore water at 70 ºC for 6 months were observed to have a penetration depth of less than 50 µm (Holgersson *et al,* 1998*).* Spherical particles have an area-volume ratio of 6/d. For particles of the same size as the average size of the backfill, i.e. of 25 mm, the theoretical spherical area-volume ratio is 240 m^{-1}. In order to achieve a penetration depth less than 50 µm as indicated in the experiments, the area-volume ratio must be at least about 4 times higher than the theoretical area-volume ratio for a spherical particle, see Figure 2. Surface measurements on crushed rock, Äspö diorite and fine-grained granite, have been performed (Byegård *et al.,* 1998). The BET-surfaces for the largest size fraction (2 – 4 mm) were almost 40 times the theoretical spherical surface area for Äspö diorite and 90 times for the fine-grained granite. There is a trend towards increasing difference between the actual surface area and the theoretical spherical surface area with increasing particle size. For crushed granite of the size fraction 12.7 to 19.05 mm actual surface areas of about 150 to 200 times larger than estimated surface areas for spherical particles are reported (Möller *et al.*, 1982). This indicates that the actual surface area-volume ratio for 25 mm particles could be in the order of 30 000 – 50 000 m^{-1}.

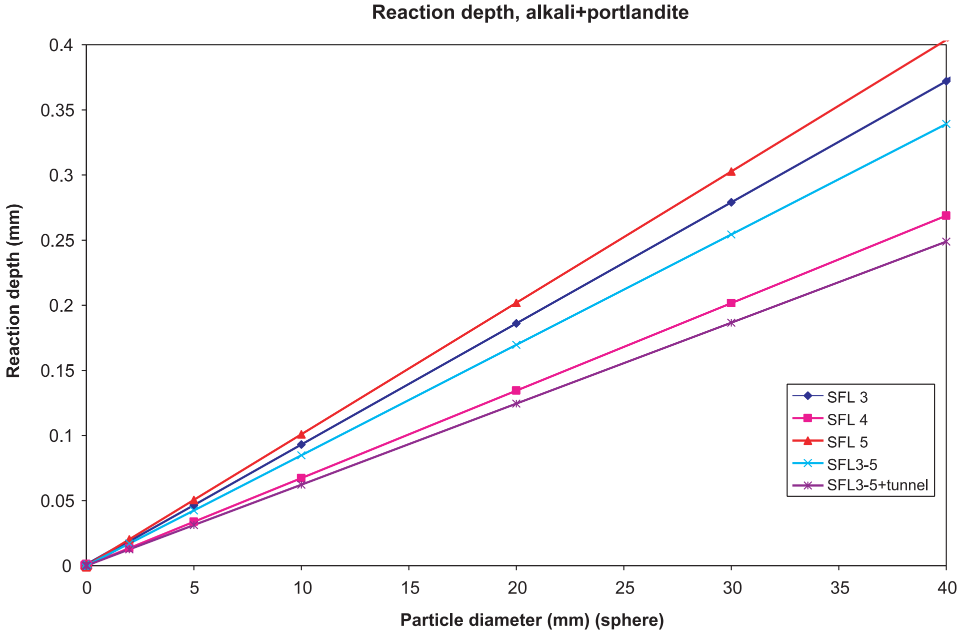

Figure 1 *Reaction depth as a function of particle diameter (sphere) if all the leached hydroxide ions from the concrete are buffered by reaction with* SiO_2 *in the sand/gravel backfill.*

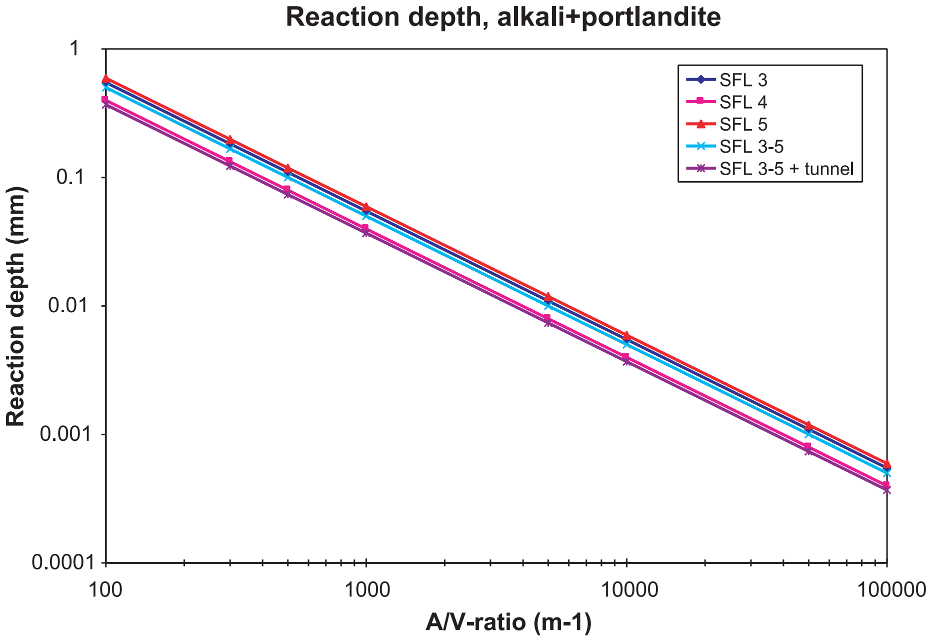

Figure 2 *Reaction depth as a function of area-volume ratio if all the hydroxide leached from the concrete in SFL3-5 is buffered by reaction with* SiO_2 *in the sand/gravel backfill.*

4 pH determined by diffusion of OH^- in concrete and dissolution of SiO_2

The formation rate of CSH-phases from OH^- and dissolved SiO_2 is dependent on both the diffusion of OH^- in concrete and on the dissolution rate of SiO_2 in the sand/gravel backfill. The dissolution rate of SiO_2 is in turn dependent on the concentration of OH^-. The balance between the diffusion and dissolution may determine the pH in the sand/gravel. The dissolution rate of SiO_2 may be determined by other factors than the pH, this is not considered here and hence this calculation of the pH in the sand/gravel backfill is approximate.

The diffusion of hydroxide from concrete can be approximated by diffusion from a semi-infinite plate with a homogeneous initial concentration, Co, and zero concentration at the boundary. The cumulative amount M(t) of released hydroxide ions is then described by:

$$M(t) = 2 \cdot C_o \cdot (D_e \cdot \varepsilon \cdot R \cdot t/\pi)^{1/2} \quad (mol\ OH^-/m^2)$$

where
D_e is the effective diffusivity (m^2/s)
ε is the porosity of the concrete
R is the retardation factor ($R=1+(1-\varepsilon)K_d\rho_s/\varepsilon$).

The dissolution rate of SiO_2 has been studied, for example by Knauss and Wollery, 1988 and by Savage *et al*, 1992. From Figure 6 in Knauss and Wollery, 1988 an expression describing the OH^- dependence of the dissolution rate at 25°C and pH > 6 is obtained:

$$k = 4 \cdot 10^{-14} \cdot \sqrt{[\mathrm{OH}]} \quad \left(mol\ SiO_2 / cm^2, s\right).$$

To determine the evolution of pH in the sand/gravel backfill in SFL3-5 a stepwise calculation was performed. The steps were: 1) Choose a time step. 2) Calculate the diffusion of OH^- and dissolution of SiO_2 during this time step. 3) Calculate the difference between the amount of OH^- that has diffused from the concrete and OH^- consumed by the reaction with dissolved SiO_2 from the sand/gravel backfill. 4) Adjust the pH in the sand/gravel.

The total diffusion during a time step is calculated as:

$$M_{diff} = M(t_n) \cdot A - M(t_n - t_{n-1}) \cdot A \quad \left(mol\ OH^-\right)$$

where
$M(t_n)$ is the amount of diffused OH^- ions until the actual time t_n (mol OH^-/m^2)
$M(t_{n-1})$ is the amount of diffused OH^- ions until the previous time t_{n-1} (mol OH^-/m^2)
A is the surface area (m).

The possible consumption of OH^- determined by the dissolution rate of SiO_2 is calculated as:

$$M_{con} = k \cdot A_{sand/gravel} \cdot \Delta t = 2.5 \cdot 10^{-2} \cdot \sqrt{[\mathrm{OH}]} \cdot (A/V) \cdot V_{sand/gravel} \cdot (t_n - t_{n-1}) \quad (mol\ OH^-)$$

where:
k is the dissolution rate (mol OH^-/m^2, year)
$A_{sand/gravel}$ is the surface area of the sand/gravel (m^2)
Δt is the time period between the actual time and the time at the previous step
A/V is the area to volume ratio (m^2/m^3)
V is the volume of the sand/gravel (m^3)
t_n is the time at the actual calculation step n
t_{n-1} is the time at the previous calculation step.

The input data used in the calculations are summarised in Table 6.

Table 6 Input data used in the calculation of pH as a function of time.

Initial amount of OH^- in sand/gravel backfill		
Initial concentration of OH^-(pH=8.2, i.e. Allard water[a])	0.00158489	mol OH^-/m^3
Pore volume in sand/gravel backfill, SFL 3	6 227	m^3
Pore volume in sand/gravel backfill, SFL 4	8 566	m^3
Pore volume in sand/gravel backfill, SFL 5	6 227	m^3
Diffusion of OH^- from concrete		
Co, initial concentration of OH^- in concrete porewater	114	mol OH^-/m^3
D_e, effective diffusivity	$3 \cdot 10^{-11}$	m^2/s
ε, porosity of the concrete	0.15	–
R, retardation factor	1 (no sorption)	–
A, diffusion area, SFL 3 *b)*	5 159	m^2
A, diffusion area, SFL 4 *c)*	32 256	m^2
A, diffusion area, SFL 5 *b)*	5 159	m^2
Consumption of OH^-		
A/V, area-volume ratio of sand/gravel backfill	240	m^{-1}
Vsand/gravel, volume of sand gravel, SFL 3	14 530	m^3
Vsand/gravel, volume of sand gravel, SFL 4	19 988	m^3
Vsand/gravel, volume of sand gravel, SFL 5	14 530	m^3

a) Allard water is well defined, easy to prepare and often used in different experiments to simulate Swedish groundwater.
b) outer area of concrete structure
c) bottom plate and unit vessels

Figure 3 shows the pH in the sand/gravel backfill as a function of time for the three repository parts. The calculations show that the diffusion of OH^- is slower than the dissolution of SiO_2 and hence the pH in the sand/gravel will decrease below nine after a few years in all three repository parts. The area-volume ratio assumed is for spherical particles with a diameter of 25 mm, i.e. the average grain size in the sand/gravel backfill. The real area-volume ratio is larger, which implies an even faster decrease in pH. Again it should be noted that the mechanisms considered here might not be governing the system. If there are limitations in the described mechanisms it is possible that the pH plume will extend for a longer time period and hence diffuse further out through the sand/gravel backfill out in the rock mass. One limitation in the above calculation is that all the sand/gravel is assumed to be immediately available, i.e. no transport resistance is accounted for.

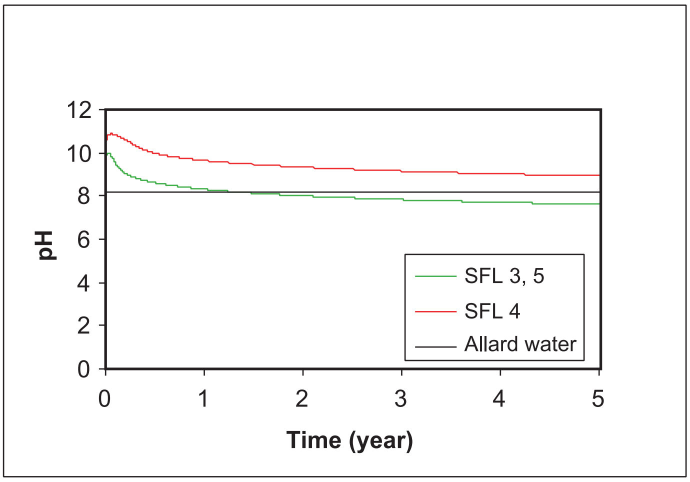

Figure 3 *pH calculated as a function of time for SFL 3, SFL 4 and SFL 5, based on limitations in the diffusion of hydroxide ions from concrete and the dissolution rate of SiO_2.*

5 Time for portlandite depletion

The time for depletion of portlandite determined by diffusion is estimated assuming instantaneous removal of leachate from the concrete surface. According to Höglund et al. 1991, the depth of depletion at different times can be estimated from the following equation:

$$x(t) = \sqrt{\frac{2\,C_{sol}\,D_e\,t}{q_0}}$$

where

C_{sol} is the solubility of portlandite (mol/m^3)
D_e is the effective diffusivity in the concrete (m^2/s)
t is the time (s)
q_0 is the initial concentration of portlandite (mol/m^3)

The input data used in the calculations are summarised in Table 7.

Table 7 Data used to estimate the time for depletion of portlandite.

Solubility of portlandite	25	mol $Ca(OH^-)_2/m^3$ concrete	Höglund et al, 1991
Effective diffusivity in leached concrete	$3\cdot10^{-11}(3\cdot10^{-12})$	m^2/s	
Initial conc. of portlandite	1 000	mol $Ca(OH^-)_2/m^3$ concrete	Table 7-3 in this report

The calculated depletion depth is shown in Figure 4 and 5 as a function of time on two different scales. The curve for an assumed $D_e = 3\cdot10^{-11}$ m^2/s indicates that portlandite depletion of a concrete barrier to a depth of one meter takes at least 50 000 years, see Figure 4.

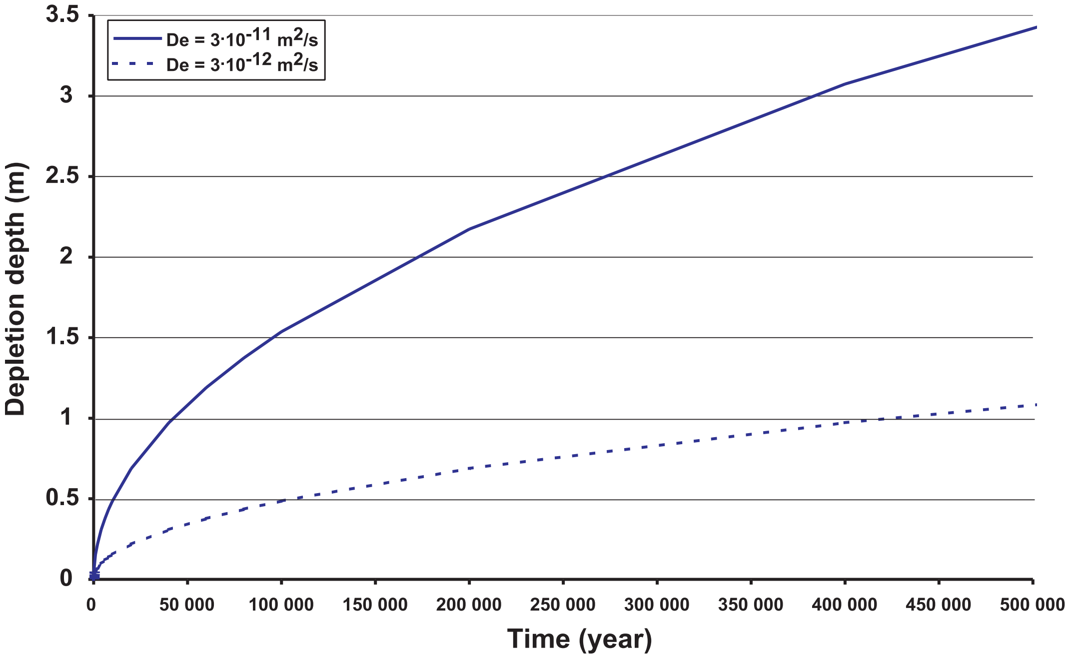

Figure 4 *Depletion depth in concrete as a function of time determined by diffusion of portlandite.*

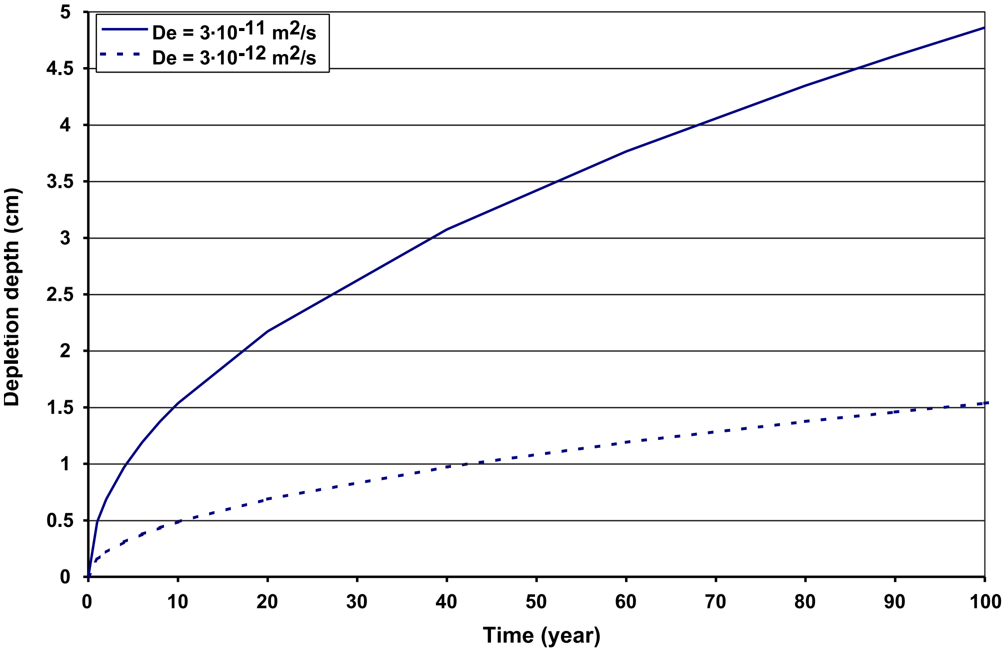

Figure 5 *Detail of Depletion depth in concrete as a function of time determined by diffusion of portlandite.*

In an old water tank the steel walls were covered by a 20 mm thick layer of mortar. Investigations of the tank show that after about 90 years in contact with fresh water is the surface carbonated, and the calcium content has decreased and the porosity increased to a depth of 5 – 8 mm. At greater depth the mortar is dense and shows only slight calcium depletion (Trägårdh et al, 1998). This is less than the calculated depletion depth of almost 5 cm obtained with the assumed data in Table 7, see Figure 5. This indicates that either diffusion is slower or that dissolution determines the depletion rate. Calculations were therefore also performed for an effective diffusivity of $3 \cdot 10^{-12}$ m^2/s, resulting in a depletion depth of 1.5 cm after 90 years, see Figure 5.

The lower effective diffusivity ($D_e = 3 \cdot 10^{-12}$ m^2/s) indicates ten times longer time for depletion of portlandite in a concrete barrier that is of the order of a meter, i.e. about 500 000 years, see Figure 4. The other possibility, as stated above, is that the dissolution rate for portlandite determines the time for depletion.

6 Discussion and conclusion

A massbalance between the leachable hydroxide ions in concrete in the SFL 3-5 repository and the available amount of quartz (SiO_2) in the granitic sand/gravel backfill shows that less than 6% of the total amount of quartz is needed to buffer the pH in the sand/gravel.

Although only a small part of the total amount of quartz present in the sand/gravel backfill is needed to buffer the pH, limited accessibility for the buffering reaction inside the sand/gravel particles may decrease the buffering capacity.

The formation rate of CSH-phases from OH^- and dissolved SiO_2 is dependent on both the diffusion of OH^- in concrete and on the dissolution rate of SiO_2. The dissolution rate of SiO_2 is in turn dependent on the concentration of OH^-. The balance between the diffusion of OH^- and dissolution of SiO_2 may determine the pH in the sand/gravel. It was shown that increased pH level in the sand/gravel would prevail during a period of some few years and that the pH plume will not reach the rock mass. The dissolution rate of SiO_2 may be determined by other factors than the pH. If there are limitations in the described mechanisms it is possible that the pH plume will extend for a longer time period and hence diffuse further out through the sand/gravel backfill into the rock mass.

The calculations performed here show that quartz will buffer the OH^- leached from concrete and hence under these circumstances only a small increase in pH under a short period is achieved in the sand/gravel backfill. There are, however, factors other than SiO_2 dissolution that may determine the pH of this system and that have not been considered. Nevertheless, from these calculations it is possible to assume that the occurrence of a plume of hydroxide ions with a relatively high pH is limited to the sand/gravel backfill and the influence of the plume on the rock mass is considered to be insignificant.

7 References

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Appendix C: Stray material potentially remaining in SFL 3-5

Contents

1 Introduction

In SFL 3-5, stray material will be introduced into the repository with the waste packages and structural materials. Stray material in the drifts will also arise from the construction and operation of the repository. In this appendix, a rough estimate is made of the quantities emanating from the construction and operation activities.

2 Estimated amounts in SFL 3-5

An estimate of the quantities of stray material emanating from the construction and deposition periods made by Larsson (1997a) for the deep repository for spent fuel, SFL 2, has been used as the basis for the estimates of stray material in SFL 3-5. The quantities of material from the construction and operation of SFL 3-5 have been estimated from information concerning the transport tunnels in the deposition area of SFL 2. The estimation of quantities for SFL 3-5 is based on a comparison of the lengths of the different tunnels in SFL 3-4 with 40 m of transport tunnels in the deposition area of SFL 2. The transport tunnels in SFL 2 are washed after blasting using high-pressure hoses and then regularly in order to control dust and impurities.

The quantities of stray material in SFL 3-5, calculated by scaling of the length of the drift to the length of the transport tunnels in SFL 2, are given in Table 1. However, not all the quantities of material are directly dependant on the length of the drift, some depend on other factors. The quantities of ”detonators with capsules and cables” and ”explosives” depend more on the blasted volume of rock than on the length of the tunnel, and since the tunnels in SFL 3-5 are larger than those in SFL 2, the amount of these materials may be slightly underestimated in Table 1. The amounts of ”hydraulic oils” and ”degreasing and washing agents” are probably also related to the amount of blasted rock. Whether or not ” asphalt flooring” will be used in SFL 3-5 is not certain. The quantities from ”wear of tires”, ”exhaust from diesel engines”, ”diesel oil”, ”battery acid”, ”shavings from wood work”, ”corrosion products”, ”urine”, ”other human refuse” and ”ventilation air” can be expected to depend on the distance driven and/or the opening time for the repository. The amount of ”metal swarf” estimated for SFL 3-5 emanates from steelwork and is small compared to the amount of steel in the waste and packagings.

Nevertheless, a scale factor based on the lengths of the drifts has been chosen as a first assumption to estimate the quantities of stray material in SFL 3-5, despite the fact that other factors affect the amount of material. The assumed length of SFL 3 and SFL 5 is 133 m respectively, and the assumed length of SFL 4 is 900 m. The same scale factor has been used for all three repository parts, even though SFL 4 is used for all the transports to SFL 3 and 5 and as a consequence SFL 4 will probably contain more stray material, per unit tunnel length. Further, it can be assumed that cleaning and high-pressure washing is less careful and extensive in SFL 3-5 tunnels than in SFL 2. The amount of remaining material could therefore increase by a factor of 5 per metre of drift compared to the transport tunnels in SFL 2 (Larsson, 1997b). This has not been considered in the estimates given here.

The quantity of concrete and other construction material in SFL 3-5 cannot be compared to the quantities in SFL 2. The quantities of structural concrete in SFL 3-5 have been derived from Forsgren (1996) and are given in Table 2. In order to compare the quantities of stray material from construction and operation to the quantities introduced into the repository with the waste and packaging, the quantities of the materials in the waste and packaging are also given, see Tables 3 and 4 (Lindgren *et al.,* 1998). In addition, the quantities remaining per 40 m of transport tunnels in the deposition area of SFL 2 estimated by Larsson (1997a) are given in Table 5.

The stray material from construction and operation activities which are of major interest, with a potential effect on the long-term function of the repository are ”degreasing and washing agents” (surfactants), ”wood shavings” (cellulose) and ”ventilation dust” (partly cellulose). However, the quantities of these materials transferred to SFL 3 during construction are relatively small in comparison to the total quantities in the waste, e.g. about 400 tonnes of cellulose. No material of this kind is transferred to SFL 4 and SFL 5 with the waste.

Table 1 Estimated amounts (tonnes) of stray materials from operation and construction remaining in SFL 3-5. Based on information concerning transport tunnels in the deposition area of SFL 2 (scale factor: length of drift).

Term	Chemical content	Quantity remaining (tonnes) [a]			
		SFL 3	SFL 4	SFL 5	SFL 3-5 [b]
Detonators with capsules and cables	Aluminium Plastic	0.02 0.2	0.1 1	0.02 0.2	0.2 1
Explosives	Nitrogen oxides	0.001	0.005	0.001	0.006
Asphalt flooring	Bitumen	0.04	0.3	0.04	0.4
Wear of tires	Rubber	0.2	1	0.2	2
Diesel exhaust	Nitrogen oxides Soot and ash	0.2 0.07	1 0.5	0.2 0.07	2 0.6
Degreasing and washing agents	Hydrocarbons and other org. material	0.03	0.2	0.03	0.3
Hydraulic and lubricating oils	Hydrocarbons	0.04	0.3	0.04	0.4
Diesel oil	Hydrocarbons	0.2	1	0.2	1
Battery acid	Sulphuric acid	0.004	0.03	0.004	0.03
Swarf of hard metal	Wolfram, cobalt	0.01	0.09	0.01	0.1
Swarf from steel work	Steel	0.05	0.3	0.05	0.4
Wood shavings	Wood	0.2	1	0.2	1
Corrosion products	Rust (FeO) Zinc	0.3 0.3	2 2	0.3 0.3	3 2
Urine		0.8	6	0.8	7
Other human refuse	Org. material	0.2	2	0.2	2
Ventilation air	Org. material	0.2	1	0.2	1

[a] *Calculated using the scale factor length of drift*

[b] *The total quantity has been calculated with a greater number of significant figures for each part of the repository than is given in the table.*

Table 2 Structural, grouting and reinforcing concrete (tonnes) in SFL 3-5 (Forsgren, 1996).

Materials	Quantity (tonnes) Concrete	Reinforcement
Spray conrete with steel fibre reinforcement	3 000	30
Structural concrete with reinforcement	22 000	800
Grouting concrete	3 500[a)] + 2 200[b)]	

a) SFL 3

b) SFL 5

Table 3 The total quantities of waste (tonnes) in each part of the SFL 3-5 repository (exkluding packaging) (Lindgren *et al.,* 1998).

Material	SFL 3	Quantity (tonnes) SFL 4	SFL 5	Total
Metals				
Aluminium	82			82
Brass and copper	2			2
Cadmium	1			1
Chromium			5	5
Hafnium			4	4
Inconel			2	2
Lead	4			4
Stainless steel	71	4 720	1 650	6 441
Boron steel		1 260	17	1 277
Carbon steel	80	3 190	280	3 550
Thorium metal	2			2
Zircaloy	3		30	33
Other[a)]	0.1		0.3	0.4
Organic material				
Ion exchange resin	230			230
Paper/wood	5			
Textile/rags	20			20
Plastic/rubber	130			130
Unspecified	1			1
Concrete				
Concrete/cement [b)]	2 580	880		3 460
Other [c)]	84			84

[a)] zinc and titanium in SFL 3, beryllium in SFL 5

[b)] stabilized waste and contaminated concrete

[c)] ashes, glass, ferrocyanide precipitates etc.

Tabell 4 **Packaging (tonnes) in each part of the SFL 3-5 repository (Lindgren *e al.,* 1998).**

Material	Quantity (tonnes) SFL 3	 SFL 4	 SFL 5	 Total
Lead	20		110	130
Carbon steel [a)]	820	1 000	440	2 260
Stainless steel	20		930	950
Concrete	5 000		7 300	12 300
Concrete (backfill)	700		10 400	11 100

[a)] *including reinforcements*

Tabell 5 **Estimated amounts (kg) of stray materials from operation and construction remaining in 40 m transport tunnel in the deposition area of SFL 2 (Larsson, 1997a).**

Term	Chemical content	Quantity[a)] (kg)
Detonators with capsules and cables	Aluminium	6
Detonators with capsules and cables	Plastics	50
Explosives	Nitrogen oxides	0.2
Asphalt flooring	Bitumen	12
Wear of tires	Rubber	60
Diesel exhaust	Nitrogen oxides	55
Diesel exhaust	Soot and ash	22
Degreasing and washing agents	Hydrocarbons and other org. material	10
Hydraulic and lubricant oils	Hydrocarbons	12
Diesel oil	Hydrocarbons	50
Battery acid	Sulphuric acid	1.2
Swarf of hard metal	Wolfram, cobalt	4
Swarf from steel work	Steel	14
Wood shavings	Wood	50
Corrosion products	Rust (FeO)	90
Corrosion products	Zinc	80
Urine		250
Other human refuse	Organic material	70
Ventilation air	Organic material	50

a) *per 40 m transport tunnels in the deposition area of SFL 2*

3 References

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Appendix D: Design alternatives

Contents

1 Introduction

The prestudy of final disposal of long-lived low and intermediate level waste (Wiborgh (ed.), 1995) was carried out for the conceptual design of the SFL 3-5 repository proposed in (Plan 93, 1993). Since then a revision has been made of the SFL 3-5 repository design and in the preliminary assessment of the SFL 3-5 repository (SKB, 1999) the revised design was used. Some of the material forming the base for the selection of backfill material is given in this appendix.

2 Important features of the backfill material

According to the conceptual design of the SFL 3-5 repository proposed in (Plan 93, 1993) the waste packages in SFL 3 will be stacked in concrete cells. The cells are backfilled with porous concrete, and the volume between the concrete structure and the rock will be filled with bentonite and sand/bentonite mixtures.

During the work with the analyses of the barrier functions in SFL 3 the necessity of having bentonite barriers in SFL 3 has been questioned, and an alternative design has been proposed where the volume between the concrete structure and the rock is backfilled with sand/gravel.

In order to minimise the release of radionuclides from SFL 3, the following functions of the barrier between the concrete structure and the rock are important:

- the barrier should minimise the water flow through the internal concrete structure, backfill and waste packages to ensure diffusion dominated transport of radionuclides through these inner concrete barriers,
- the retardation of radionuclides in the barrier itself should be high,
- the barrier should be permeable to gas, thereby allowing gas generated in the interior of SFL 3 to escape without pressure build-up and expulsion of contaminated water,
- the chemical and physical properties of the barrier should be stable over long times,
- the barrier should restrict physical and chemical degradation of the internal concrete structure, the porous concrete backfill and the waste packages.

A comparison is made between bentonite barriers and a sand/gravel backfill what concerns the above listed barrier functions in Sections 2.1 to 2.5.

2.1 Minimise water flow through concrete structure and waste packages

Here a comparison is made of the water flow in the concrete structure for a sand/bentonite backfill or a sand/gravel backfill surrounding the concrete structure. To ensure diffusion dominated transport of radionuclides through the internal concrete structure, the backfill between the concrete structure and the rock should restrict water flow through the internal parts. Both a sand/bentonite backfill and a sand/gravel backfill can act as a hydraulic barrier. The hydraulic conductivity of a sand/gravel backfill is several orders of magnitude higher than the concrete structure and its interior filled with concrete. The main part of the water flows in the sand/gravel backfill and the flow through the structure is very small (Holmén, 1999). Changing the backfill material to a less permeable material reduces the flow rate through the backfill significantly, but simultaneously the water flow rate through the concrete structure increases. The effect of the hydraulic conductivity of the backfill material on the release rate of chloride from SFL 3 has been investigated assuming a specific groundwater flow of 10 l/m^2, year (Pettersson *et al.,* 1999). It has been found that when the hydraulic conductivity of the backfill material is decreased from a very large value to about ten times that of the rock, the maximum release rate from the repository is increased by a factor of about two. Additional decrease of the hydraulic conductivity of the backfill results in a slight decrease in the maximum release rate.

How effective the two alternative barriers are to limit the water flow through the internal concrete structure depends not only on their hydraulic properties, but also on the hydraulic properties of the surrounding rock and the internal concrete structure. As a part of the modelling of the groundwater flow in SFL 3-5, the flow in a tunnel with a concrete structure inside the tunnel has been investigated (Holmén, 1997). The effect of different contrasts in hydraulic conductivity in the different barriers was calculated. Based on these results, the total flow in the concrete structure obtained with a sand/bentonite barrier and with a sand/gravel backfill was estimated.

The calculated total flow in the concrete structure is given in Table 1 as a factor of the regional groundwater flow. In addition, the ratio of the total flow in the concrete structure for a sand/bentonite barrier and a sand/gravel backfill is given in Table 1. The basic assumptions are that the hydraulic conductivity in the sand/bentonite barrier is 10^{-9} m/s and that the hydraulic conductivity in the sand/gravel backfill is of the order of 10^{-5} – 10^{-7} m/s. It is believed that it will be difficult to construct a sand/bentonite barrier with a hydraulic conductivity lower than 10^{-9} m/s, and that the hydraulic conductivity in a sand/gravel backfill probably will be closer to 10^{-5} m/s than to 10^{-7} m/s. Table 1 indicate that a sand/gravel backfill with a hydraulic conductivity of 10^{-5} m/s is more effective as a hydraulic barrier for the internal concrete structure than a sand/bentonite barrier if the groundwater flow in the rock is evenly distributed in the rock mass.

The figures in Table 1 represent a situation where the groundwater flow in the surrounding rock is equally distributed over the whole rock mass, uniform continuum approach. If the flow of groundwater in the rock preferentially occurs in one or several fracture zones, the flow through the barrier and the concrete structure is higher than for a homogeneous rock mass. However, the results indicate that a sand/gravel barrier with a hydraulic conductivity of 10^{-5} m/s is to prefer in comparison to a sand/bentonite barrier, see Table 2.

Table 1 **Factor between the total flow in concrete structure and the regional groundwater flow with a sand/bentonite barrier or a sand/gravel barrier, and the ratio between these factors. Continuum flow in the rock outside the barriers (along SFL 3).**

Conductivity [m/s]		Factor between total flow in concrete structure and regional groundwater flow			$\frac{\text{Factor}_{\text{(sand/bentonite)}}}{\text{Factor}_{\text{(sand/gravel)}}}$	
rock	concrete structure	sand/bent. 10^{-9} m/s	sand/gr. 10^{-7} m/s	sand/gr. 10^{-5} m/s	sand/gr. 10^{-7} m/s	sand/gr. 10^{-5} m/s
10^{-9}	10^{-12}	3	0.4	0.006	7.5	500
	10^{-10}	25	4	0.06	6.2	417
	10^{-9}	100	40	0.6	2.5	167
	10^{-8}	1 000	400	6	2.5	167
	10^{-7}	3 500	2 500	60	1.4	58
10^{-8}	10^{-12}	3.5	1	0.06	3.5	58
	10^{-9}	20	10	0.6	2	33
	10^{-8}	100	100	6	1	17
	10^{-7}	700	900	60	0.8	12
	10^{-6}	1 800	4 000	600	0.5	3

Table 2 **Factor between the total flow in concrete structure and the regional groundwater flow with a sand/bentonite barrier or a sand/gravel barrier, and the ratio between these factors. Flow (along SFL 3) in fractures in the rock outside the barriers.**

Conductivity [m/s]		Factor between total flow in concrete structure and regional groundwater flow			$\frac{\text{Factor sand/bentonite}}{\text{Factor sand/gravel}}$	
rock	concrete structure	sand/bent. 10^{-9} m/s	sand/gr. 10^{-7} m/s	sand/gr. 10^{-5} m/s	with 10^{-7} m/s	with 10^{-5} m/s
10^{-9}	10^{-9}	700	160	2	4.4	350
	10^{-8}	1 700	1 000	20	1.7	85
10^{-8}	10^{-8}	300	500	20	0.6	15
	10^{-7}	700	2 000	200	0.4	4

2.2 Retardation of radionuclides in the barrier

Here a comparison is made of the possible retardation in different backfill materials, (bentonite, sand/bentonite mixture and sand/gravel). The retardation of radionuclides in the barrier between the internal concrete structure and the rock will also be of importance for the release of radionuclides from SFL 3. This retardation depends on whether advection or diffusion is the dominating transport mechanism and on the sorption capacity in the barrier. A measure of the radionuclide retardation due to sorption in a barrier is given by the capacity of the barrier, which is defined as:

$$C = \varepsilon + (1-\varepsilon) \cdot K_d \cdot \rho = \frac{D_e}{D_a}$$

where ε = porosity in the barrier

K_d= distribution coefficient between solid and liquid, m^3/kg

ρ = solid density of the barrier material, kg/m^3

D_e= effective diffusivity in the barrier, m^2/s

D_a = apparent diffusivity in the barrier, m^2/s

The capacities in bentonite barriers and in a sand/gravel backfill are given in Table 3. The data used to calculate the capacities are given in (Wiborgh (ed.), 1995). The distribution coefficients for sand/gravel are for a pH in the range 8-10.

The capacity in the sand/gravel backfill is somewhat lower than that in a pure bentonite barrier, except for Cs, Sr, Ra, Be, Cd, Am, Cm, Eu and I where the capacities in the sand/gravel are somewhat higher. Compared to a sand/bentonite backfill, the capacity in the sand/gravel backfill is higher for all nuclides. The relations between the capacities in the different barriers are a bit surprising in the sense that a mixture between two barrier materials with similar capacities gives a barrier material with lower, and for some nuclides much lower, capacity.

Table 3 Barrier capacities for different backfill materials.

Element	Bentonite	Sand/bentonite (90/10)	Sand/gravel
Cs	10	1	88
Sr	10	1	18
Ra	10	1	175
Ni, Co, Fe	100	10	35
Be, Cd	100	10	175
Am, Cm, Eu	$1.0 \cdot 10^3$	100	$5 \cdot 10^3$
Np, Pa, Pu, Th, U	$1.0 \cdot 10^4$	$1 \cdot 10^3$	$9 \cdot 10^3$
Tc, Zr, Nb	$1.0 \cdot 10^4$	$1 \cdot 10^3$	$4 \cdot 10^3$
I	0.1	0.01	0.3

For a non-sorbing nuclide like iodide, the capacity should be equal to the porosity of the barrier. Using the proposed values of the effective and apparent diffusivities to calculate the capacity to retain iodide in bentonite and sand/bentonite gives values of the capacities lower than the proposed porosity, which is 0.6 for bentonite and 0.25 for sand/bentonite (90/10). There are experimental results that indicate that the porosity accessible to anions in bentonite and bentonite/sand mixtures is lower than the porosity accessible to cations. It is also possible that the accessible porosity is lower than the total porosity. What seems a bit strange is the difference in capacity for iodide between a pure bentonite and a sand/bentonite mixture obtained with the proposed effective and apparent diffusivities. These capacities indicate that the porosity accessible for iodide in pure bentonite is 6 times lower than the total porosity and 25 times lower than the total porosity in a 90/10 sand/bentonite mixture. A re-evaluation of the apparent and effective diffusivities proposed for sand/bentonite is therefore suggested. The proposed apparent diffusivity in sand/bentonite is for all elements ten times higher than in pure bentonite. The effective diffusivity is the same for all elements except for iodide that has a ten times lower effective diffusivity.

2.3 Gas pressure build-up and expulsion of water

There are large amounts of metals in the concrete interior of SFL 3 that may corrode and generate gas. If this gas cannot escape through the concrete structure and surrounding barriers the internal gas pressure will increase and water may be expelled from the concrete interior. If this water contains radionuclides, a pressure build-up in the concrete interior may increase the release of radionuclides from SFL 3 (Skagius *et al.,* 1999).

The comparison between bentonite barriers and a sand/gravel backfill in this context is made for the following two different assumptions concerning the concrete structure:

- the concrete structure contains micro-fractures with an aperture and frequency large enough to allow gas to escape through the concrete structure without pressure build-up, and

- the concrete structure is impermeable to gas.

Furthermore it is assumed that the gas conductivity in the surrounding rock is high enough to not restrict gas flow.

If the first assumption is valid, no pressure build-up and expulsion of water from the concrete interior will occur if the structure is surrounded by a sand/gravel backfill. In case of a sand/bentonite backfill at the top of the concrete structure, an over pressure of about 50 kPa has to be reached in the concrete interior before gas can escape through the sand/bentonite backfill and further out through the rock (Pusch, 1985). If a pressure of 50 kPa is obtained, non-capillary bound water in the concrete interior will be expelled.

If the second assumption is valid, i.e. the concrete structure is impermeable to gas, the internal gas pressure will increase until fractures are created in the concrete through which gas can escape. If this over-pressure is larger than the over-pressure required for gas flow through a sand/bentonite barrier, the same amount of water will be expelled from the concrete interior both with a sand/bentonite barrier and a sand/gravel backfill. If the over-pressure is smaller, the expulsion of water in case of a sand/gravel backfill will be determined by this over-pressure and, thus, be smaller than if the concrete structure is surrounded by bentonite barriers where the over-pressure needed for gas escape through the sand/bentonite determines the minimum amount of water expelled.

The effect of expulsion of all non-capillary bound water in the concrete interior, into surrounding bentonite barriers or a sand/gravel backfill, on the radionuclide release has been calculated (Skagius *et al.,* 1999). The results show that the maximum release rate from SFL 3 is not affected for the studied nuclides. However, expulsion of contaminated water results in an earlier release.

2.4 Long-term stability

Different alteration processes may change the initial properties of the backfill material with time. Properties of importance for the radionuclide migration and release are the homogeneity of the barrier, the hydraulic and gas conductivity, the diffusivity and the retention capacity.

The presence of concrete in SFL 3 is probably the major cause for chemical alteration of bentonite. The high pH of concrete leachates may in contact with the smectite in the bentonite barrier lead to the formation of zeolites and hydrosilicates. These minerals do not have the same plasticity as smectite, and may therefore increase the possibility of fracturing of the barrier if exposed to mechanical impact. However, it is possible that reactions between hydroxyl ions and bentonite require elevated temperature (Wiborgh (ed.), 1995). If so, the high pH in SFL 3 will not cause a hydrolysis of the bentonite in a sand/bentonite barrier in SFL 3.

The bentonite may be converted to illite by replacement of sodium by potassium leached from the concrete. Illite is a brittle material with little or no swelling property, which would reduce the plasticity of the bentonite and thereby increase the risk for cracking. The conversion to illite is greatly enhanced by elevated temperature (Wiborgh (ed.), 1995).

Sodium in the bentonite may be replaced by calcium leached from the concrete causing a loss in swelling pressure and thereby an increase in hydraulic conductivity. This process is expected to gain importance when the leaching of the alkali hydroxides in the concrete is completed and the concentration in the cement porewater of Ca^{2+} starts to increase and Na^+ decreases (Wiborgh (ed.), 1995).

Chemical reactions between components dissolved from the bentonite, or naturally present in the groundwater, and components leached from the concrete may cause precipitation of calcite and brucite. This may lead to a blocking of pores in the barrier and thereby reduced porosity, but also to a cementation of the barrier with a loss in plasticity and increased risk for fracturing as a consequence. A bentonite barrier is also sensitive to the salinity of the groundwater. An increased salinity of the water will increase the hydraulic conductivity of the barrier for low bentonite densities.

However, none of the alteration processes is expected to significantly change the retardation (sorption) capacity of a bentonite barrier or a sand/bentonite barrier.

The above listed alteration processes may with time increase the hydraulic conductivity of a sand/bentonite barrier and some of them also increase the risk for preferential flow paths through the barrier. This could mean a decrease in efficiency of the sand/bentonite as a barrier for radionuclide migration and release, but not necessarily a decrease in the efficiency of the SFL 3 barrier system. It depends on how large these changes are, and how important the sand/bentonite barrier is in relation to the other barriers in the system.

An increase in the already high hydraulic conductivity in a sand/gravel backfill is of no importance for the efficiency of the barrier, and furthermore processes causing an increase are difficult to identify. However, a redistribution of the sand/gravel material or blocking of porosity may create preferential flow paths through the sand/gravel backfill, thereby reducing the accessible retention capacity. Settling of the sand/gravel material and movements of rock blocks may not necessarily create preferential flow paths through the sand/gravel itself. Chemical reactions between components leached from the concrete and components in the groundwater may cause precipitation of calcite and brucite in the sand/gravel backfill.

The minerals in the sand/gravel material may be altered in contact with highly alkaline water. This may change the retention capacity of the material, but probably increase the capacity rather than decrease it.

2.5 Protection of inner concrete structure and barriers

Both bentonite barriers and a sand/gravel backfill will act as a mechanical support for the surrounding rock and thereby to some extent protect the inner concrete structure from mechanical impact by rock blocks caving in. However, a bentonite barrier is probably more effective as long as it maintains the initial plasticity and swelling pressure.

What concerns the chemical alteration of the inner concrete structure and barriers, bentonite and sand/bentonite barriers may limit the supply of aggressive species in the groundwater and the release of components leached from the concrete. A sand/gravel backfill can lead to a lower water flow rate through the concrete structure than a sand/bentonite barrier (see Section 2.1), but the water flow rate outside the structure will be higher. The importance of this effect is difficult to assess.

In the negative sense, bentonite barriers may act as a source for species that may react with the concrete, for example sulphate, while a sand/gravel backfill probably is inert in this sense.

3 Backfill in tunnel and waste packages in SFL 4 or not?

According to the conceptual design of the SFL 4 repository proposed in (Plan 93, 1993) the waste is packed in steel vessels, which are piled on a concrete bottom plate in the tunnel system connecting the SFL 3 and SFL 5 repository parts. The steel vessels are not backfilled, but before repository closure the tunnels are backfilled with sand/gravel and the access tunnel is plugged.

One question regarding the design of SFL 4 concerns the importance of backfill in the tunnels and the waste packages for the radionuclide migration and release from SFL 4. Therefore, a first attempt has been made to estimate the effect of backfill in tunnels and waste packages on the retention capacity and transport parameters (water fluxes and diffusivities) of importance for radionuclide migration and release, see Section 3.1-3.2.

3.1 Transport parameters

The water flow in SFL 4 has been estimated as a function of the average hydraulic conductivity in the tunnel (Holmén, 1997). For a horizontal flow along or perpendicular to SFL 3 and SFL 5, the water flow through SFL 4 is independent of the hydraulic conductivity of the backfill material as long as the backfill conductivity is 10^4 times that of the rock or higher.

The conductivity of SFL 4 may influence the flow in the SFL 3 tunnel. Results presented in Holmén (1997) show that backfilling SFL 4 will increase the water flow rate through SFL 3 in comparison with the case when SFL 4 is not backfilled.

The effect of backfill in the waste packages on the transport parameters describing the radionuclide release from the packages is difficult to estimate, since it cannot be guaranteed that all waste in the packages are surrounded by backfill. The only difference that can be accounted for is the difference in sorption capacity that determines the radionuclide concentration in the water in the waste packages.

3.2 Retention capacity

The capacity of the barrier is defined in Section 2.2. The total retention capacity in the barrier is obtained by multiplying the capacity defined with the volume of the barrier.

The effect of backfilling the waste packages in SFL 4 with either sand or concrete has been calculated. This has been done for:

- a sand/gravel backfill in the waste packages with a filling degree of 50 or 100 %
- a concrete backfill in the waste packages with a filling degree of 50 or 100 %.

The waste to be deposited in SFL 4 consists mainly of metals. The waste packages (steel vessels) are not backfilled and the major part of the packages is void. The retention capacity of the waste package is therefore based on the void volume only. The distribution coefficients and material data used are given in (Wiborgh (ed.), 1995). The distribution coefficients used are for sand/gravel at a pH in the range 8-10 and for leached concrete.

The results are shown in Table 4 as retention capacity in backfilled packages relative unfilled packages. For all sorbing elements, a backfill in the waste packages will decrease the concentration in the waste package and thereby the radionuclide release from the package compared with an unfilled waste package. A concrete backfill is in general more efficient than a sand/gravel backfill. The effect on low-sorbing nuclides (e.g. inorganic carbon and strontium in sand/gravel and iodide and strontium in concrete) is limited. For non-sorbing nuclides (organic carbon, hydrogen and iodide (in sand)) the capacity equals the void volume. Backfilling the waste packages has thus a negative effect since the concentration increases.

Table 4 Effects of backfill in waste packages on the retention capacity.

Element	Retention capacities in backfilled packages relative to unfilled packages			
	packages filled with sand to:		packages filled with concrete to:	
	50%	100%	50%	100%
Cs	44	88	115	230
Sr	9	18	24	46
Ni, Co, Fe	18	35	115	230
Ra, Be, Cd	88	175	58	115
Am, Cm, Eu	2 626	5 250	5 738	11 475
Np, Pa, Pu, Th, U	4 376	8 750	5 738	11 475
Tc	1 751	3 500	2 296	4 590
Zr	1 751	3 500	5 738	11 475
Nb	1 751	3 500	2 296	4 590
C (inorg)	1.5	2.1	1 148	2 295
C (org)	0.7	0.3	0.6	0.2
I	0.7	0.3	4.0	7.0
H	0.7	0.3	0.6	0.2

The capacity of the tunnel not filled with waste packages has been neglected in the results presented above. Backfilling the SFL 4 tunnel with sand/gravel is an option being discussed. The effect of backfilling the tunnel has therefore also been analysed in terms of retention capacity. The volume of waste packages to be deposited in SFL 4 and the volume of tunnel backfill required for the part of SFL 4 occupied by the waste are roughly equal, i.e.:

$$\frac{V_{waste}}{V_{tunnel\ backfill}} \approx 1$$

Based on this relationship between volume of waste packages and tunnel backfill material, the total retention capacity has been calculated for a tunnel backfilled with sand/gravel and waste packages filled with either sand/gravel or concrete. The filling degree in packages is assumed to be 50 % or 100 %. The results are compared with the total capacity obtained if the waste is backfilled but the tunnel is not.

Table 5 shows the effect of a sand/gravel backfill in the tunnel if the waste packages are a) backfilled with sand/gravel or b) backfilled with concrete. The additional retention capacity obtained by not only backfilling the waste packages but also the SFL 4 tunnel is in general about a factor of two. This is related to the assumption that the volume of tunnel backfill and waste packages are the same. The relative effect of backfilling the tunnel with sand/gravel is higher when the waste packages are filled with sand than when filled with concrete. The total capacity is, however, higher for a concrete backfill.

Table 5 Effects of backfill in waste packages on the retention capacity.

Element	**Retention capacities relative retention capacities for backfilled packages but unfilled tunnel.**			
	Sand/gravel filled tunnels and			
	packages filled with sand to:		packages filled with concrete to:	
	50%	100%	50%	100%
Cs	2.9	2.0	1.7	1.4
Sr	2.6	1.9	1.7	1.4
Ni, Co, Fe	2.8	1.9	1.3	1.1
Ra, Be, Cd	3.0	2.0	4.0	2.5
Am, Cm, Eu	3.0	2.0	1.9	1.5
Np, Pa, Pu, Th, U	3.0	2.0	2.5	1.8
Tc	3.0	2.0	2.5	1.8
Zr	3.0	2.0	1.6	1.3
Nb	3.0	2.0	2.5	1.8
C (inorg)	1.4	1.3	1.0	1.0
C (org)	0.6	0.5	0.6	0.4
I	0.6	0.5	0.9	0.9
H	0.6	0.5	0.6	0.4

The effect of backfilling the SFL 4 tunnel if the waste packages were not backfilled would be just as pronounced as the effect of backfilling waste packages in an empty tunnel as shown in Table 4. This is, however, not considered to be an alternative since the unfilled waste packages probably would not be able to take the load of the tunnel backfill.

4 Conclusions

This comparison between different backfill material for the SFL 3 tunnel showed that:

- Both a sand/bentonite barrier with hydraulic conductivity of 10^{-9} m/s and a sand/gravel backfill with hydraulic conductivity of 10^{-7} to 10^{-5} m/s will function as a hydraulic barrier for the internal concrete system. Of the alternatives compared here, a sand/gravel backfill with a hydraulic conductivity of 10^{-5} m/s is to prefer.

- There is no obvious advantage with bentonite barriers compared to a sand/gravel backfill what concerns the radionuclide retention in the barriers. The retention capacity in the sand/gravel backfill is comparable to the retention capacity in a pure bentonite barrier, but higher than in a 90/10 sand/bentonite barrier. This could in fact mean that the sand/gravel backfill is a better barrier to radionuclide transport and release than a 90/10 sand/bentonite barrier. However, it should be noted that diffusivity and sorption data in bentonite systems are difficult to determine and proposed values are associated with large uncertainties.

- A sand/gravel backfill will not cause pressure build-up and water expulsion, but bentonite barriers will. If the concrete structure are impermeable to gas, and this causes pressure build up in the interior and expulsion of water, both bentonite barriers and a sand/gravel backfill is in general effective enough to capture nuclides in the expelled water without causing increased maximum release rates of nuclides.

- The hydraulic properties of bentonite barriers may be affected in a negative way by alteration processes initiated by the presence of concrete. The probability of occurrence and the effects on the hydraulic properties are difficult to assess. In addition, the consequences of potential changes in hydraulic properties for the migration and release of radionuclides depends on the relative importance of the barrier in the whole barrier system. The important properties of a sand/gravel backfill is probably more inert and less sensitive to alteration processes, and no major negative changes in hydraulic or retention properties are expected.

- There seems to be no obvious advantage with bentonite barriers compared to a sand/gravel backfill regarding the chemical protection of the inner concrete structure and barriers. However, a bentonite barrier may be more effective to mechanically protect the internal system as long as it maintains the initial plasticity and swelling pressure.

In summary, the comparison indicates that a sand/gravel backfill is good enough as a barrier for radionuclide migration and release for low regional groundwater flows. A sand/bentonite barrier may be equally good or even better, but data on transport properties are difficult to obtain and therefore associated with large uncertainties. In addition, potential changes in transport properties due to alteration of bentonite barriers are difficult to predict. Therefore, sand/gravel is proposed as a backfill material in SFL 3.

The comparison of retention capacities for SFL 4 indicates that a sand/gravel backfill in the waste packages will be efficient in lowering the release of radionuclides from SFL 4. A concrete backfill will in general be even more efficient. The additional effect obtained by backfilling the tunnel as well is generally small. Backfilled tunnels and unfilled packages are not an alternative since the packagings will probably not sustain the mechanical load from the tunnel backfill. Backfilling SFL 4 will, however, increase the water flow rate through SFL 3.

5 References

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