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Technical Note

2014:48

Independent assessment of groundwater sulphide content in the long-term

Main Review Phase

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SSM perspektiv

Bakgrund

Strålsäkerhetsmyndigheten (SSM) granskar Svensk Kärnbränslehantering AB:s (SKB) ansökningar enligt lagen (1984:3) om kärnteknisk verksamhet om uppförande, innehav och drift av ett slutförvar för använt kärnbränsle och av en inkapslingsanläggning. Som en del i granskningen ger SSM konsulter uppdrag för att inhämta information i avgränsade frågor. I SSM:s Technical note-serie rapporteras resultaten från dessa konsultuppdrag.

Projektets syfte

Syftet med detta uppdrag är göra en utvärdering av giltigheten för SKB:s metod för att bestämma representativa halter av sulfid i grundvatten, som inkluderar urval av prover, grunden för att utesluta vissa grundvattenprover, samt även en analys av det möjliga tidsberoendet för en utveckling av grundvattnets sulfidkoncentrationer.

Författarens sammanfattning

Grundvattnets innehåll av svavelväte är en viktig faktor för analys av tiden för kopparkapslarnas livslängd på grund av dess roll i korrosion av koppar. SKB har baserat analysen av kapsellivslängder på en fördelning av uppmätta sulfidkoncentrationer som antas gälla under hela den tid som täcks in i analysen av långsiktig säkerhet. Fördelningen är baserad på expertbedömningar för att fastställa urvalet av prover som kan betraktas som representativa. Syftet med denna rapport är att göra en bedömning av giltigheten av SKB:s metod.

Sulfid i grundvattnet kommer från biogeokemiskt alstrad omvandling av sulfat. Sulfidkoncentrationer i grundvatten med normal mikrobiell aktivitetsnivå, lösta järnkoncentrationer och halter av organiskt kol är generellt lägre än 10^{-4} mol.dm^{-3}. Dessa nivåer styrs av långsam kinetik för sulfatreduktion och/eller påverkan av upplösta sulfidkoncentrationer från kemisk jämvikt med fasta järnsulfidfaser. Jämviktsmodellering visar att uppmätta sulfidhalter ligger under mättnadsnivåerna för järnmonosulfid, så antingen är det reduktionshastigheten som styr uppmätta koncentrationer eller så är andra järnsulfidfaser inblandade.

Nästan alla grundvattenprover från Forsmark har HS- koncentrationer under $1{,}1\text{x}10^{-4}$ mol.dm^{-3} och de flesta har värden under $1\text{x}10^{-5}$mol.dm^{-3} med många under detektionsgränsen $3\text{x}10^{-7}$mol.dm^{-3}. SKB har tilldelat $1.1\text{x}10^{-4}$mol.dm^{-3} som det högsta värdet från en fördelning av valda data som tolkas som representativa för dagens ostörda grundvatten. Valet av fördelning utgår från ett ganska litet antal prover, så det förekomma grundvatten med högre in situ halter av sulfid som inte har blivit provtaget, men enligt min bedömning som grundar sig på data från andra liknande grundvattensystem är det osannolikt att halterna skulle kunna vara betydligt högre. Prover med högre koncentration än $5\text{x}10^{-4}$ mol.dm^{-3} har uppmätts i Forsmark, men denna information har uteslutits från fördelningen av sulfidkoncentrationer eftersom det är frågan om en lokaliserad störning som har orsakat ett tillfällig toppvärde för sulfid. Det finns andra fall av övergående höga sulfidhalter i prover från Forsmark, även i Olkiluoto Finland och tidigare data från Äspö. Det är viktigt att detta fenomen kan förstås mot bakgrund av att sulfidhalter är betydelsefulla för korrosionsberäkningar.

Den sannolika omfattningen av osäkerhet på grund av variationer i sulfidinnehåll och risken för att det finns okända störningar under provtagningen kan enligt min bedömning inte undergräva värdet och tillförlitligheten hos valda sulfiddata för användning inom säkerhetsanalysen. Detta gäller så länge som osäkerheter behandlas pessimistiskt och så länge som lämpliga känslighetsanalyser kopplade till korrosionsberäkningarna har utförs. SKB:s metod för val av data och hantering av osäkerheter är rimlig som en del av ett praktiskt sätt att erhålla parametrar för användning inom säkerhetsanalysen.

Ytterligare provtagning under konstruktionsfasen kommer att erfordras för att bekräfta de valda sulfidhalterna för aktuella bergvolymer i berggrunden. Det behövs en stabil och väl kontrollerad metod för provtagning av sulfid, mikrober och geogaser för användning i tunnlar, sonderingshål, osv. som kan utesluta förekomst av okontrollerade störningar. Variationer av sulfidhalter i nuläget och i den framtida utvecklingen av grundvattensystemet styrs av tillgång till svavel, av sulfatreduktion, samt genom kontroll av sulfidhalter via kemisk jämvikt med järnsulfid. Sulfatreduktion och produktion av sulfid förekommer aktivt i grundvatten på förvarsdjup och det finns en förväntan att sulfidproduktionen kommer att fortsätta på detta sätt. Mikrobiologiska och geokemiska data ger dock inte ge en klar bild av de biogeokemiska processer som påverkar den rumsliga och tidsmässiga fördelningen av sulfid. Förutom att löst sulfid begränsas av jämvikt med järnsulfid, finns det också en yttersta begränsning som styrs av massbudgeten av svavel som finns tillgänglig för grundvattensystemet med beaktande av hastigheten för frigörelse från olika källor, dispersion eller utfällning av sulfid från vattenfasen. Vissa överslagsberäkningar har utförts i denna rapport av dessa materialbalanser och processhastigheter som illustrerar frågeställningar och effekter kopplade till extrema scenarier.

SKB har använt modellering av hydrodynamisk blandning och hydrogeokemiska processer för att förutse den potentiella utvecklingen av sulfid genom både tempererade och glacial/ peri-glaciala perioder. Denna modellering utforskar på ett bra sätt omfattningen av sulfidvariabilitet som beror på kemiska koncept, antaganden och förenklingar. SKB har dock inte använt dessa modellers beräkningar av sulfidhalter i säkerhetsanalysen SR-Site, med motiveringen att de är pessimistiskt höga och inte jämförbara med de uppmätta data i dagens system. SKB använder istället dagens sulfidhalter för hela referensutvecklingen genom både tempererade och periglaciala/istider. Det är mycket troligt att långsiktiga sulfidkoncentrationer kommer att kontrolleras på låga nivåer som liknar de som observerats i de nuvarande systemen.

Jag drar slutsatsen att SKB: s tolkning av biogeokemi för sulfid i grundvattensystemet är den mest sannolika modellen. Den mest pessimistiska extrapolationen av den biogeokemiska modellen in i framtiden skulle vara ett scenario med ökande tillförseln av organiskt kol, antingen naturligt eller från material som har tillförts slutförvaret, i en form som skulle vara tillgängligt för mikrobiell respiration. Detta skulle främja en snabb produktion sulfid. I detta fall skulle grundvattnets innehåll av sulfid kontrolleras genom kemisk jämvikt med fasta järnsulfider eller genom tillgängligheten för sulfat.

SKB:s metod som utgår från användningen av en konstant sulfidhalt genom hela utvecklingen av slutförvarssystemet är försvarbar eftersom den är enkel. Den har använts i korrosionsberäkningarna med en känslighetsanalys som visar de potentiella effekterna av tänkbara scenarier för sulfidinnehåll. SKB borde dock även ha testat det pessimistiska tillståndet i vilket sulfid halterna etablerats är de högre nivåerna som ges av kemisk jämvikt med järnsulfid.

Projektinformation
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Diarienummer ramavtal: SSM2011-3637
Diarienummer avrop: SSM2013-2218
Aktivitetsnummer: 3030012-4067

SSM perspective

Background

The Swedish Radiation Safety Authority (SSM) reviews the Swedish Nuclear Fuel Company's (SKB) applications under the Act on Nuclear Activities (SFS 1984:3) for the construction and operation of a repository for spent nuclear fuel and for an encapsulation facility. As part of the review, SSM commissions consultants to carry out work in order to obtain information on specific issues. The results from the consultants' tasks are reported in SSM's Technical Note series.

Objectives of the project

The objective of this assignment is to make an assessment of the validity of SKB's approach for determining representative groundwater sulphide content involving both sample selection, and the basis for omitting some samples as well as an analysis of possible time dependencies of sulphide concentration evolution.

Summary by the author

Groundwater sulphide content is a key factor in the determination of canister lifetimes because of its role in corrosion of copper. SKB has based the canister lifetime analysis on a distribution of measured sulphide concentrations which are assumed to apply throughout the long-term analysis period. The distribution is based on expert judgement in the selection of samples that are regarded as representative. The objective of this report is to make an assessment of the validity of SKB's approach.

Sulphide in groundwater derives from biogeochemically-mediated redox transformation of sulphate. Sulphide concentrations in groundwaters with normal microbial activities, dissolved iron concentrations and organic carbon contents are generally lower than 10^{-4} mol.dm^{-3} because of low sulphate reduction kinetics and/or because of control of dissolved sulphide concentrations by iron sulphide equilibrium. Equilibrium modelling shows that measured sulphide contents are below saturation levels for iron monosulphide, so either reduction rate is controlling concentrations or another iron sulphide phase is involved.

Almost all groundwater samples from the Forsmark site have HS- concentrations below 1.1×10^{-4} mol.dm^{-3} and most have values below 1×10^{-5} mol.dm^{-3} with many below the detection limit of 3×10^{-7} mol.dm^{-3}. SKB has assigned 1.1×10^{-4} mol.dm^{-3} as the maximum of a distribution of selected data that are interpreted to be representative of present-day unperturbed in situ groundwaters. The selections are from a rather low number of samples, so there may be higher in situ sulphide contents that have not been sampled though my judgement based on data from similar groundwater systems is that they are unlikely to be substantially higher. A higher concentration of 5×10^{-4} mol.dm^{-3} has been measured at Forsmark but this has been excluded from the selected sulphide values on the basis that localised perturbation has caused a transient peak of sulphide. There are other cases of transiently high sulphide contents in samples from Forsmark, and also at Olkiluoto in Finland and in historical data from Äspö HRL, so this is a phenomenon that needs to be understood in view of the significance of sulphide for corrosion calculations.

The likely magnitude of uncertainties due to the variations of sulphide contents and the possibilities of poorly understood perturbations during sampling does not, in my opinion, undermine the value and reliability of selected sulphide data for use in safety analysis as long as the uncertainties are treated pessimistically and appropriate sensitivity tests of the corrosion calculations are carried out. SKB's approach to data selection and handling of uncertainties is reasonable as a practicable way of achieving parameters for use in safety analysis.

Additional sampling during a construction phase will be needed to confirm the range of in situ sulphide in the target volume of bedrock. A robust and well-controlled sampling method for sulphide, microbes and gases that will exclude uncontrolled perturbations is needed for use in tunnels, probe holes, and so on.

The variability of sulphide at the present time and through the future evolution of the groundwater system is governed by the sources of sulphur, by the rate of reduction of sulphate, and by control by iron sulphide. Sulphate reduction and production of sulphide is actively occurring in groundwaters at repository depth and there is an expectation that sulphide production in this way will continue. However the microbiological and geochemical data do not offer a clear picture of the biogeochemical processes affecting the spatial and temporal distribution of sulphide. In addition to dissolved sulphide being limited by iron sulphide equilibrium, it is also ultimately constrained by the mass budget of sulphur available to the groundwater system, by the rates of release from these various sources and the rates of dispersion or removal of sulphide from solution. Some scoping calculations of these mass budgets and process rates illustrate the issues and the impacts of extreme scenarios.

SKB has used hydrodynamic mixing and hydrogeochemical modelling to forecast potential evolution of sulphide through both the temperate and glacial/periglacial periods. This modelling usefully explores the scale of sulphide variability for the various hydrogeochemical concepts, assumptions and simplifications. However SKB has not used these modelled sulphide contents in the safety analysis for SR-Site, reasoning that they are pessimistically high and do not compare with the measured data in the present-day system. Instead, SKB use the present-day sulphide contents for the entire reference evolution through temperate and periglacial/glacial periods. It is highly likely that long-term sulphide concentrations will be controlled at low levels similar to those observed in the present systems.

I conclude that SKB's interpretation of sulphide biogeochemistry in the general groundwater system is the most likely model. The most pessimistic extrapolation of that biogeochemical model into the future would be a scenario of increasing inputs of organic carbon, either naturally or from introduced materials in the repository, in a form that would be available for microbial respiration and would promote rapid sulphide production. In that case, groundwater sulphide contents would be controlled by iron sulphide equilibrium or by sulphate availability.

SKB's approach using constant sulphide contents throughout the evolution of the system is defensible because it is straightforward. It has been used in corrosion calculations with a sensitivity analysis that shows the potential impacts of plausible scenarios for sulphide contents, although the pessimistic condition where sulphide contents are at the higher levels given by iron sulphide equilibrium should also have been tested.

Project information
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Contents

1. Introduction

SSM’s scope of work for this assignment states:

Groundwater sulphide content is a key factor in the determination of canister lifetimes. SKB has based the canister lifetime analysis on a distribution of measured sulphide concentrations which are assumed to apply indefinitely. The distribution is based on expert judgement in the selection of samples that are regarded as representative. The objective of this assignment is to make an assessment of the validity of SKB’s approach, including sample selection, treatment of uncertainties in the method for analysis, and the basis for omitting some samples as well as an analysis of possible time dependencies associated with the long-term evolution of sulphide concentration. SKB’s omission of time dependency is not necessarily a deficiency as long as the present groundwater situation can be shown to be at a reasonable and/or at a conservative level. Associated microbial or inorganic reactions in the groundwater that either directly or indirectly affect the distribution of sulphide concentrations should be addressed to the extent possible. In case the SKB distribution is judged to be insufficient or non-conservative, the author(s) may provide a justified alternative distribution that can be used as a basis for SSM’s independent modelling work.

The structure of this report is as follows:

Chapter 2 assesses SKB’s approach to sample and data selection for groundwater sulphide contents.

Section 2.1 summarises the methods used for sampling and analysis for sulphide and the results obtained from deep surface-based boreholes at Forsmark. It also gives some background interpretation of the measured sulphide concentrations and of the constraints on present-day production and concentrations of sulphide in groundwaters.

Section 2.2 presents some information relating to SSM’s motivation in commissioning this assessment. The relevant parts of SSM’s advice on applying the regulations are recapped, especially the relevant requirements in terms of safety functions and performance of the engineered and natural barriers. Recommendations in the regulations concerning the development of scenarios and the identification and evaluation of uncertainties are abstracted. The safety implications of groundwater sulphide are discussed in terms of processes in the buffer that would influence the amount of sulphide reaching the surface of the copper canister, and processes in groundwaters that would affect the concentration of sulphide at the rims of deposition holes. Some aspects of the safety analysis calculations that give insights of the tolerance to uncertainties in sulphide contents are discussed.

Section 2.3 provides my assessment of SKB’s approach to sample and data selection for groundwater sulphide contents. A background of general knowledge and available data for sulphide concentrations in groundwaters in aquifers and crystalline rocks is reviewed. Then data reported for Forsmark and the validity of sample and data selection by SKB are assessed. The biogeochemical parameters and processes that are involved in the production of sulphide are summarised and the state of knowledge about them is reviewed. These processes, and the associated uncertainties, are the basis for estimating potential fluxes of sulphide from groundwater into the engineered barrier system.

Chapter 3 assesses SKB's approach to understanding and constraining the potential time dependences of sulphide contents, as inputs to the long-term analysis of canister corrosion.

Section 3.1 summarises SKB's interpretative models for sulphide production in buffer and backfill and for transport of sulphide to the buffer-canister interface. Then the main issues of how groundwater sulphide contents in the temperate, periglacial and glacial periods of the long-term reference scenario have been treated in SKB's performance analysis are reviewed. The arguments made by SKB to support their choices of values for sulphide contents in groundwaters adjacent to deposition holes at various times are abstracted.

Section 3.2 refers back to Section 2.2 for relevant extracts from the regulatory guidance. Then the potential safety implications of sulphide contents and the factors that might affect sulphide in the long term evolution of the system are summarised. The implications of uncertainties in sulphide contents, processes and variables affecting sulphide are discussed.

Section 3.3 contains my assessment of SKB's decision to use the present distribution of sulphide contents as being representative for all stages of future evolution in the long-term analysis of corrosion. Firstly, the data and processes for sulphide in the buffer and backfill are reviewed since these will be the barriers between groundwater and canisters. Then the state of knowledge about biogeochemistry of sulphide production in the natural groundwater system is described. This is rather similar to what is described in Section 2.3 except that the understanding of processes is used to discuss the ways that the biogeochemical system might respond to future changes of groundwater conditions. Various scoping calculations are presented to examine the potential 'worst case' scenarios for increased sulphide contents, and also to examine the mass budgets of sulphide, sulphate and iron in groundwaters as the three key variables that can be constrained geochemically.

Chapter 4 presents my overall assessment of SKB's approach to these issues and also some suggestions for future investigations during construction and operation that might increase knowledge and confidence.

Section 4.1 deals with the issues of sample and data selection. Section 4.2 deals with the issues of future evolution of sulphide contents and choice of sulphide data for corrosion analysis in the stages of the reference evolution. Section 4.3 draws together some succinct general conclusions.

Chapter 5 contains a full list of references to work that has been cited in this report.

Appendix 1 contains a list of SKB reports, and of the pertinent sections, in the SR-Site portfolio that have been reviewed for this task.

Appendix 2 contains my comments on SKB's response to a request for complementary information that was submitted by SSM in 2011. The request for further information pertains to two related issues: (i) the forms and availability of dissolved organic carbon for microbial sulphate reduction, and (ii) the hypothesis that microbial reduction of methane (anaerobic oxidation of methane) does not occur in Forsmark groundwaters.

2. Assessment of SKB's approach to sample and data selection

2.1. SKB's presentation

2.1.1. Sampling and analysis for dissolved sulphide

The Site Description report, SDM-Site Forsmark (SKB 2008), contains information about the sampling and analyses for sulphide (HS^-) and sulphate (SO_4^{2-}) concentrations in groundwaters. These data, plus associated parameters for dissolved iron (Fe^{2+}) concentrations, redox and microbiological populations are the basis of SKB's description and interpretation of the present-day contents, sources, *in* situ production and other controls of dissolved HS^- contents in groundwaters at Forsmark.

Modelled predictions of future copper canister corrosion by HS^- for the long-term safety analysis, SR-Site, rely on projections of dissolved HS^- concentrations at various stages of the future evolution of conditions at repository depth at Forsmark. Therefore data for present-day contents would appear to be of subsidiary importance for the safety case. However, as will be explained below, SKB justifies the use of present-day distributions of HS^- as a proxy for future contents.

Water samples for HS^- analyses were collected routinely during water sampling for 'complete chemical characterisation' (CCC) and also, occasionally but not always, from other types of water sampling procedures including multiple sampling in time series from monitoring systems installed at identified flowing features in the percussion (HFM) and cored (KFM) boreholes. All or most of the associated hydrochemical parameters were obtained in each CCC sampling operation, so that many of these borehole intervals have the most complete and most representative sets of data for the sulphide system: pH, Eh potential, ferrous iron (Fe^{2+}) and total iron, sulphate (SO_4^{2-}), dissolved organic carbon (DOC), and stable isotopic composition of sulphur in SO_4^{2-} ($\delta^{34}S$). In a smaller number of cases, dissolved gases and microbial populations were sampled and analysed in specialist laboratories.

The various methods by which water samples for sulphide analyses have been collected are described and discussed in Tullborg et al. (2010).

Sulphide concentrations in groundwater samples have been analysed by spectrophotometry, using either the in-house SKB laboratory or an external laboratory. The detection limit for the SKB analyses is 0.006 mg/L though a reporting lower limit of 0.02 mg/L has generally been applied (Section 4 in Kalinowski et al. 2008). The external laboratory had a reporting/detection limit of 0.01 mg/L. The analytical uncertainties for the two laboratories are ±25% and either ±0.02 mg/L or ±12% respectively.

2.1.2. Sulphide concentration data for groundwaters

Water samples and resulting analytical data have been subjected to quality classification, depending on the operational parameters of sampling and field observations that pertain to the reliability and representativeness of each sample (Smellie et al., 2008). Reported HS^- data have been selected and qualified by SKB as the most representative of in situ conditions.

Table 1 lists the HS^- concentrations and some other relevant hydrochemical parameters for samples that are assessed by SKB to fall in quality categories 1 to 3. These data are extracted from an SKB spreadsheet for the ‘extended SDM 2.3’ data freeze around mid-2007. Category 1 samples are the most representative. SKB states that category 1 and 2 data are required for “geochemical equilibrium calculations, modelling of redox conditions, and for specialised studies on microbes, organics and colloids” (SKB 2008). Category 3 and 4 data, together with category 1 and 2 data are judged to be adequate for use in interpreting “overall site understanding (e.g. groundwater distribution, origin and evolution and integration with hydrogeology).”

Table 1 includes some time series data from sampling campaigns that are separated typically by a few months to a year, and also some time series that are separated only by a few days within a single sampling campaign. These time series examples, comprising samples with adequate levels of reliability, give an idea of the variability of HS^- contents in these different sampling conditions. Many more time series of HS^- data are presented in Appendices 1 and 2 of Tullborg et al. (2010), as discussed below, but these samples have a wider range of sample quality categories.

HS^- analyses, qualified and approved by SKB in the ‘extended 2.3’ spreadsheet (dated 30 Dec 2007), for CCC samples taken from percussion (HFM) and cored (KFM) boreholes soon after drilling are below 1 mg/L (*i.e.* $<3\times10^{-5}$ mol/L) with one exception (HFM19/-137.1). Several analyses are below detection limits (which varied from to 0.002 to 0.03 mg/L, usually around 10^{-7} mol/L).

Table 1: Sulphide (HS^-), iron (Fe^{2+}) and selected other hydrochemical data for groundwater samples in quality categories 1 to 3 from percussion (HFM) and cored (KFM) boreholes at Forsmark. Extracted from SKB spreadsheet Forsmark_2_3_updated_Dec30_2007, sheets 'Extended F23 (+SFR)' & 'F23 corrected' (SKB document 1344208 dated 2012-05-15). 'T' prefix in quality category values are time series samples.

Borehole	Sample number	Quality category	Date	Elevation, metres	Drill water, %	pH	Eh mV	TDS mg/L	Cl^- mg/L	SO_4^{2-} mg/L	HS^- mg/L	Fe^{2+} mg/L	DOC mg/L
HFM01	12757	3	2007/04/10	-37.02		7.72		1660	739	180	<0.006	0.79	9.5
HFM02	12006	3	2005/11/09	-39.91		7.82		949	396	84	0.026	0.43	9.8
HFM02	12503	T3	2006/10/17			7.60		1914	945	155	0.031	0.82	8.6
HFM04	12003	1	2005/11/07	-57.92		7.71		325	56	45	0.047	0.35	8.3
HFM04	12519	T1	2006/10/31			7.69		326	59	45	0.055	0.34	8.8
HFM13	12009	1	2005/11/09	-138.63		7.34		8754	5020	476	0.023	3.47	2.2
HFM13	12510	T1	2006/10/24			7.32		8913	5150	431	0.005	3.62	1.9
HFM16	12379	3	2006/10/06	-57.19		7.78		651	187	101	0.011	0.59	13.0
HFM19	12010	1	2005/11/09	-137.10		7.21		9372	5330	565	1.57	5.36	35.7
HFM21	12758	3	2007/04/10	-18.82		7.54		715	241	105	<0.006	1.03	7.6
HFM27	12506	3	2006/10/17	-45.60		7.35		4779	2660	347	0.020	2.77	4.6
KFM01A	4538	2	2003/02/24	-111.74	0.8	7.62	-195	7771	4563	316	0.014	0.95	1.5
KFM01A	4620	T2	2003/03/07	-176.26	6.5	7.41		8985	5187	533	<0.030	1.85	3.3
KFM01A	4663	T2	2003/03/14		5.6	7.41		9036	5220	534	<0.030	1.11	1.1
KFM01A	4665	T2	2003/03/20		5.2	7.41		8896	5091	537	<0.030	0.81	4.1
KFM01A	4724	2	2003/03/31		4.8	7.41	-188	9179	5329	547	<0.030	0.47	2.3
KFM01D	12771	3	2007/04/18	-252.53		7.60		6298	3680	212	0.287		8.0
KFM01D	12366	3	2006/08/22	-253.31	9.0	7.56		6699	3890	279	0.009		4.1
KFM01D	12343	1	2006/07/13	-445.17	0.8		-260	9800	5960	31.1	0.01	0.76	11.0

Borehole	Sample number	Quality category	Date	Elevation, metres	Drill water, %	pH	Eh mV	TDS mg/L	Cl^- mg/L	SO_4^{2-} mg/L	HS^- mg/L	Fe^{2+} mg/L	DOC mg/L
KFM02A	8100	3	2003/11/18	-108.85	0.4	7.53		1309	642	90	0.008		11.0
KFM02A	8272	2	2004/02/23	-414.81	2.2	7.11		9141	5380	434	<0.002	0.73	<1.0
KFM02A	12002	2	2005/11/04	-417.80	2.6	7.36		9431	5440	435	0.058	1.36	1.2
KFM02A	12502	T2	2006/10/10			7.44		9677	5590	502	0.129	1.74	1.5
KFM02A	12004	2	2005/11/07	-494.97	3.4	7.19		9526	5540	507	0.066	2.26	1.5
KFM02A	12311	T2	2006/06/20			7.16		9565	5480	493	0.065	1.84	1.5
KFM02A	12507	T2	2006/10/18			7.25		9362	5370	437	0.167	1.97	2.2
KFM03A	8011	2	2003/09/16	-379.06	0.6	7.37		9407	5440	515	0.004	0.56	1.3
KFM03A	8017	2	2003/10/24	-440.79	0.3	7.58		9338	5430	472	<0.030	0.92	1.2
KFM03A	8284	2	2004/04/15	-442.35	0.4	7.29	-176	9494	5330	511	0.047	1.11	
KFM03A	12512	3	2006/10/24	-631.10		7.43		9589	5700	216	0.538	0.84	1.2
KFM03A	12001	2	2005/11/07	-631.10	5.7	7.49		9550	5640	230	0.701	1.06	1.4
KFM03A	8281	3	2004/03/29	-930.50	8.8	7.40	-245	13968	8560	73.9	0.058	0.21	1.5
KFM03A	12005	2	2005/11/07	-969.13	2.8	6.27		17254	10500	47	0.838	1.36	13.0
KFM03A	12513	T2	2006/10/25			7.11		16838	10400	45	0.587	0.66	1.8
KFM03A	8152	3	2003/12/08	-977.67	3.9	8.26		15678	9690	46.7	0.033	0.03	1.4
KFM04A	8160	3	2004/02/05	-197.00	7.1	7.28		9653	5550	511	<0.002	2.17	
KFM04A	8287	3	2004/05/10	-302.75	6.5	7.33		10234	5780	590	0.005	2.16	1.7
KFM06A	12399	3	2006/10/09	-298.54		7.38		7861	4620	186	0.108	2.39	2.0
KFM06A	8809	3	2005/03/07	-303.24	7.7	7.33	-155	7668	4560	151	<0.002	1.11	<1.0
KFM06A	12398	3	2006/10/09	-622.78		7.42		10334	6200	115	0.368	0.92	1.8
KFM06A	8785	2	2005/01/31	-645.95	1.6	8.22	-200	11541	7080	36	0.018	0.05	1.6
KFM07A	8843	3	2005/03/24	-759.72	0.6	8.04		23890	14400	103	0.062	0.26	2.0

Borehole	Sample number	Quality category	Date	Elevation, metres	Drill water, %	pH	Eh mV	TDS mg/L	Cl^- mg/L	SO_4^{2-} mg/L	HS^- mg/L	Fe^{2+} mg/L	DOC mg/L
KFM08A	12000	2	2005/10/31	-546.32	5.1	8.00		10054	6100	91.5	0.012	0.73	<1.0
KFM08D	12803	T2	2007/05/29	-540.63	8.9	8.30		12064	7300	109	<0.006	0.60	<1.0
KFM08D	12804	T2	2007/05/31		8.2	8.30		11995	7270	104	0.006	0.43	1.1
KFM08D	12805	T2	2007/06/04		7.0	8.30		12222	7280	104	0.009	0.21	<1.0
KFM08D	12806	T2	2007/06/08		6.2	8.30		12233	7340	104	<0.006	0.09	<1.0
KFM08D	12816	T2	2007/06/11		5.7	8.30		12464	7490	104	0.010	0.03	<1.0
KFM08D	12817	T2	2007/06/14		5.7	8.30		12370	7400	102	0.009	0.02	<1.0
KFM08D	12818	2	2007/06/18		5.4	8.30	-260	12468	7460	101	<0.006	<0.01	<1.0
KFM08D	12753	T3	2007/04/09	-664.06	8.2	8.00		13262	7910	159	<0.006	<0.01	2.2
KFM08D	12762	T3	2007/04/12		7.3	8.00		13191	7990	156	<0.006	<0.01	2.6
KFM08D	12766	T3	2007/04/16		6.3	8.00		13401	8050	155	0.067	<0.01	2.0
KFM08D	12773	T3	2007/04/18		6.3	8.00		13214	7950	152	0.052	0.01	1.2
KFM08D	12774	T3	2007/04/23		4.9	8.00		13439	8070	152	0.054	0.05	1.2
KFM08D	12775	T3	2007/04/26		4.5	8.00		13448	8080	149	0.082	0.08	1.2
KFM08D	12776	3	2007/04/30		4.3	8.00		13583	8160	156	0.068	0.11	<1.0
KFM09A	12243	2	2006/04/27	-614.21	1.8	8.10		24928	14800	118	0.004	0.10	1.3
KFM10A	12552	2	2006/11/26	-214.77	4.5	8.20	-281	6878	4050	215	0.027	1.43	2.0
KFM10A	12769	3	2007/04/17	-299.83	7.2	7.41		8553	4900	511	0.056	7.04	2.9
KFM10A	12508	T3	2006/10/18	-328.08	1.0	7.70		7841	4420	479	0.008	8.97	4.7
KFM10A	12509	3	2006/10/23		0.7	7.70		8372	4730	494	0.013	7.24	3.5
KFM10A	12517	T3	2006/10/30		3.6	7.70	-258	6500	3690	400	0.065	15.40	15.0
KFM12A	12791	T3	2007/05/15	-439.26	1.2	7.41		10587	6190	373	0.023	0.26	1.9
KFM12A	12792	3	2007/05/21		0.5	7.54		10446	6130	381	0.034	0.28	1.1

A larger set of data for HS^- concentrations have been considered in a comprehensive compilation and interpretation of groundwater sulphide contents for SR-Site (Tullborg et al., 2010). All HS^- analyses for groundwater samples collected from HFM and KFM boreholes, including both CCC samples and samples from the long-term monitoring systems, up to 2009 are shown in Figure 1. Appendix 1 in Tullborg et al. compiles all of these data, along with contemporaneous data for Fe, Mn and DOC, and comments on the trends in values at each sampling point over time. Data from a sampling campaign in spring 2010 are also added to Appendix 1 in Tullborg et al. and are commented on in relation to prior data, but have not been taken into account in the body of the report and in the main figures, such as Figure 1 here, and tables.

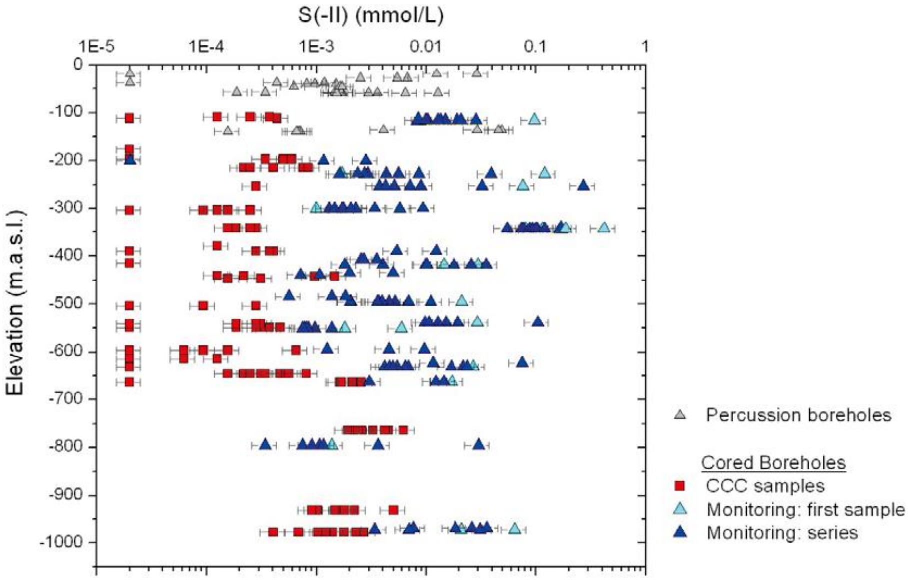

Figure 1: Depth variations of HS^- contents for all groundwater samples from CCC samplings and long-term monitoring installations, in all quality categories, collected up to 2009 from percussion (HFM) and cored (KFM) boreholes at Forsmark. Time series samples appear as horizontal series, i.e. at same elevations. The maximum HS^- value shown is 13.4 mg/L ($4.2\text{x}10^{-4}$ mol/L) in a sample from KFM01D at -343 m a.s.l. Data below detection limit are all shown at $2\text{x}10^{-8}$ mol/L (Figure 4-1 in Tullborg et al., 2010).

Time-series samplings of the monitoring installations produced water samples that had rather large variations of HS^- contents. Figure 1 shows that the ranges of HS^- contents seen in monitoring samples are generally up to 1 to 2 orders of magnitude higher than contents in CCC samples. In many, but not all, of the time series from monitoring installations, the ranges of HS^- variation are about an order of magnitude. In several cases, one or more samples contained HS^- at levels not otherwise observed in these groundwaters. The phenomenon of a relatively high HS^- content in the first sample in a time series occurs in many cases although the severity varies. An example of this phenomenon for samples from KFM01D/-252.53 is shown in Figure 2.

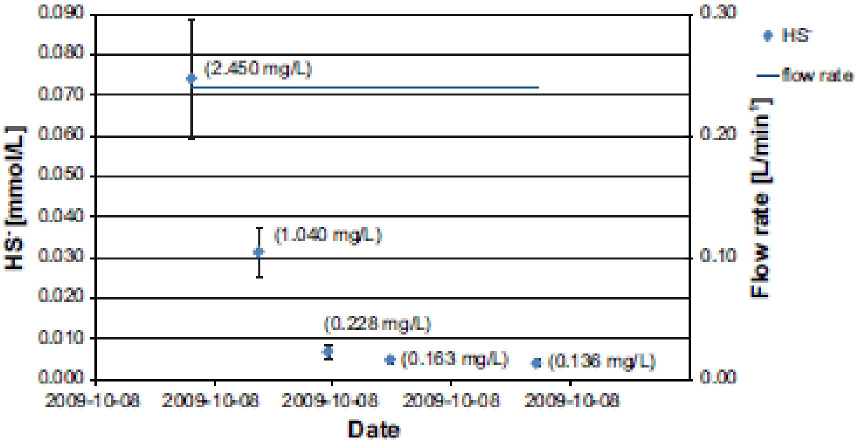

Figure 2: Time series of HS^- concentrations in water samples from borehole KFM01D at -252.53 m elevation. (Note the labels on the x-axis are erroneous unless all samples were taken in a single day). (Fig 3-2 in Tullborg et al., 2010).

The highest HS^- concentration observed, 15.9 mg/L ($5x10^{-4}$ mol/L), was in a sample collected in 2010 from the monitoring installation at -343.03 m elevation in borehole KFM01D (Figure 3). As in the example shown in Figure 2, measured HS^- concentrations decreased through the time series, *i.e.* as cumulative amount of water pumped from the intervals increased. The CCC ('complete chemical characterisation') water sample obtained from an adjacent interval at -341.93 m elevation in borehole KFM01D had HS^- content of only 0.009 mg/L ($2.8x10^{-7}$ mol/L).

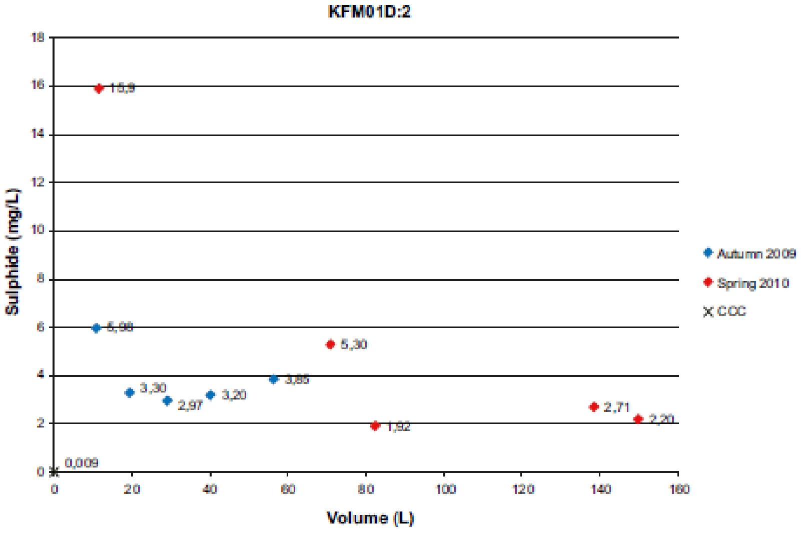

Figure 3. Time series of HS^- concentrations from two sampling exercises in 2009 and 2010 from a long-term monitoring installation in KFM01D at -343.03 m elevation (Figure A1-3 in Tullborg et al., 2010).

Similar time series of initially high HS^- followed by a generally decreasing trend of HS^- have been observed in samplings of monitoring installations in boreholes KFM 01A, 01D, 02A, 03A, 07A, 08A, 08D (Appendices 1 and 2 in Tullborg et al. 2010). Time series samples from monitoring installations in other boreholes showed no substantial anomalies or trends of HS^-. Fe^{2+}, DOC and $\delta^{34}S$ values also show no clear trends or correlations that shed light on the cause of the variations of HS^-.

Time series samples from monitoring installations were not analysed for microbial populations or for dissolved gases.

The aim of the Tullborg et al. report is “to assess realistic, representative and reliable sulphide groundwater concentrations at present conditions in Forsmark and also to evaluate possible changes during different climatic conditions covering the repository operation period, post-closure conditions and the proceeding temperate period”. Its approach is described by the statement “In order to avoid bias due to having many samples in some borehole sections and a few in other locations, a group of samples representing the sulphide concentrations in the different sampling points has been selected”.

In other words, representative present-day sulphide groundwater concentrations have been selected for each sampling point from the varying values that were observed in the time series up to 2009. Note that the additional time series data from the sampling campaign in Spring 2010 were not considered in the selection of HS^- values that are representative and appropriate for use in safety analysis. The comments on time series variations and the justifications for the selections of representative HS^-, Fe, Mn and DOC concentrations for each sampling point (CCC and monitoring system) are in Appendix 1 of Tullborg et al. (2010)

The selected data are presented in Table 4-1 in Tullborg et al. (2010). This table comprises 42 more-or-less complete hydrochemical analyses of specific water samples, taken at various times from cored boreholes by either CCC sampling or from monitoring installations. 16 of these samples also have microbiological data and a smaller number of samples have dissolved gases data, though several of these are incomplete. The microbiological analyses were originally reported in Hallbeck and Pedersen (2008b). Microbiological analyses for 3 additional samples have been extracted from SKB’s Site Investigation Reports (‘P’ series). These 19 sets of microbiological data, plus associated hydrochemical data and dissolved gases data, where available, are compiled in Table 2. Data in Tables 1 and 2 in this report present slightly different compilations of data but are essentially very similar to Table 4-1 in Tullborg et al. (2010) which is the basis of HS^- data that SKB has been taken forward into the safety analysis modelling. Table 1 contains approved hydrochemical data from samples that have been assessed as being in quality categories 1-3 and that are documented in the data spreadsheet for the ‘extended SDM 2.3’ data freeze; Table 2 contains data for all samples with reported microbiological analyses, including provisional data for 3 samples that post-date the compilation in Table 4-1 of Tullborg et al. (2010).

Table 2. Microbiological and related hydrochemical data for water samples taken from deep boreholes at Forsmark (Hallbeck and Pedersen, 2008; P-07-53, 177 & 198). Hydrochemical data are from SKB spreadsheet “Forsmark_2_3_updated_Dec30_2007_F23 corrected” except for samples marked * for which hydrochemical data have not been qualified by SKB. Microbiological and dissolved gases data for ^ samples are from Table 4-1 in Tullborg et al. (2010). Depths for * samples have been estimated because qualified values are not available. ‘T’ prefix in quality category values are samples from monitoring installations. MPN = ‘most probable number’ of cultivable microorganisms; A&H = total of autotrophic and heterotrophic cells. Where ‘~’ values for microorganisms are shown, these values have been estimated from data points in graphical illustrations in SDM reports.

Borehole	Sample number	Qual cat	Elev metres	Drill water %	Total no of cells mL^{-1}	IRB MPN mL^{-1}	SRB MPN mL^{-1}	Methanogens A&H MPN mL^{-1}	Acetogens A&H MPN mL^{-1}	Eh mV	SO_4^{2-} mgL^{-1}	HS^- mgL^{-1}	Fe^{2+} mgL^{-1}	DOC mgL^{-1}	CH_4 $mL\ L^{-1}$	H_2 $\mu L\ L^{-1}$	Drill water %	SI (FeS)
KFM01A	4538	2	-111.75	0.7	58000	4000	1.2	~1	~1.2	-195	316	0.014	0.95	1.5	-	-	0.7	-1.43
KFM01A	4724	2	-176.27	4.8	39000	4	0.2	~1.6	~1.7	-188	547	<0.03	0.47	2.3	-	-	4.8	
KFM01D	12326	T2	-341.93	6.3	250000	80	7	<0.2	2100	-263	126	0.006	2.04	3.7	0.14	<2.8	6.3	-1.36
KFM01D	12354	T1	-445.17	0.9	270000	220	13000	<0.2	34000	-260	38	0.005	1.23	10	4.60	<3.4	0.9	-1.89
^KFM02A	8016	4	-503.47	6.8			1.40			-143	498	0.009	1.70	2.1	0.04	199		
KFM03A	8017	2	-440.79	0.3	100000	~10	~20	~100	~1	-176	472	<0.03	0.92	1.2	-	-	0.3	
^KFM03A	8284	2	-442.35	0.4	100000	11	17	8.7	180	-176	511	0.047	1.11	1.3	0.03	213	0.4	-1.13
KFM03A	8273	2	-631.91	4.3	21000	22	30	1.7	28	-196	197	<0.002	0.23	1.6	0.07	<2.7	4.3	-1.07
KFM03A	8281	3	-930.50	8.8	61000	<0.2	500	17	23900	-245	73.3	0.058	0.21	1.5	0.06	44.0	8.8	-1.18
KFM03A	8152	3	-977.67	3.8	58000	<0.2	24	5	32		46.7	0.033	0.03	1.4	0.05	<3.8	3.8	-1.85
*KFM06A			-302		72000	30	0.8	0.2	54									
			-302		52000	23	0.4	0.6	48									
KFM06A	8785	2	-645.95	1.6	17000	2.3	0.2	<0.2	8.8		36	0.018	0.05	1.6	0.09	<3.2	1.6	-1.80

Borehole	Sample number	Qual cat	Elev metres	Drill water %	Total no of cells mL^{-1}	IRB MPN mL^{-1}	SRB MPN mL^{-1}	Methanogens A&H MPN mL^{-1}	Acetogens A&H MPN mL^{-1}	Eh mV	SO_4^{2-} mgL^{-1}	HS^- mgL^{-1}	Fe^{2+} mgL^{-1}	DOC mgL^{-1}	CH_4 mL L^{-1}	H_2 µL L^{-1}	Drill water %	SI (FeS)
^KFM07A	8879	T3	-759.72	0.35	10000	<0.2	<0.2	0.2	0.7		99.3	0.134	0.16	<1	0.04	<4.8	0.4	-0.83
KFM08A	12000	2	-546.42	5.1	42000	17	500	<0.2	1600		92	0.012	0.73	<1	0.03	<4.3	5.1	-1.34
KFM08D	12818	2	-540.63	5.4	21000	4	13	<0.2	132	-260	101	0.006	0.006	<1	0.09	<2.9	5.4	-3.30
*KFM08D			-664	4.3	11000	>1600	2.3	<0.2	88		156	0.07	0.11	<1	0.06	<3.3	4.3	-1.21
KFM10A	12552	2	-214.77	4.5	46000	500	500	0.2	1100	-281	215	0.027	1.43	2.0	0.06	<3.8	4.5	-0.21
KFM11A	12706	T4	-389.68	4.9	13000	2850	140	0.2	1300	-203	244	<0.006	0.21				7.1	

An example of how the range of HS^- variations has been truncated by the data selection is given by the data for borehole KFM01D. The maximum analysed HS^- concentration in samples from borehole KFM01D at -343.03 m elevation up to 2009 is 13.4 mg/L ($4.2x10^{-4}$ mol/L; this is surpassed by the value of 15.9 mg/L or $5x10^{-4}$ mol/L in the same interval in the Spring 2010 sample), whereas the selected representative value for this sampling point 3.85 mg/L ($1.2x10^{-4}$ mol/L) which is the concentration in the last of the time series samples taken in 2009 (see Figure 3). This value is also the highest HS^- concentration in the selected data set as in Table 4-1 of Tullborg et al. The corresponding selection from Fe^{2+} data, which have a range of just over an order of magnitude, is 0.139 mg/L. It is not clear from the presented data whether variations of the individual HS^- and Fe^{2+} analyses are positively or inversely correlated, the latter being expected if FeS equilibrium is involved. No correlation is expected if FeS is below saturation.

Representative single values for HS^- contents, and also for Fe, Mn and DOC contents, for each CCC sampling and each monitoring section have been selected by Tullborg et al. (2010) on the basis of sampling observations, patterns in time series and overall consistency. The highest HS^- concentration from monitoring installations that has been qualified and reported by SKB in its selected data set for use in SR-Site is about $1.2x10^{-4}$ mol/L.

Figure 4 illustrates these data as a depth profile of all analyses, so the correspondence between selected HS^- values from CCC samples and from monitoring samples can be seen. In the cases for CCC and monitoring samples can be compared, samples from the long-term monitoring installations generally have higher HS^- values than CCC samples, (Figure 4; see also Figure 5-5b in Tullborg et al. 2010).

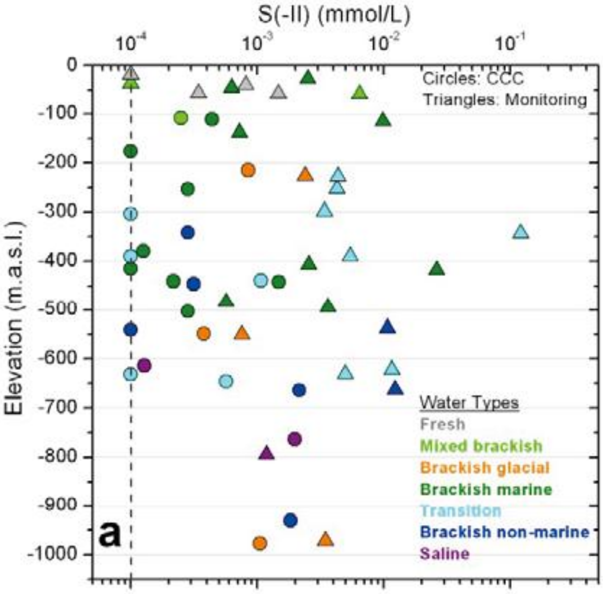

Figure 4: HS^- contents for CCC and monitoring groundwater samples, selected as being representative for each sampling point in percussion (HFM) and cored (KFM) boreholes at Forsmark, as listed in Table 4-1 of Tullborg et al. (2010). A single value has been selected as representative for each time series from monitoring installations. Data below detection limit are all shown at 10^{-4} mol/L (Fig 5-5a in Tullborg et al., 2010).

There is a trend in Figure 1 towards increasing HS^- concentrations in the CCC samples below 600 m depth. This pattern is not evident in the monitoring samples for which the highest values occurred in samples from around 350 m depth.

SKB states that dissolved HS^- is systematically low, possibly due to precipitation of amorphous Fe(II)-monosulphide and that formation of HS^- at low temperature is "undoubtedly related to activity of sulphate-reducing bacteria (SRB)" (Tullborg et al. 2010, p 15). Deeper than 600 m, increasing HS^- concentrations are observed (Figure 1), although this is not evident in the data for samples from monitoring installations. Increasing HS^- with depth is interpreted to be consistent with a corresponding decrease of Fe^{2+} concentrations which are considered to be controlled by crystalline iron oxides, mainly hematite (SKB, 2011, p 134).

In summarising long-term buffering of redox and its potential influence on the evolution of HS^- concentrations, SKB concludes that Eh in brackish groundwaters (between about 100-650 m depth) is controlled mostly by amorphous Fe(III) oxyhydroxide (Tullborg et al. 2010, p 11). This inference is supported by the detection of fine-grained amorphous oxyhydroxides. The long-term redox buffering capacity of the fracture system, provided by *e.g.* chlorite and pyrite, is considered sufficient to have not been exhausted by any previous oxidising episodes.

Concerning identified limitations of data, it is noted in the Data Report (SKB 2010a, p 183) that HS^- concentrations obtained before construction of the HRL at Äspö were found to be systematically higher than those obtained from complete chemical characterisation of borehole sections at Forsmark (and also at Simpevarp/Laxemar site) (SKB 2010a, p 187). It is suggested that "several questions regarding the values for sulphide remain in SR-Site" (SKB 2010a, p 187).

2.1.3. Present-day production of sulphide

Safety function R1 states that the host rock should 'provide chemically favourable conditions'. This includes, in addition to a requirement for low HS^- concentrations, a requirement that concentrations of reductants that may be used by sulphate-reducing bacteria to produce HS^- should also be 'low' (SKB 2011, p 259). These reductants or electron donors are dissolved hydrogen (H_2), methane (CH_4) and dissolved organic carbon (DOC). SKB's safety function criterion is that concentrations of these should be 'low' but there are no quantitative limits.

SKB asserts that the present concentrations of HS^- represent the steady state between microbially-mediated reduction of SO_4^{2-} for the coexisting concentrations of H_2, CH_4 and DOC and the precipitation of sulphide minerals (SKB 2011, p 360). From that basis and the low concentrations of H_2 and CH_4, from which low fluxes of these two gases are inferred, $<3x10^{-10}$ $mol.m^{-2}.y^{-1}$ (Delos et al 2010), it is concluded that the contribution to HS^- from active SO_4^{2-} reduction is 'minor' (SKB 2011, p 361).

DOC is rather complex as a potential reductant because "a large part of this carbon is relatively nonreactive in large molecules, like humates and fulvates, which have complex chemical structures" (SKB 2011, p 361). The analysed DOC contents in groundwaters from below 50 m depth (43 samples) at Forsmark are between 10^{-3} mol/L and the detection limit of $3x10^{-5}$ mol/L, mostly around 10^{-4} mol/L (SKB 2011, Fig. 10-43, p 362). SKB argues that most of this DOC is not readily accessible by sulphate-reducing bacteria or to fermenting bacteria that could produce smaller, more labile, organic molecules, on the basis that it coexists with relatively large

SO_4^{2-} concentrations that would otherwise react with the DOC (SKB 2011, p 362). Therefore SKB argues that HS^- concentrations used for copper corrosion modelling the safety analysis do not need to be increased to take account of a hypothetical increase that might arise from SO_4^{2-} reduction by DOC. SKB also states that the proportion of the DOC that would be available for reaction over a very long timescale "cannot be established".

It is likely that natural DOC will be enhanced in the vicinity of a repository by organic substances that would be introduced during construction and operation. From an estimated inventory of such organics, and by consideration of degradation pathways, maximum amounts of HS^- that could be produced by SRB activity in deposition tunnels and other cavities in the repository have been estimated (Hallbeck et al. 2006). These amounts are 1.22 and 36 µmol/L respectively, which equate to dissolved concentrations of 0.06 and 1.2 mg/L of HS^-. The same calculation was used to infer that "the maximum amount of sulphide that can be generated microbially is ~10 moles for each deposition hole, which, if it was able to react completely with the canister, would be equivalent to a corrosion of less than 10 µm if distributed evenly" (Auqué et al. 2006). The reasoning behind this interpretation of the original information is not provided.

Concentrations of Fe^{2+}, which plays a role in regulating HS^-, are interpreted by SKB to be controlled by a "complicated set of reactions including slow dissolution of Fe(II)-silicates such as chlorite and biotite, precipitation of Fe(II)-sulphides, and redox reactions" (SKB 2011, p 363). Fe^{2+} concentrations in future groundwaters have been modelled by equilibrating with Fe(III)-oxyhydroxide at the calculated Eh. The resulting Fe^{2+} concentrations (as shown in SKB 2011, Fig 10-44) have been used with Fe(II)-sulphide equilibrium to calculate HS^- concentrations.

Studies of the transient production of HS^- in deep groundwaters during sampling and monitoring operations were carried out in two boreholes at Äspö and Laxemar (Rosdahl et al. 2010). Boreholes KLX06 and KAS09 were sampled via monitoring installations at about 480 m and 110 m depth. General chemical compositions, HS^-, microorganisms, dissolved gases and stable S isotopes were analysed in time series samples in KLX06 with a 9 week pause of pumping. The initial HS^- content was 7 mg/L which decreased as pumping progressed, but after the pause of pumping the HS^- content of water was high again at maximum 9 mg/L. The high contents of HS^- were associated with high SRB numbers and also with high DOC up to 367 mg/L. Pumping caused a progressive increase of salinity (though remaining only fresh/brackish at maximum 1480 mg/L Cl^- and about 700 mg/L SO_4^{2-}). Fractionation of S isotope ratios between SO_4^{2-} and HS^- indicated that there was active sulphate reduction occurring.

The much older borehole, KAS09, had not been pumped for 2 years or so. Initial water samples taken from the standpipe in KAS09 had very high HS^- concentrations up to 102 mg/L, associated with high DOC up to 148 mg/L. In this borehole and another one at Äspö, KAS03, the standpipes had been in place for more than 20 years. When removed, black sludge and deposits on the piping were found. The high HS^- analyses in water, indicating highly supersaturation with respect to FeS, were attributed to the presence of suspended sulphide particles as well as truly dissolved HS^- (Rosdahl et al. 2010).

These two sets of observations in Laxemar and Äspö boreholes are interpreted as adding to the evidence discussed in Tullborg et al. (2010) that different chemical and microbial conditions prevail in stagnant water in isolated borehole sections in monitoring installations. The phenomenon of excessive HS^- contents seems to be related to growth of SRB due to the materials and surfaces introduced into the boreholes, combined with the transient perturbations of local redox and biogeochemical conditions by sampling. The exact roles of these materials, microorganisms and dissolved gases in the metabolic processes causing raised HS^- are left as an open question, as also is the implication of these observations for the possibility of raised HS^- concentrations in the undisturbed groundwater system (Rosdahl et al. 2010).

2.2. Motivation of the assessment

This assessment is motivated by the significance of dissolved sulphide (HS^-) as the main corrodant that could threaten the integrity of the copper canisters in the KBS-3 concept for deep geological disposal of spent fuel.

In the long term, HS^- will diffuse into the buffer from groundwater surrounding deposition holes. The compacted bentonite buffer in the KBS-3 concept has a critical role in limiting the migration of groundwater HS^- between the bedrock-buffer interface and the buffer-canister interface. If the bentonite buffer remains intact and highly compacted, the migration of HS^- through it is diffusive and is controlled by the concentration gradient through the buffer. The safety analysis assumes that the HS^- concentration at the canister surface will be zero because HS^- will be consumed by the corrosion reaction with copper to form Cu_2S. Therefore the rate of transport of HS^- will be controlled by the concentration in near-field groundwater at the outer surface of the buffer. The higher the HS^- content of this groundwater, the greater the flux of HS^- through the buffer will be and the greater the rate of copper corrosion.

The buffer plays a second role in inhibiting biogeochemical reduction of sulphate (SO_4^{2-}) to HS^- in the vicinity of the canister. In the long term, SO_4^{2-} will enter the buffer from groundwater diffusively, in the same way as dissolved HS^-. The potential mass budget of S in groundwater SO_4^{2-} is orders of magnitude greater than the content of sulphide, so there is a strong requirement to understand the biogeochemical potential and capacity for SO_4-HS^- transformation within the buffer and also the long-term evolution of SO_4^{2-} concentration in near-field groundwaters.

In the reference evolution of the engineered barrier system (EBS), it is presumed on the basis of experimental evidence that sulphate-reducing bacteria (SRB) will not be active in compacted bentonite and therefore that HS^- will not be generated in this way adjacent to the canister.

However a variant evolution, whereby bacteria are viable in the buffer and thus can reduce SO_4^{2-} to HS^-, must also be considered in the safety analysis. One way this could happen would be if buffer erosion and mass loss were to cause loss of compaction. Another possibility to be considered is that the limited experimental evidence of microbial inactivity might not be applicable to *in situ* buffer in the long term.

These issues are discussed further below in Section 3.1.3.

There are other principal sources of HS^- that might reach the outer surface of the canister: (i) dissolution of sulphide mineral, pyrite, that is contained as a trace component of bentonite, (ii) microbially-mediated reduction of dissolved SO_4^{2-} in bentonite pore water that is also subject to a concentration gradient and in-diffusion of SO_4^{2-} from surrounding groundwater. In the long-term, the second process is the greater potential source of HS^- at the canister should microbially-mediated reduction be a viable process in the buffer. It is considered in the next section.

Data for HS^- contents of water that will, or potentially could, come into contact with the canister in each deposition hole are therefore a necessary input to the safety analysis. This assessment is concerned primarily with HS^- contents of groundwaters in the vicinity of deposition holes. These concentrations are the boundary conditions for HS^- that can diffuse through the buffer to the canister. In addition, the potential for HS^- contents of groundwaters to be enhanced by reduction of dissolved SO_4^{2-} has to be taken into account.

The processes controlling present-day HS^- contents are hydrogeochemical and biogeochemical and require mineralogical characterisation. Understanding and modelling of HS^- requires data for concentrations of dissolved SO_4^{2-} and Fe^{2+}, mineral sources of sulphide, sulphate and iron, and also populations of microorganisms that catalyse the redox transformations controlling HS^-. To the extent possible in a groundwater system that has a low level of organic activity, the energy and nutrient sources for microbial activity also need to be characterised.

The motivation for assessing SKB's selection of data from the overall database of HS^- measurements in groundwater samples is whether that selection is somehow underestimating the actual variability of HS^- concentrations in the groundwater system around the proposed repository volume at Forsmark. Opportunities for groundwater sampling during the surface-based site investigation at Forsmark have been limited by the practicalities of constructing and testing boreholes. They have especially been limited by number of intersected fractures that have sufficient transmissivity to yield water samples of acceptable quality in relation to in-mixing of drilling water and perturbation by the pumping and sampling process.

Dissolved HS^- is especially vulnerable to these limitations and perturbations because it is present in groundwaters in trace quantities. These practical challenges and the various strategies adopted by SKB to achieve a representative set of data for HS concentrations in groundwaters at Forsmark are described in Tullborg et al. (2010). Expert judgement has been used, with SKB's normal sample quality categorisation procedures, to reject or accept analyses as representative of *in situ* conditions. Therefore the issue for this assessment is whether this data selection might have discounted, on the basis of unacceptable sample quality, higher concentrations that should be taken into account in the range of HS^- contents used in safety analysis.

The second issue that motivates this assessment is whether the relatively sparse distribution of samples and measured HS^- contents, in relation to the target volume of bedrock for proposed repository construction, is adequate in terms of confidence in spatial variability. In other words, is it possible that there are groundwaters in the target volume that have not been tested by the site investigations but might have unacceptably high contents of dissolved HS^-?

It has to be remembered that the analysis of long-term safety requires data for the evolution of future HS^- contents, rather than the contents measured at the present-day in the site investigation programme. The modelled data for future HS^- contents depend on the understanding of relevant processes that can be justified by interpretation of present-day HS^- contents. Interpretation concerns the biogeochemistry and sinks and sources of sulphide in the groundwater-rock system.

This assessment therefore considers whether the dataset for HS^- contents in present-day groundwaters and the biogeochemical model of processes are an adequate basis for forecasting likely values of future HS^- contents and the maximum plausible values.

These issues and the analysis of potential evolutions of future HS^- contents are the topic dealt with in Section 2.3 of this report.

2.3. The Consultant's assessment

2.3.1. General knowledge of sulphide in groundwaters

There are surprisingly few reliable and meaningful data elsewhere in the literature for concentrations of sulphide, HS^- and S^{2-} species, in groundwaters. Dissolved sulphide in neutral-pH conditions occurs primarily as HS^- species. An understanding of HS^- in groundwater requires the geochemical sulphur cycle to be taken into account. Sulphur is one of the more mobile and reactive major geochemical component elements. Its reactivity is enhanced by redox transitions between the S(-II) and S(VI) oxidation states in the natural environment. These redox states are biogeochemically reactive because of microbial mediation. Therefore the kinetics of transformations between dissolved S species and the relative distributions of the main oxidised and reduced dissolved sulphur species, SO_4^{2-} (abbreviated hereafter as SO_4) and HS^-, might be understood in terms of ambient redox and populations and activity of microbes.

Sulphide in sedimentary rock aquifers

Sedimentary rock aquifers and other relatively shallow groundwaters generally contain measureable concentrations of HS^- if the redox conditions in the aquifers have evolved sufficiently to become anaerobic and reducing. The normal process of evolution towards reducing groundwater conditions is a sequence of reactions between electron donors (reducing agents) and electron acceptors (oxidised species) in groundwater and reactive minerals. These redox-active substances may be natural solutes and solids (possibly including colloidal material) or introduced contaminants. The sequence is controlled by the order of free energies for the half-reactions. SO_4 is a relatively unreactive electron acceptor and requires a strong electron donor, *e.g.* organic C, to promote reduction. The reduction of SO_4 to HS^- at low temperatures such as those of the normal groundwater environment is usually feasible only with microbial mediation of the reaction.

It is evident from studies of water-rock reaction in aquifers that, although they are theoretically stronger electron acceptors, Fe-oxide and Mn-oxide minerals do not inhibit the onset of SO_4 reduction. That is probably because heterogeneous redox reactions, between solid and solution, are likely to be slow relative to homogeneous redox reactions where the electron acceptor is in solution. It is also evident from aquifer studies that SO_4 and HS^- coexist in many groundwater systems (as is observed in Forsmark groundwaters). This might reflect the stabilisation of electrochemical redox potential corresponding to that ratio of S(-II)/S(VI), or it might reflect the slow kinetics of SO_4-HS transformation where microbial activity is low. The latter is likely to be the case in crystalline rock groundwaters such as those at Forsmark, in which the energy sources and nutrients promoting activity of microorganisms such as sulphate-reducing bacteria (SRB) are sparse.

HS^- and SO_4 concentrations and transformations were studied in a shallow glacial sands aquifer, overlain by organic-rich soils, in northern Germany (Massmann et al. 2003). It can be inferred that reducing conditions prevailed throughout the aquifer because of the abundance of organic C. SO_4 concentrations varied from about $3.5x10^{-3}$ to $<1x10^{-3}$ mol/L, whilst HS^- varied from about $3x10^{-5}$ to $<5x10^{-6}$ mol/L. These concentration changes plus the additional evidence from $^{34}S/^{32}S$ stable isotopes confirmed that SO_4 is being reduced with a half-life varying between the orders of days and years depending on the abundance and lability of organic C for the microbially-mediated process. Concentration of dissolved HS^- did not exceed $3x10^{-5}$ mol/L (1 mg/L), despite a rapid reduction rate, presumably because it was being controlled by FeS precipitation although this was not confirmed by mineralogical analyses of aquifer material.

Similar limits on dissolved HS^-, up to maxima of about $7x10^{-6}$ mol/L, have been observed in other systems that are biogeochemically favourable for reducing SO_4 to HS^-, such as organic-rich shallow aquifers (*e.g.* Jessen et al. 2008) and shallow groundwaters affected by leachate from a landfill (*e.g.* He et al. 2002).

HS^- occurrence in a deep aquifer with low DOC and in an aquifer matrix in which organic solids are absent or sparse is exemplified by a sandstone aquifer in the U.K. (Edmunds et al. 1982). This type of aquifer is probably a reasonable biogeochemical analogue for groundwaters in crystalline bedrock, having no organic contamination, low indigenous organic carbon and presumably low microbial activity. DOC throughout the aquifer is $\leq 3x10^{-5}$ mol/L. SO_4 concentrations in the upgradient oxidising and aerobic part of the aquifer are between $1x10^{-4}$ and $1x10^{-3}$ mol/L. Further down gradient, in the deeper aquifer, redox conditions become slightly reducing with Eh down to -50 mV, presumably reflecting redox control by Fe^{2+}-$Fe(OH)_3$ reaction. HS^- concentrations are $<1x10^{-5}$ mol/L (<0.2 mg/L). SO_4 concentrations are up to about $4x10^{-3}$ mol/L, because anhydrite is being dissolved or sulphate-rich groundwaters are entering the aquifer from adjacent formations. Fe^{2+} concentrations increase, as expected, as the redox conditions become more reducing; Fe^{2+} varies between $2x10^{-6}$ and $4x10^{-5}$ mol/L (0.1 and 2 mg/L) in the deep aquifer. In this case, low HS^- concentrations are probably determined by the very low biogeochemical reactivity of the hydrogeochemical system and possibly by localised FeS precipitation. The highest HS^- concentration corresponds to the highest SO_4 concentration.

The conclusions from aquifer studies concerning the hydrogeochemistry of sulphide are:

- SO_4 coexists with HS^- and whether HS/SO_4 is controlled by redox equilibrium depends on the biogeochemical reactivity of the system and the availability of organic C and other microbial nutrients.

- High HS^- concentrations, *i.e.* $>1x10^{-4}$ mol/L, are generally not found in groundwaters that have normal to low biogeochemical activities, because of low SO_4 reduction kinetics and/or because of control of dissolved HS^- concentrations by FeS precipitation equilibrium.

Sulphide in crystalline rock groundwaters

HS^- data for groundwaters in crystalline rocks come from investigations by SKB and Posiva in Fennoscandian Shield bedrock. Redox, SO_4 and Fe^{2+} data have been reported from the AECL programme in Canadian Shield bedrock at Whiteshell, northern Canada, but quantitative analyses of HS^- and DOC are missing except that ‘dissolved H_2S’ is reported to be ‘mostly absent’ (Gascoyne 1997, 2004). Data from the Swedish and Finnish sites are shown in Table 3.

Table 3. HS$^-$, SO$_4^{2-}$, Fe^{2+} and DOC contents (mg/L) of groundwaters sampled in Fennoscandian crystalline bedrock.

Location	Boreholes	HS$^-$	SO$_4^{2-}$	Fe^{2+}	DOC	Ref
Swedish granites						
Äspö	HA,HD,KA	0.01-7.69		<.004-7.6		SKB (2005) & SKB SDM 1.2 database)
	PA,SA,SM	<0.01-3.7		<0.05-7.9		
	KC-KR	<0.01-1.4		<0.02-1.0		
	KXB-KXT	<0.01-0.4		0.35-1.15		
	HAS02-13 (0-100m)	<0.01	100-285	2.69	1-27	
	KAS02-12 (0-920m)	<0.01-5.6	31-709	0.02-1.6	0.1-6.9	
Ävrö	KAV01-04A (0-819m)	<0.01-1.2	38-390	0.3-3.2	4.8-11	
Bockholmen		0.09-0.15		2.9		
Finnsjön	BFi1-Fi9	<0.005-0.44	7-410	<0.005-24	5.7	
Fjällveden	Fj2-8	<0.01-1.5		<.005-8.2		
Gideå	KGI02-04	<0.01-0.13		0.05-7.5	2	
Kamlunge	HKM20	0.01		13.0-16.7		
	KKM03-13	<0.01-0.03		0.04-18.3		
Klipperås	KKL01-09	0.01-0.41	1.3-4.4	0.002-0.5		
Länsjarv	KLJ01	<0.01-0.01		0.001-0.009		
Svartboberget	KSV04-05	<0.01-0.07		0.03-25		
Taavinunnanen	KTA01	<0.01-0.04		<0.01-1.7		
Stripa		<0.01-0.2	0.1-105	0.01-0.15	1-25	
Forsmark	PFM,SFM	<0.03-0.57	1-364	0.003-8.7	3-31	SKB (2005) & P reports
	KFR	0.01-2.2		0.3-6.2		
	HFM01-38 (0-200m)	0.01-1.57	19-550	0.35-4.4	1.3-36	
	KFM01A-KFM12A	<0.01-3.29	35-550	<0.001-15	<1-34	
Laxemar	HLX01-43 (0-200m)	0.03	6-102	0.03-0.09	3-8	SKB (2006) & P reports
	KLX01-09 (0-1600m)	<0.01-7.4	4-1205	0.002-14.9	1-140	
	KLX10A-20A (0-900m)	<0.01-4	5-425	0.03-15	1.5-10	
	KLX21B-27A (0-650m)	0.12	48-176	0.03-16	2.1	
Oskarshamn	KOV01	<0.01-0.07		0.1-3.0		
Simpevarp	PSM	0.01-0.02		0.17-0.9		
	HSH02-05 (0-200m)	0.12	29-122	15.8	2.1-3.9	
	KSH01A-03B (0-600m)	0.01-3	25-600	0.002-1.75	<1-240	
Finnish metagneiss & granites						
Olkiluoto	PVP,PP,PR	<0.01-0.2	0.1-105	0.01-0.15	1-25	Posiva (2003) & WR reports
	KR1-47	<0.01-12.4	0.1-730	<0.01-8.3	1.3-188	

HS^-, SO_4, Fe^{2+} and DOC in crystalline rock groundwaters in Sweden and Finland can be summarised as follows:

- At all of the sites, many of the groundwaters have HS^- at below the detection limit which in most cases was 0.01 mg/L ($3x10^{-7}$ mol/L). The maximum HS^- concentration is 12.4 mg/L ($3.9x10^{-4}$ mol/L) in a single sample at Olkiluoto. A high value of 15.9 mg/L was measured in a monitoring sample from borehole KFM01D at Forsmark and subsequently discounted from the selected HS^- used in SR-Site. Most of the historical HS^- data have maxima <1 mg/L ($3x10^{-5}$ mol/L), though there are rather few analyses. The three Swedish sites with the most intensive samplings are Äspö, Simpevarp/Laxemar and Forsmark from which the maximum of selected data is 7.7 mg/L ($2.4x10^{-4}$ mol/L)for a sample at Äspö, though the majority of analyses are <3 mg/L ($9.4x10^{-5}$ mol/L).

- SO_4 concentrations vary over 3-4 orders of magnitude, from 0.1 mg/L ($1x10^{-7}$ mol/L) in a sample from Stripa to a maximum of 1205 mg/L ($1.26x10^{-2}$ mol/L) in a sample from about 1390 m depth in KLX02 at Laxemar. Groundwaters at that depth at Laxemar are saline and are interpreted to contain the highest proportion of the deep 'Shield brine' end-member that is a component in deep groundwaters at Forsmark. Most of the groundwater samples from Forsmark, Äspö and Simpevarp, have moderate SO_4 contents and are from intermediate depth range of about 100-600 m; SO_4 in these waters derives predominantly from Littorina water. The variability of SO_4 with respect to Cl^- suggests that it is being depleted gradually by reduction and production of HS^-; $^{34}S/^{32}S$ stable isotope studies tend to confirm SO_4 reduction as the cause of variability and not addition of SO_4 *e.g.* from *in situ* oxidation of sulphide minerals. Deep groundwaters at Olkiluoto have very low SO_4 contents, in contrast to groundwaters at similar depths at Forsmark (Geier et al. 2012).

- Fe^{2+} varies over 2 to 3 orders of magnitude in crystalline rock groundwaters, from analytical detection levels at <0.01 mg/L ($1.8x10^{-7}$ mol/L) to maxima between 15-25 mg/L ($2.7x10^{-4}$ to $4.5x10^{-4}$ mol/L). There is no particular pattern of values and most of the sites have similar ranges. High values of Fe^{2+} and of HS^- are mutually exclusive, in other words high Fe^{2+} concentrations correlate with low HS^-. This supports the concept that HS^- concentrations are controlled by iron monosulphide, FeS, equilibrium. Otherwise Fe^{2+} and HS^- concentrations are rather scattered (Figure 5).

- Dissolved organic carbon, DOC, concentrations very from detection limit around 1 mg/L to a high value of 140 mg/L at the Swedish sites. That high value was measured in a sample from a monitoring installation in KLX02 at Laxemar; a high value of 240 mg/L was measured in a sample, also from a monitoring installation, at a similar depth in KSH02 at Simpevarp. Values around 90 mg/L were measured in water samples from about 1350 m depth in KLX02. A single high value of 188 mg/L was measured in KR2 at about 820 m depth. It is unclear what might account for these isolated anomalies, and whether they represent natural sources of organics or artefacts of borehole operations and sampling. Otherwise DOC is in the range 1 to 40 mg/L, so amounts are potentially significant with respect to biogeochemical reactions although the molecular form and availability of the organics as energy sources for microbial activity is not known.

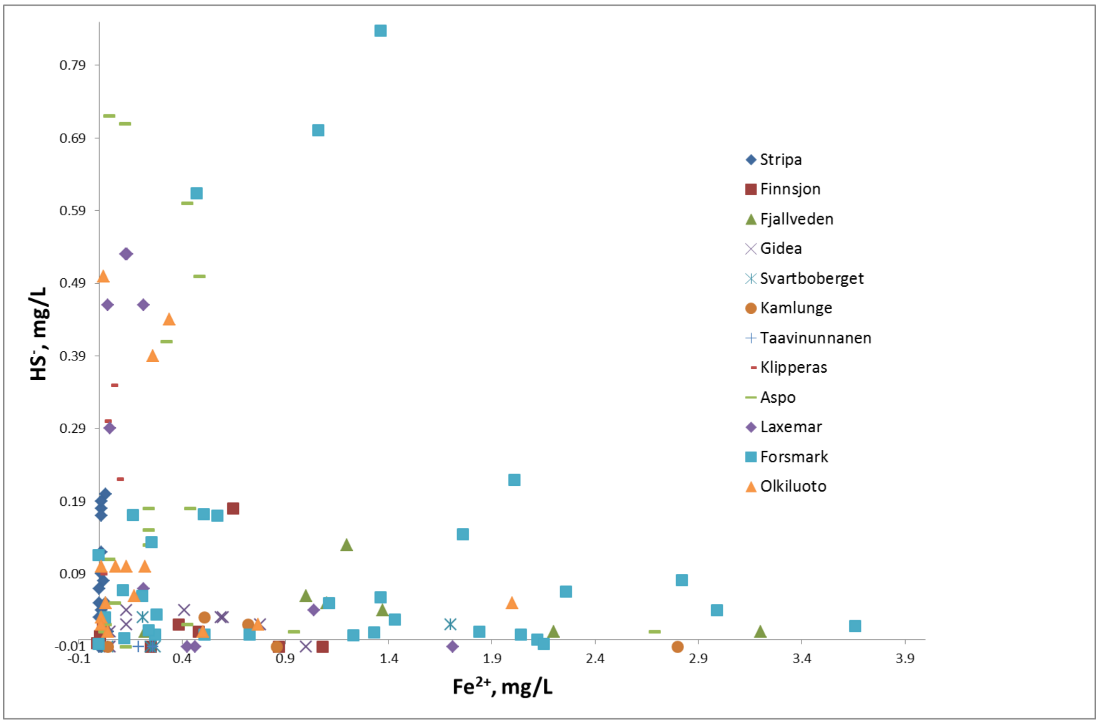

Figure 5. HS$^-$ versus Fe^{2+} in Swedish and Finnish crystalline rock groundwaters (see Table 3). Note that the few samples with HS$^-$ >0.85 mg/L and Fe^{2+} >4 mg/L have been omitted from the crossplot so that the variability of the majority of data is shown at a suitable scale.

2.3.2. Sulphide in groundwater at Forsmark

Tables 1 and 2 are my compilations of SKB’s key data for HS$^-$ and associated parameters in percussion and cored boreholes at Forsmark. They are based on SKB’s hydrochemical data spreadsheets “Forsmark_2_3_updated_Dec30_2007, sheets ‘F23 corrected’ and ‘Extended F23 (+SFR)’. Data for dissolved gases and microbial populations (from Hallbeck and Pedersen, 2008) have been supplemented by unqualified data that have been extracted from SKB ‘P’ reports and from Tullborg et al. (2010).

The maximum HS$^-$ in Table 1 is 1.57 mg/L (4.9x10^{-5} mol/L) and in Table 2 is 0.134 mg/L (4.2x10^{-6} mol/L). The range of concentrations in these compilations is similar to, but slightly different from, the range of HS$^-$ concentrations in Table 4-1 in Tullborg et al. (2010) that SKB has selected as being the best representation of HS$^-$ contents of groundwaters at Forsmark. The difference is due to Table 4-1 including 17 samples from monitoring installations that post-date the extended SDM 2.3 data freeze, i.e. after 2007. The HS$^-$ contents of these 17 samples selected by Tullborg et al. are between 0.024 and 3.85 mg/L (1.2x10^{-4} mol/L), mostly being above 0.1 and below 0.4 mg/L.

Another difference between the two tables is that ‘Fe^{2+}’ values in Table 1 are mostly values obtained by spectrophotometry, whereas ‘Fe’ values listed in Table 4-1 of Tullborg et al. (2010) are ICP-MS analyses of total iron.

Saturation Indices (SI) of FeS have been calculated for the analyses in Table 2 using the geochemical speciation and equilibrium code PHREEQC (Parkhurst and Appelo 1999). The thermodynamic database used was modified to change the log K value for FeS from -3.91 to -3, as was also done in SKB's calculations (see Gimeno et al. 2006; Appendix 3 in R-06-70). The calculated SIs of $FeS_{(am)}$ are negative which means that these groundwater compositions are undersaturated with respect to amorphous FeS. They are oversaturated with respect to more crystalline forms of FeS such as mackinawite and heavily oversaturated with respect to pyrite (SI values between +7 and +11). They are slightly undersaturated with respect to $FeCO_3$ (SI between zero and -2). Siderite has not been reported as a common secondary mineral in fractures at Forsmark.

Undersaturation with respect to $FeS_{(am)}$ suggests that release of Fe^{2+} from relevant minerals, *e.g.* chlorite or biotite, is controlling dissolved Fe^{2+} and similarly that microbially-mediated reduction of SO_4 to HS^- is a slow process. It is reasonable to suggest that there are localised zones in the groundwater system where Fe^{2+} and/or HS^- concentrations might be high enough to reach saturation and thus to precipitate $FeS_{(am)}$. Thus FeS is likely to be the dominant sink for Fe^{2+}, as well as for HS^-, although $FeS_{(am)}$ has not been reported in the observed fracture mineral assemblage (Tullborg et al. 2010, p44). The observation of pyrite, FeS_2, rather than amorphous FeS in fractures, and the widely varying S stable isotope ratios suggest that biogenic FeS has formed in low-temperature groundwater conditions and has transformed over time to pyrite. SKB's interpretation of these hydrogeochemical processes is reasonable and reflects the current paradigm for dissolved Fe^{2+} and HS^- in normal groundwater systems.

Figure 6 shows the best representation of variations of HS^- contents versus depth. It includes data in Tables 1 and 2 plus data selected by SKB and reported in Table 4-1 of Tullborg et al. (2010). Data from groundwater samples, mostly from monitoring installations, to which SKB has attributed transient perturbations of HS^- content are excluded. The highest such HS^- concentration is 15.9 mg/L analysed in an early sample from KFM01D/-343.02 in 2010 (see Figure A1-3 in Appendix 1 of Tullborg et al. 2010).

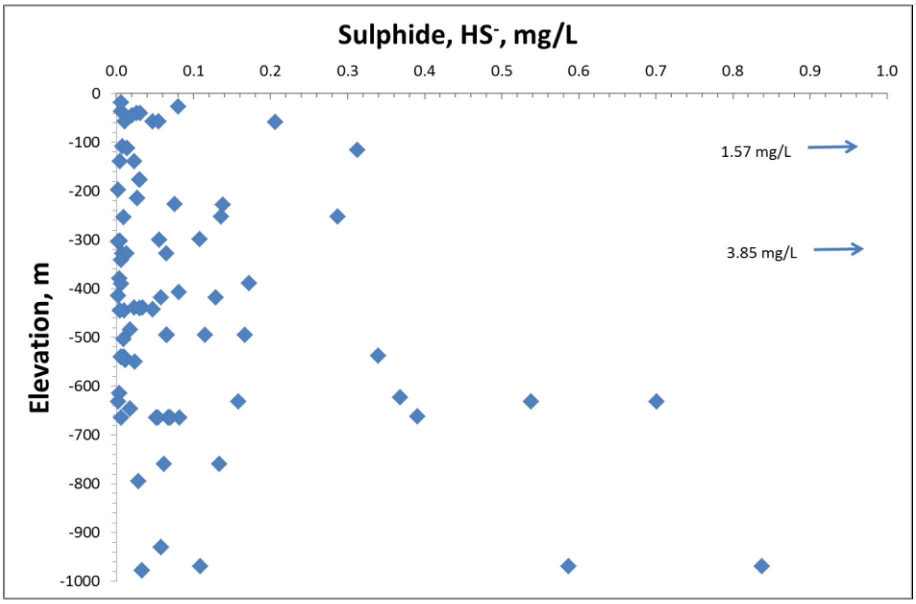

Figure 6. Dissolved sulphide, HS^-, in Forsmark groundwater samples versus depth. Data reported by SKB from Tables 1 and 2 in this report plus data in Table 4-1 in Tullborg et al. (2010) are shown. High HS^- concentrations that are attributed to transient perturbations in samples from long-term monitoring installations are not shown (up to 15.9 mg/L HS^-; see Figure 4-1 and Appendix 1 in Tullborg et al.).

Figure 6 shows that localised high values of HS^- have been found in samples at elevations of -137 m, -343 m, -631 m and -969 m. Microbiological data are not available for any of the these groundwater samples with anomalously high HS^- or for those with transient perturbations giving high HS^- (Table 2) so it is not possible to say whether these high HS^- contents are associated with anomalously high SRB numbers or high SRB activity. Some of the high HS^- values in Table 1 are associated with high DOC contents, e.g. HFM19/-137.10, KFM03A/-969.13, but there is not a consistent correlation.

Overall, the data shown in Figure 6 indicate that HS^- concentrations are generally below 0.4 mg/L with occasional higher values that do not have any evident common origins or associations with e.g. DOC or SO_4. The range and pattern of HS^- contents is consistent with other sites in the Fennoscandian Shield (Table 3).

2.3.3. Validity of sample and data selection

The process that has been used by SKB for selecting HS^- values from 'complete chemical characterisation' (CCC) and time series data for monitoring samples is explained clearly in Tullborg et al. (2010). Tullborg et al's data set includes a number of samples that postdate the SDM 2.3 (extended) data freeze. Inclusion of these more recent data from monitoring installations is valuable because some anomalously high HS^- concentrations from monitoring installations are disclosed and discussed. The selection criteria are close to those used in the general quality classification: stability of major ion chemistry through sampling, drilling water tracer content (though this is not useful for monitoring samples that have too much prior test history such as injection testing with tracer), and charge balance. Other criteria are variations of HS^- and associated species such as Fe^{2+}, DOC and SO_4, and supersaturation with respect to amorphous Fe-monosulphide on the assumption that precipitation of FeS is a fast and limiting process. Rejecting samples whose analyses are supersaturated with FeS obviously tends to exclude the higher HS^- values.

Although there is a rationale for selecting a single groundwater sample and HS^- value as being representative for each sampled point in the groundwater system, uncertainty remains about the likelihood of occurrences of high HS^- contents in other locations in the target bedrock volume and at future times. It is difficult to constrain this uncertainty because of the absence of clear evidence and understanding of what causes the higher values and transient variations of HS^-. Without that understanding and confidence that the selected analyses were for water samples with the least perturbation, it cannot be proven that the selected data are representative of the actual spatial variability of *in situ* groundwater compositions and that there are no circumstances where natural HS^- concentrations might locally exceed the range of selected analyses.

Nevertheless, it is evident that the range of HS^- concentrations in the selected dataset represents the general order-of-magnitude variability of sulphide contents, even taking account of both apparently perturbed samples and unperturbed samples, i.e.

all data. There is no compelling evidence from theory or from the general hydrochemical observations that there is a possibility of groundwaters with *in situ* contents of HS^- exceeding this range being widespread and able to dominate volumetrically over groundwaters with low HS^- contents. The only observations at Forsmark of significantly higher concentrations are the monitoring samples from the single interval at KFM01D/-343.03, for which all the circumstantial evidence points to a local perturbation due to the monitoring system. The same phenomenon is likely to be the cause of similarly anomalous and transient HS^- concentrations in monitoring samples from boreholes KAS09 and KLX06 at Äspö/Laxemar (Rosdahl et al. 2011).

Therefore I accept that the *general* variability of sulphide contents can be adequately, and probably conservatively, represented by the selected data. SKB's approach for corrosion calculations in the safety analysis has been to use the 90-percentile value of HS^- in the probability distribution, $1x10^{-5}$ mol/L (Figure 6), for all deposition hole positions and at all times in the reference evolution assuming that buffer remains intact in all positions (SKB 2010b, Section 5.3.4).

In view of this value being almost the maximum of the distribution (Figure 5), with the only exception being a single sample from the selection of representative values with a content of $1.2x10^{-4}$ mol/L, this is a reasonable simplification considering the sparse data and the absence of any reason to expect higher HS^- contents in the long term. Using random assignments from the full HS^- data distribution, as could erroneously be misunderstood from the SR-Site Main Report (p 603), would lower the assigned HS^- values and therefore be less pessimistic. SKB has rightly calculated an even more pessimistic variant case in which that single higher value of $1.2x10^{-4}$ mol/L is assigned to all deposition holes at all times. The result of that is that the probabilistic corrosion rate distribution for the various DFN variants has a maximum at around 10^{-3} micrometres per year which would still be below the rate that would penetrate a canister in 1 million years (SKB 2010b, Section 5.3.4). Thus the hydrogeological DFN model for transport of HS^- to the buffer and the diffusion model for HS^- through the buffer are the dominating controls on corrosion rates and HS^- concentrations, even pessimistically high values, play a subsidiary role. SKB's selection of HS^- values for use in corrosion calculations in the safety analysis is described in Section 3.1.3.

Whether the larger dataset of HS^-, with a lesser degree of data selection or culling, or the existing highly-selected dataset is more valid of that *general* statistical variability is a matter of expert judgement. A dataset with a lower degree of culling or selection would include all or some of the higher values (*e.g.* up to 15.9 mg/L HS^-) that have been discounted from the more selective dataset. The distribution would be wider but the mean would be similar and, because the highest values are isolated anomalies, simplification of the distribution to a representative single value for use in corrosion calculations would result in a value close to the above 90-percentile value. The safety analysis, being concerned with the aggregate corrosion of copper over a long timescale, anyway should use a HS^- concentration, or range of concentrations, that is characteristic of the long-term average. In my opinion, SKB's decision to use the 90-percentile HS^- value from the selected is a sensible and reasonable choice for a simplification that is most likely to be appropriate for 'typical' or average long-term HS^- contents.

In summary, my assessment of how data have been selected to give a relatively small set of values for HS^- contents and their spatial variability is that it makes reasonable assumptions about their representativeness for actual contents, both at the present-day and far into the future.

2.3.4. Biogeochemistry of sulphide and sulphate reduction

Buffering by S and Fe redox couples

Redox potentials due to the SO_4/HS^- and $SO_4/FeS_{(am)}$ couples have been calculated by SKB (Gimeno et al. 2008) and have been found to be close to the range of measured values. A similar modelling exercise, calculating Eh according to the thermodynamics of the redox couples SO_4/HS^-, Fe^{3+}/Fe^{2+} and $Fe(OH)_3/Fe^{2+}$, was done for SSM by Bath and Hermansson (2009). The measured Eh is probably poised by the electrochemically-active SO_4/HS^- couple which is a homogeneous (*i.e.* single phase) redox system although the number of electrons involved in the reaction mean that it may not be responsive at the Eh electrode.

In contrast to the S system that is mostly restricted to dissolved components, the $Fe(OH)_3/Fe^{2+}$ redox couple is a heterogeneous (*i.e.* solid + solution) reaction that has the possibility of strong buffering by Fe^{2+} released by mineral dissolution. It is therefore likely that the Fe system is the basis of long-term buffering of redox in the Forsmark groundwater system. This may be coupled to greater or lesser degrees with other redox couples, *i.e.* SO_4/HS^-, DOC/CO_2 and CH_4/CO_2. The relationship between the S and Fe redox couples is presumably dependent on the kinetics of the relevant reactions, *i.e.* the reduction of SO_4 and the release of Fe^{2+} from Fe-containing minerals.

Microbial mediation of sulphate reduction

Microbially-mediated SO_4 reduction was the focus of a research project in the early period of Äspö HRL development, during and soon after construction (Laaksoharju, 1995). The research involved geochemical and isotopic analyses of water samples from sea-bed sediments, surface-based KAS boreholes, shallow boreholes and inflows to short boreholes in the HRL tunnel, and also of iron sulphide mineral sampled from sediments and bedrock fractures.

The research concluded that SO_4 reduction is an ongoing process in both the pore waters of the sea-bed sediments and the 'SO_4-rich' seawater-derived groundwaters that are in the bedrock around the tunnel excavations down to several hundred metres depth. It also deduced that SO_4 reduction has occurred in the geological past resulting in the secondary pyrite that is seen in bedrock fractures. The evidence for these conclusions was drawn mainly from SO_4/HCO_3 ratios in groundwaters, on the basis that HCO_3 should increase if organic C is being consumed as the electron donor as well as SO_4 decreasing, and also from $^{34}S/^{32}S$ stable isotope ratios of mineral sulphide and dissolved SO_4. At that early stage of SKB's investigations, there was scant microbiological data and, as is still the case, there was uncertainty about the reducing agent (electron donor), *i.e.* whether it is DOC and/or dissolved H_2, and whether there are threshold concentrations of DOC and SO_4 below which SO_4 reduction is negligible.

Initial evidence of SRB facilitating the reduction of SO_4 in groundwaters at Äspö/Laxemar came from limited experimentation with groundwater from borehole KLX01. Using lactate as the C source, the rate of HS^- production by unattached

SRB was measured as 8-114 x10^{-6} mol.m^{-3}.d^{-1} and by SRB attached in a biofilm was 0.2-9 x10^{-6} mol.m^{-2}.d^{-1} (Pedersen and Ekendahl 1992). These empirical results are not directly comparable because the former rate is per water volume whilst the latter rate is per surface area, but they suggest that (a) SRB attached as biofilms to mineral surfaces are more efficient at producing sulphide than when not attached, and (b) that up to 290 µg of H_2S per day could be produced by SRB in a biofilm per m^2 of the surfaces of a fracture with 1 mm aperture. It is noted that these experimental rates were apparently not constrained by available carbon because an artificial source, *i.e.* lactate, was added. Thus the rates would be expected to represent an upper limit relative to unperturbed natural conditions where dissolved organic carbon (DOC) and/or bacteriogenic acetate is the sole C source, although the study described below suggests otherwise.

Observations made during a 90-day closed loop circulation 'MICROBE' experiment in a fracture 43.8 m from the tunnel wall at 447 m depth in Äspö HRL, provided *in situ* evidence for SO_4 reduction coupled with acetate production and consumption in unperturbed deep groundwaters (Hallbeck and Pedersen 2008a). Interpreted rates of production of HS^- and acetate (HA) during the main part of the closed circulation MICROBE experiment were 0.08 mg(HS).L^{-1}.d^{-1} and 0.14 mg(HA).L^{-1}.d^{-1}. The HS^- production rate converts to 2.4x10^{-3} mol.m^{-3}.d^{-1} which surprisingly is several orders of magnitude higher than the rate in experiments (described above) where lactate was the C source. Rates broadly corresponded with the measured cell populations of SRB and acetogens in solution which were inferred to be indicative of much larger populations of active microbes attached to fracture surfaces in biofilms. It is speculated that the higher rate of HS^- production in the *in situ* experiment compared with lab experiments could be due to the difficulty of maintaining reducing anaerobic conditions in the latter case, and perhaps also to a greater propensity for active biofilms in the former case.

It is reasonable to infer from the variability of SO_4 contents of groundwaters that SO_4 reduction is also occurring at Forsmark. In brackish groundwaters down to about -500 m elevation, SO_4 concentrations are very variable with a maximum of 590 mg/L and a minimum of 31 mg/L. In saline groundwaters at greater depths, maximum SO_4 decreases sharply to 230 mg/L at -630 m and 110 mg/L below -760 m (Figure 7).

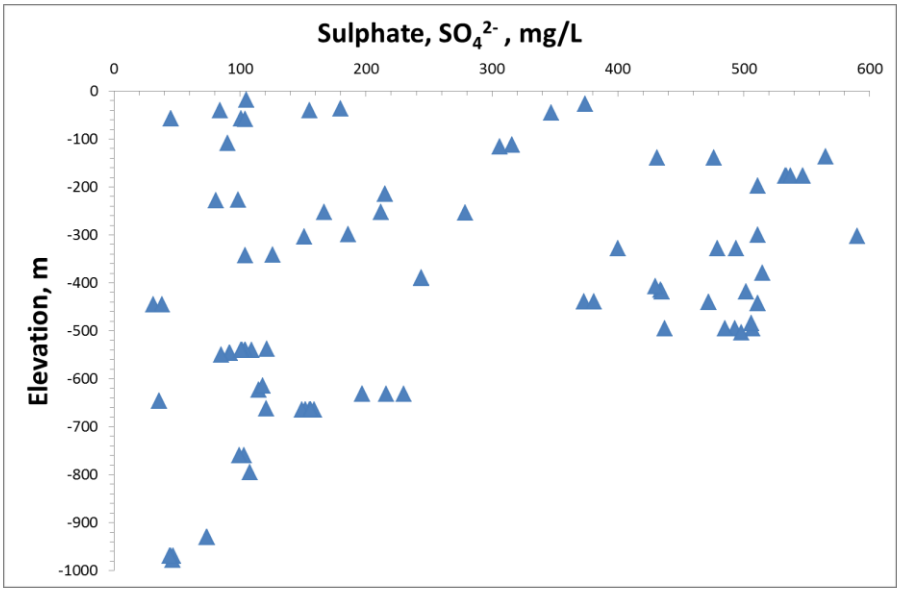

Figure 7. Dissolved sulphate, SO_4^{2-}, in Forsmark groundwater samples versus depth. Data reported by SKB from Tables 1 and 2 in this report plus data in Table 4-1 in Tullborg et al. (2010) are shown.

Role of dissolved organic carbon in sulphate reduction

Dissolved organic carbon, DOC, potential as an energy source and electron donor for SO_4 reduction is limited both by its sparse concentration in crystalline rock groundwaters and by the amount of carbon that is not readily available to microbial respiration.

It has been suggested that evidence of SO_4 reduction (*i.e.* lowered SO_4 and raised HCO_3 concentrations) in Äspö groundwaters corresponds with relatively high contents of DOC, >10 mg/L (Puigdomenech et al. 2000).

DOC concentrations at Forsmark vary from below detection level, <1 mg/L, up to 36 mg/L (Table 1). DOC values in CCC water samples are mostly <10 mg/L with a maximum reported concentration of 15 mg/L. The highest DOC values are mostly in samples from long-term monitoring installations and are sometimes associated with transient anomalously high HS^- concentrations, but there is not a general correlation between higher HS^- contents and higher DOC.

The resistance of humic organics to microbial degradation in anaerobic environments is generally supported by Lovley et al. (1996). However those authors find evidence that humics might be usable by microorganisms as an electron acceptor for the anaerobic oxidation of organics and hydrogen by, for example, sulphate. That might also provide a pathway by which other more resistant electron acceptors such as Fe^{III} oxides could be reduced because humics could act as 'shuttles' to move electrons around between different electron acceptors. Essentially, these types of complex microbially-mediated pathways that would facilitate the reducing, *i.e.* electron-donating, efficiency of DOC or H_2 or CH_4 are potentially key to understanding how SO_4 reduction might take place in crystalline rock groundwaters. Acetate may be an intermediate C compound in the reduction process.

This issue has been considered further in the context of SKB's response to a request from SSM for complementary information, and my comments on SKB's response (see Appendix 2).

Significance of microbial data for Forsmark

The data for microbial populations in Forsmark groundwaters shown in Table 2 do not in general give a clear indication of the relationships between measured numbers of cells and the biogeochemistry of redox reactions, specifically sulphate reduction. It has to be remembered that of the total numbers of cells, $<10^5$ mL^{-1}, the proportion which are cultivable anaerobic cells is mostly <1% except at KFM01A/-112m, KFM01D/-445, KFM03A/-930, KFM08A/-546, KFM08D/-664, KFM10A/-214 and KFM11A/-390.

Analysed SRB numbers are very variable, from <1 mL^{-1} to a maximum of 13000 mL^{-1} in KFM01D/-445, close to repository depth. However this interval with high SRB has low HS^- contents, whereas other intervals in the same borehole, KFM01D/-253 and KFM01D/-342, have higher HS^- contents (see Table 1 and also Appendix 1 in Tullborg et al. 2010). Thus there is no correlation between SRB numbers and high content of HS^-. The monitoring interval with high SRB numbers has a relatively low SO_4 concentration of around 38 mg/L (see Figure 9), so this suggests that SO_4 reduction is active at this bedrock location. The conjunction of high SRB, low HS^- and low SO_4, can be reconciled by inferring that FeS precipitation is keeping HS^- values low; this is supported by the observation of relatively high Fe^{2+} concentration although the calculated saturation index for $FeS_{(am)}$ is negative (Table 2), suggesting that a more crystalline form of FeS might be controlling HS^- and Fe^{2+}. Overall, however, general conclusions cannot be drawn from these observations of microbial and hydrochemical relationships in 3 sampled intervals in a monitoring installation in a single borehole, KFM01D. It is probable that, as SKB has tentatively inferred, these are transient phenomena caused by some sort of perturbation due to this particular monitoring installation.

Numbers of acetogens are mostly much greater than the numbers of methanogens. At repository depth, the nearest 3 samples (KFM01D/-445, KFM03A/-441 and KFM03A/-442m) have very different numbers of methanogens and acetogens with no clear dominance. Many of the samples with higher numbers of acetogens also have relatively high numbers of SRB (*e.g.* KFM01D/-445 and KFM03A/-920), suggesting microbial respiration whereby SRB use acetate to reduce SO_4 to HS^-. These waters also tend to have the lower Eh values.

Overall, the microbiological and geochemical data do not offer a clear picture of the biogeochemical processes and relationships at repository depth at Forsmark, although it is reasonably evident that SO_4 reduction and production of HS^- is actively occurring. The data do not indicate, for example, that SO_4 reduction occurs preferentially in some depth interval or in a particular water type. Biogeochemical HS^- production is more likely to occur in groundwaters that are dominated by the Littorina component, mainly because this is the dominant source of dissolved SO_4 and also because it would be expected to contain DOC originating from seabed sediments. However there is no compelling evidence of such a simple correlation.

It is probably the case that analysed cell populations in water samples provide a semi-quantitative indication of larger microbial populations on mineral surfaces. Microorganisms attached to rock surfaces in ‘biofilms’ have greater population density and are expected to be more active than microorganisms dispersed in groundwater. This would be especially the case for rock surfaces ‘contaminated’ by organic carbon from substances introduced by repository construction.

Interpretations of microbial data for other sites

Comparable microbiological and hydrochemical data for Simpevarp/Laxemar (SKB 2006a,d; Pedersen, 2005; Hallbeck and Pedersen 2008c) do not give any better evidence of biogeochemical processes than the Forsmark data. Data are generally too sparse and variable to identify distinct relationships between SRB, SO_4 and HS^-. The depth trends of SO_4 concentrations at the two sites are different. At Forsmark, SO_4 contents decrease with increasing salinity (Figure 9). At Laxemar, in contrast, SO_4 increases with overall salinity reaching a maximum of 700-800 mg/L in saline waters at 1000 m depth.

As at Forsmark, populations of acetogens in Simpevarp/Laxemar water samples were consistently higher than populations of both methanogens and SRB. The maximum population of acetogens was 2500 cells mL^{-1} at 412m depth. It is noteworthy that higher numbers of methanogens were measured in samples from

Äspö HRL (Kotelnikova and Pedersen 1998; Pedersen 2005), and this might be due to disturbance of that system by excavation.

Similar biogeochemical investigations have been carried out by Posiva in deep boreholes at the Olkiluoto/ONKALO site in Finland (Pedersen 2006, 2008). Total numbers of microorganisms in deeper groundwaters were similar to those for Forsmark samples. SRB range from ~1000 mL^{-1} to zero (below detection limit) and do not show a clear depth trend. Methanogens range from >10 to zero cells mL^{-1} and acetogens range from 1000 to zero mL^{-1}. Dissolved HS^- is mostly <0.2 mg/L down to ~200 m depth, has some higher values up to a maximum of ~12 mg/L between 200-400 m, and then decreases to <0.3 mg/L below 400 m.

SO_4 has relatively high concentrations at Olkiluoto up to maximum ~550 mg/L between 90-320 m depth then goes to very low values, <10 mg/L, below 470 m. Thus SO_4 in deep groundwaters at Olkiluoto is markedly different to concentrations at and below proposed repository depth at Forsmark which are variable but go as high as 500 mg/L (Geier et al. 2012).

It may be that SO_4-containing deep groundwaters had existed in the distant past at Olkiluoto and that all the SO_4 has been reduced to HS^-. Alternatively, the deep groundwaters at Olkiluoto never had a significant SO_4 content. The first explanation implies SO_4 reduction by a process such as anaerobic oxidation of methane (‘AOM’, see below) although this has not hitherto been observed to take place in this type of geochemical environment having low organic C and thus low activities of SRB.

The significance of this for future evolution of Forsmark groundwaters is that it leads to an expectation that SO_4 in deep groundwaters will continue to be progressively reduced to HS^-. Groundwaters at proposed repository depth at Forsmark have very variable SO_4 contents which supports the idea that SO_4 reduction is ongoing. These contents vary spatially up to a maximum of ~500 mg/L, indicating the potential for production over a period of time of a large amount of HS^-. The rate of production and the resulting concentrations will depend on various factors, including the biogeochemical reduction kinetics, mineral sources and sinks of SO_4, concentrations of dissolved Fe^{2+} to react with HS^- and precipitate FeS, the mineral sources of Fe^{2+}, and the rate of release of Fe^{2+} from those solid phase sources. The dynamics of groundwater movement and thus the inwards and outwards fluxes of the biogeochemically reactive solutes, including microbial energy sources such as DOC, CH_4 and H_2, are also factors affecting the evolution of HS^-.

Reduction of sulphate by methane

Anaerobic oxidation of methane (AOM) coupled with SO_4 reduction has been suggested to be a significant process of Olkiluoto, but there is no direct evidence to confirm this (Pedersen 2008). The peak of dissolved HS^- at around 300 m depth corresponds to a step increase of CH_4 (10-100 mL/L), a locally higher population of SRB (up to 100 cells mL^{-1}), and slightly higher populations of methanogens (up to 40 cells mL^{-1}). It is thought that SRB and methanogens are able to cooperate to oxidise CH_4 to produce H_2 and then use this H_2 to reduce SO_4 to HS^- (Pedersen 2008). The property of Olkiluoto deep groundwaters that may trigger this process is the higher concentration of CH_4 relative to the deep groundwaters at the Swedish sites.

Although there is no indication that SRB use CH_4 rather than, or in addition to, DOC or acetate as the carbon source in groundwaters at Forsmark, a role for acetogens in SO_4 reduction at the Swedish sites is supported by microbiological data and hydrogen concentrations. Acetate concentrations have not been routinely analysed at any of these sites, but acetate analyses are mentioned (but data not reported) in Rosdahl et al. (2011).

Anaerobic oxidation of methane, AOM, is discussed above as a possible though unproven process in crystalline rock groundwaters at Forsmark and, more probably, at Olkiluoto. AOM is a biogeochemical process that links C and S redox transformations by mechanisms that are mediated by complex microbial communities and reaction pathways. Similarly, biogeochemical processes that link S and Fe redox transformations have to be considered as being relevant to the long-term evolution of SO_4 and HS^- in the Forsmark groundwater system. The particular issue is the role that Fe^{III} oxide, which is present in fractures mostly as the secondary mineral hematite, might have in controlling HS^- concentrations.

Studies of AOM have not been carried out in crystalline rock groundwaters. However biogeochemical observations and experiments in sediments have shown that SO_4 reduction can proceed concurrently with Fe^{III} oxide reduction due to the development of distinct microbial communities that facilitate both production of HS^- and its consumption in reducing Fe^{III} to Fe^{2+} (Coleman et al. 1993; Kwon et al. 2013). Presumably the produced Fe^{2+} would further control HS^- concentration by precipitating FeS. Whilst these biogeochemical processes are probably significant for S and Fe hydrogeochemistry only in sediment or groundwaters that have abundant labile organic carbon (C availability in the experiments was amended by addition of lactate), the conclusion is that Fe^{III} oxides might be a reactant and control on HS^- in geochemical environments where SO_4 reduction is very active.

Overall, the evidence discussed in this section and previous sections suggests that, even in crystalline rock groundwaters that are generally ‘carbon-poor’, sulphur geochemistry is closely interdependent on carbon and iron geochemistry. In the long-term, unless reactive Fe becomes highly depleted in the groundwater system and the biogeochemical productivity of the system is enhanced by influx of reactive carbon, it is concluded that HS^- concentrations will be controlled at low levels similar to those observed in the present systems.

This issue has been considered further in the context of SKB’s response to a request from SSM for complementary information, and my comments on SKB’s response (see Appendix 2).

SKB’s proposed model for sulphide production at Forsmark

The model proposed by SKB for SO_4 reduction in groundwaters at Forsmark utilises short chain organic acids, such as acetate, which are produced by acetogenic bacteria, as the normal sources of carbon and energy for SRB (Hallbeck and Pedersen 2008a; Hallbeck et al. 2006). The sequence of reactions is:

a. Production of acetate from H_2 and CO_2, mediated by autotrophic acetogens;
b. Reduction of SO_4 by acetate (possibly coupled with H_2) or by DOC, mediated by SRBs;
c. Control of dissolved HS^- by reaction with Fe^{2+} to precipitate FeS and FeS_2.

The general implication of this model is that the HS^- production rate potentially has a number of constraining factors: the fluxes of SO_4, DOC and H_2 and possibly also of CH_4, as well as the viability and activity of acetogens, SRB and maybe also methanogens. It is inferred that the generally low populations of microorganisms reflects the low concentrations and fluxes of the main energy sources, *i.e.* DOC and H_2. Equally, it is evident that the overall constraint on HS^- production is the flux of dissolved SO_4 (assuming that sources of SO_4 by sulphide mineral oxidation are relatively minor). Within repository depth range at Forsmark, where SO_4 is at moderate concentrations, it seems that other factors are limiting the process, *e.g.* supply of naturally-occurring DOC and/or H_2.

In addition to the constraint on microbial activity posed by availability of energy sources, DOC and H_2, there is the basic constraint on microbial viability which is posed by the availability and mass transfer of nutrients that are necessary for cell growth. These nutrients include nitrogen and phosphate compounds. Minerals and groundwaters at repository depth in crystalline rocks are extremely poor suppliers of nutrients, *i.e.* an 'oligotrophic' environment. Dissolved nitrogen, mainly as NH_4, is reported in the SKB hydrochemical database at concentrations up to mg/L level. The higher concentrations of NH_4 in this range are found in brackish groundwaters that are dominated by the Littorina component. Dissolved phosphate occurs at the μg/L level or below detection limit. Lower typical concentrations of N and P are quoted for Forsmark groundwaters in Hallbeck and Pedersen (2008a); the reason for the discrepancy is not explained. A future evolution of groundwater composition at repository depth in which the concentrations of N and P were significantly higher is not envisaged, so nutrient supply has been assumed to persist in the long term as a constraint on SO_4 reduction.

Rate of sulphide production

The biogeochemical factors that need to be taken into account of prognosing the likely maximum rate of production and concentration of HS^- in geosphere groundwaters at repository depth are:

- SO_4 concentration and inwards flux of SO_4-containing groundwaters;
- Population and viability of SRB and acetogens;
- Concentration and inwards flux of DOC that is one of the sources of C to acetogens and SRB;
- Temperature, salinity, minor nutrients (N & P compounds) and other environmental factors that affect microbial proliferation and activity;
- Concentration and production rate of Fe^{2+} from Fe-oxide minerals, mediated by IRB, which reacts with HS^- to precipitate FeS and FeS_2, and thus limits dissolved HS^-.

There is not much literature on kinetic modelling of SO_4 reduction, and moreover all of this literature refers to biogeochemical conditions in sediments and sedimentary rocks, in which carbon and nutrient sources are generally higher than in crystalline rocks. So the studies of SO_4 reduction kinetics described in the following paragraphs have generally assumed that organic C is not the limiting factor, and may not be directly relevant to the carbon-poor and nutrient-poor geosphere environment of interest here. If organic C is sparse, SRB utilise H_2 or acetate as energy sources for SO_4 reduction, and there is little if any research on the kinetics of these reactions.

In the literature on SO_4 reduction in organic-rich sediments, it is coupled to the rate of organic C oxidation, *e.g.* (Hunter et al. 1998; van Cappellen and Wang 1996):

$$2CH_2O + SO_4^{2-} + H^+ \rightarrow 2CO_2 + HS^- + 2H_2O$$

Utilization of organic C for microbial metabolism is represented by a Monod rate expression (van Cappellen and Wang 1996):

$$R_i = R_{max} \frac{[SO_4]}{[SO_4]_{lim}} \text{ for } [SO_4] < [SO_4]_{lim}$$

where $[SO_4]_{lim}$ is a limiting concentration above which the rate of reduction is independent of $[SO_4]$, and R_{max} is the rate of organic C oxidation where $[SO_4] \geq [SO_4]_{lim}$.

In experiments with artificial labile organic substrates, SO_4 reduction rates varied from 0.007 - 0.17 $kg.m^{-3}.h^{-1}$, depending on initial SO_4 concentration which was varied from 1000 – 10000 mg/L (Moosa et al. 2002).

$[SO_4]_{lim}$ has a range of literature values from 0.001 to 1.6 mmol/L (Hunter et al. 1998; van Cappellen and Wang 1996).

The first order rate constant for oxidation of dissolved organic carbon, k^{DOC}, is in the wide range of 10^{-7} to 10^{-3} yr^{-1} (Hunter et al. 1998; van Cappellen and Wang 1996), *i.e.* the rate of DOC oxidation overall is:

$$R^{DOC} = k^{DOC} [DOC]$$

So that if DOC is, for example, $1x10^{-4}$ mol/L, then R^{DOC} is likely to be in the range 10^{-6} to 10^{-1} mol/L per year. If SO_4 is the dominant electron acceptor and exceeds 90 mg/L (*i.e.* $1x10^{-3}$ mol/L, or possibly less), then the corresponding rate of SO_4 reduction mediated by SRB will be in the range 10^{-11} to 10^{-1} mol/L per year. The lower part of this range is probably appropriate for groundwater conditions at Forsmark. This is considerably lower than the empirical rate reported from experiments with labile organic matter which are above $6x10^{-1}$ mol/L per year (Moosa et al. 2002). A further factor to be considered is what fraction, if any, of the low concentrations of DOC in these groundwaters is labile in biogeochemical reactions. It has been suggested that the humic fraction of DOC could facilitate SO_4 reduction by transferring electrons from otherwise-refractory organics, as discussed earlier (Lovley et al. 1996).

The role, if any, of CH_4 in the kinetics of SO_4 reduction raises the question, mentioned earlier, of whether anaerobic oxidation of methane (AOM) occurs to any significant extent in crystalline bedrock groundwaters (Lovley and Klug, 1983; Lovley et al. 1982; Boetius et al. 2000; Nauhaus et al. 2002):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

In AOM, SRB do not utilise CH_4 directly, but form a consortium with archaea (single-celled microorganisms without nuclei) to cause SO_4 reduction (Boetius et al.

2000; Hallam et al. 2004). Studies of AOM in organic-rich sediments with high levels of microbial activity have found that the rate of SO_4 reduction may be very high where methane abundance is not limiting, *e.g.* up to 1.8 mol/L per year (Nauhaus et al. 2002), or very low where methane is not abundant ($<3.6\text{x}10^{-4}$ mol/L per year).

AOM is considered further in the context of SKB's response to a request from SSM for complementary information, and my comments on SKB's response (see Appendix 2).

In cases where organic C is not the electron donor, the Monod rate expression is not appropriate for SO_4 reduction kinetics. The Michaelis-Menten kinetics equation has been suggested for use (Liu 2006):

$$R = R_{max}\frac{[SO_4]}{[SO_4]+K_M}$$

where R is the rate of SO_4 reduction, R_{max} is a maximum reduction rate (presumably similar to $[SO_4]_{lim}$ in the Monod equation) and K_m is the Michaelis constant for the particular microbially-mediated reaction. Reaction rates for SO_4 reduction, derived like those above from surficial sedimentary systems, of 9 x 10^{-10} mol(SO_4).yr^{-1}.cell^{-1} (Hallam et al. 2004).

For a deep location with only 100 SRB cells per mL, this would correspond to a rate of about $1\text{x}10^{-4}$ mol(SO_4)/L per year. This is roughly in the middle of the range of SO_4 reduction rates inferred above (*i.e.* 10^{-11} to 10^{-1} mol/L per year) for the cases where DOC is the electron acceptor. It would mean, if representative, that the microbially-mediated reduction of most or all of available SO_4 (*e.g.* 500 mg/L or $5.2\text{x}10^{-3}$ mol/L) could occur within a relatively short timescale of about 50 years. This suggests that HS^- production would be constrained by SO_4 flux and concentration and not by reduction kinetics. However this hypothetical model calculation has to be considered against the evidence that SO_4 has a considerably longer 'half-life' in the Forsmark groundwater system than 50 years. The bulk of the dissolved SO_4 originates from Littorina seawater and has therefore been in the rock for about 5000 years.

Flux of sulphate into repository volume

The flux of dissolved SO_4 into the repository volume is significant for HS^- contents because it is one of the constraints on the rate of HS^- production and the total potential HS^- production integrated over time. It can be estimated in two ways: (i) the amount of SO_4 that would enter the tunnels and deposition holes during resaturation in the early post-closure period, and (ii) the amount of SO_4 contained in the flow of groundwater through the repository volume after the restoration of natural hydraulic conditions.

1. According to the Safety Case, the total empty pore volume contained in a 300 m long deposition tunnel with 50 deposition holes to be resaturated after closure and sealing will be ~1250 m^3, including 20% extra water to allow for leakage through the tunnel plug (SKB 2011, Vol 2, p 306). Assuming that the SO_4 content of resaturation water is 500 mg/L, *i.e.* it is predominantly brackish groundwater with a high proportion of Littorina

seawater, then the total influx of SO_4 to each deposition tunnel and set of deposition holes is:

$5 \times 10^{-3} \times 10^{3} \times 1250 = 6.25 \times 10^{3}$ mol(SO_4) per tunnel

If all that SO_4 were to be distributed uniformly to the canister surfaces, *i.e.* it all diffused into buffer in each deposition hole and eventually migrated to the canister surface and if it were reduced to HS^-, then that would amount to:

$6.25 \times 10^{3} / 50 = 125$ mol(HS) per canister

2. If the hydraulic gradient at repository depth is assumed to be 0.01 (SKB 2008, p 369), the equivalent porous medium hydraulic conductivity is assumed to be 10^{-8} $m.s^{-1}$ (SKB 2008, p 426), then the flux of groundwater, Q, in whatever direction the hydraulic gradient is directed is:

   $10^{-8} \times 0.01 = 10^{-10}\ m^3.m^{-2}.s^{-1} = 3.2\times10^{-3}\ m^3.m^{-2}.yr^{-1}$

   Assuming that SO_4 concentration in groundwater at repository depth is 500 mg/L, then the SO_4 flux per unit cross-sectional area is:

   $5 \times 10^{-3} \times 10^{3} \times 3.2 \times 10^{-3} = 1.6\times10^{-2}$ mol(SO_4).$m^{-2}.yr^{-1}$

   Estimating the area of the repository footprint to be 5 km^2, and that the repository contains 6000 deposition holes, and assuming that all of the SO_4 flux were uniformly distributed among the deposition holes and eventually migrated to the canister surface and if all that SO_4 were reduced to HS^-, then that would correspond to:

   $1.6 \times 10^{-2} \times 5 \times 10^{6} /(6 \times 10^{3}) = 13$ mol(HS) per canister yr^{-1}.

As was also discussed in the previous section, the fact that Littorina-derived SO_4 is still remaining in the groundwater system at repository depth and has not been reduced to HS^- indicates that these illustrative calculations represent extreme and ‘worst case’ scenarios. They are unrealistic because they assume (a) that all of the SO_4 would be reduced to HS^-, either in the bedrock or in buffer; (b) that all dissolved SO_4 throughout the repository volume will end up in groundwaters around deposition holes; and (c) that SO_4 or produced HS^- will migrate through buffer to the canister surface. The third of these assumptions would be more relevant to the buffer erosion scenario where SO_4 and HS^- could be transported advectively to the canister surface.

SKB’s conceptual model and interpretation of observed HS^- contents, excluding those anomalously high values due to local transient perturbation, is that they represent a steady state of HS^- production and precipitation of FeS. My conclusion is that this is consistent with wider considerations of biogeochemical reaction kinetics and fluxes of SO_4, Fe^{2+} and DOC.

3. Analysis of potential time dependences of sulphide contents

3.1. SKB's presentation

In SKB's safety analysis for the reference evolution, corrosion of the canisters (safety function Can1) will occur due to diffusive migration of HS^- from the buffer and from groundwater at the buffer-bedrock interface to the buffer-canister interface. In a variant scenario, dissolved HS^- could be transported advectively to the canister surface if sufficient buffer had been eroded to allow free groundwater movement through the buffer (SKB 2011, p 31; SKB 2010b).

Tolerance for HS^- content of groundwater is therefore coupled with the buffer erosion scenario. The overall containment function of the canisters is dependent, *inter alia*, on "limited groundwater flow rates and low groundwater concentrations of sulphide to limit corrosion, in particular if the buffer has been eroded" (SKB 2011, p 42).

The Summary of SR-Site states that "For the majority of the 6000 deposition positions, all safety functions relating to the canister, the buffer, the deposition tunnel and the host rock are assessed to be satisfactorily upheld during the reference evolution". It goes on to summarise the conclusions regarding compliance with the safety function criteria among which is that for sulphide which would corrode the canister (safety function R1d): "Concentrations of HS^- are expected to not exceed present-day concentrations" and "If sulphate reduction is involved, the sulphide produced is expected to react with the iron(II) from the corrosion and increased sulphide levels will not occur due to this mechanism" (SKB 2011, p 29).

The following sections summarise SKB's presentation of their modelling and qualitative arguments that support the conclusions concerning potential time dependence of HS^- contents during the reference evolution and that justify the simplifications used in SR-Site. The first and second sections deal with the temperate and glacial periods respectively. The third section describes how HS^- concentrations have actually been represented in the safety analysis in SR-Site.

3.1.1. Groundwater sulphide in the future temperate period

A basic constraint on future HS^- concentrations is equilibrium with FeS in reducing conditions (SKB 2011, p 360):

$$HS^- + Fe^{2+} = FeS(s) + H^+$$

for which $\log_{10}K = \log_{10}([H^+]/([Fe^{2+}]\,[HS^-])) \approx 3$. At pH 7 to 8, $\log_{10}([Fe^{2+}][HS^-]) \approx -10$ to -11.

In most groundwaters $\log_{10}[Fe^{2+}] \geq -6$ which sets the maximum $\log_{10}[HS^-]$ in the range -4 to -5. Modelled HS^- values using these present-day Fe^{2+} concentrations are “exceptionally high, representing only a very low percentage of analyses” (Salas et al. 2010, p 40 & Fig 6-22, p 63). They are an order of magnitude or more higher, above $1x10^{-5}$ mol/L. This is consistent with the generally negative saturation indices for FeS that are calculated with analyses of present-day groundwaters (Tullborg et al. 2010, Table 4-1).

SKB discounts that approach and instead selects HS^- concentrations obtained when applying Fe^{2+} values from equilibrium with Fe(III)-oxyhydroxide. SKB’s description of their approach is rather unclear, but presumably HS^- is modelled in this case by assuming redox equilibration between SO_4^{2-} and HS^-, with independently modelled Eh and Fe^{2+} values.

Salas et al. (2010, p 40) indicate that, for the temperate period after closure, spatial variations of HS^- and Fe^{2+} have been modelled by hydrodynamic mixing of the reference waters using the transient groundwater flow model and assuming one of three variant sets of assumptions regarding redox and controls on HS^- and Fe^{2+}. Those variant models are: (a) equilibrium with $Fe(OH)_3$ and a coupled S-Fe-C redox system; (b) equilibrium with $Fe(OH)_3$ but uncoupled redox so that HCO_3 is not reduced; and (c) equilibrium with FeS and coupled redox.

Modelling of HS^- concentrations resulting from reference water mixing requires assumptions to be made about the controls on HS^- and Fe^{2+} concentrations in the reference waters.

HS^- in the Littorina reference water was fixed by equilibrating it with FeS (Salas et al. 2010, p 56). It is unclear how HS^- in the deep-saline reference water was fixed with a very low concentration, 10^{-15} mol/L, but it seems to derive from the model variant in which S(VI)/S(II) speciation is uncoupled from Eh (Salas et al. 2010, Table 4-2, p 37). The same table of equilibrated end-member compositions for modelling of future mixing and evolution has similar very low HS^- concentrations for the ‘uncoupled’ variant for the ‘old meteoric’ and ‘altered meteoric’ end-members, but a significant amount of HS^-, 10^{-7} mol/L, for the glacial end-member water.

These data seem to be inconsistent with the statement in the SR-Site Main Report that only two reference waters, marine and deep-saline, were assumed to contain HS^- (SKB 2011, p 362). The two most significant reference waters in terms of HS^- contents, on the basis of statements in Salas et al. (2010), are the marine (Littorina) and glacial waters. The basis for modelling future HS^- concentrations, as shown in Fig 10-44 of SKB 2011 needs to be clarified.

Fe^{2+} concentrations in the deep-saline and the ‘old meteoric’ reference waters was fixed by imposing equilibrium with hematite, whereas Fe^{2+} in the glacial water and ‘altered meteoric’ end-members were fixed by equilibrium with Fe(III)-oxyhydroxide at the calculated Eh value.

The range of HS^- concentrations calculated with the three variants is very wide, approx. 10^{-11} to 10^{-5} mol/L, because redox control alternately by $Fe(OH)_3$ and FeS gives a wide range of redox. According to Salas et al., the lower end of the range of HS^- is unrealistic because it simply reflects dilution due to the increasing proportion of the meteoric water reference water (which is assumed to have zero HS^-), rather than a redox or equilibrium control.

Control of Fe^{2+} concentrations in this model of mixing between reference waters and varying equilibria is complex and is not clearly described. The model suggests that Fe^{2+} will be constrained within a range slightly narrower than 10^{-7} to 10^{-4} mol/L throughout the temperate period.

HS^- and Fe^{2+} concentrations were modelled in this way for positions in the proposed repository volume at the present-day and for 1000, 3000, and 7000 years into the future (SKB 2011, Fig 10-44, p 363). The statistical distributions of HS^- at each of those times is shown in Figure 8 as box-and-whisker diagrams. Median HS^- concentrations are just above 10^{-6} mol/L except at 7000 years ahead when they are modelled at just below 10^{-6} mol/L. Total Fe is just below 10^{-5} mol/L at the earlier times and just above 10^{-5} mol/L at 3000 and 7000 years ahead. The modelled HS^- concentrations for the present day can be compared with HS^- analyses which are shown in Figure 4. Analysed values are in the range of 10^{-5} (with one outlier at 10^{-4}) mol/L to detection limit (which is 9×10^{-7} to 6×10^{-8} mol/L).

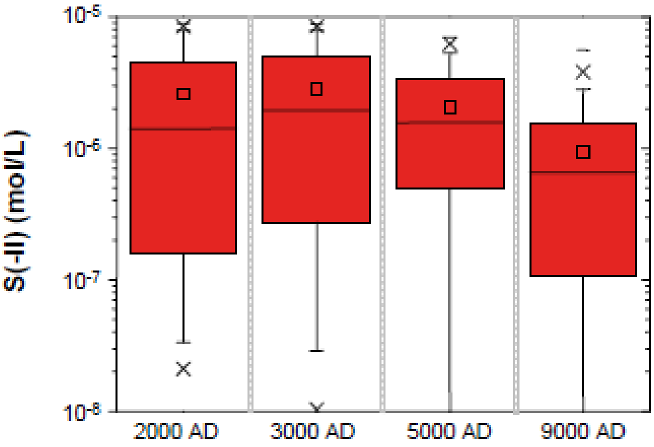

Figure 8. Box-and-whisker plots showing statistical distribution (median, mean, max, min, 1st, 25th, 75th and 99th percentiles) of calculated HS^- concentrations at positions in target volume at present day and 1000, 3000 and 7000 years into the future (from Figure 6-16 in Salas et al. 2010, also Figure 10-44 in SKB 2011, p 363).

Similar box-and-whisker diagrams showing the output HS^- concentrations from modelling with the variant model conditions for hydrogeochemical equilibria, described above, are shown in Figures 6-22 and 6-23 in Salas et al. (2010).

These results and the understanding of processes lead to SKB’s conclusion that “during the initial temperate period following repository closure the sulphide concentrations in the groundwaters will remain at the levels found at present in Forsmark, that is $\leq 10^{-5}$ mol/L for most deposition positions with a probability that for some deposition holes the surrounding groundwaters will have sulphide concentrations as high as $10^{-3.9}$ mol/L, as shown in Figure 10-41, and iron concentrations are expected to gradually increase but to remain below 10^{-4} mol/L” (SKB 2011, p 362). Furthermore “sulphide concentrations in a given fracture are expected to vary to some extent over a temperate period, but it cannot be concluded that the temporal variations will be sufficiently large that the time averaged concentration would correspond to the average of sulphide concentrations sampled at Forsmark today”.

3.1.2. Groundwater sulphide in a future glaciation

Evolution of groundwater compositions during future periglacial/permafrost and glacial periods has been modelled for SKB by Vidstrand et al. (2010) and Hartikainen et al. (2010). The hydrogeological modelling has produced forecasts of salinity changes at repository depth, from which the evolving proportions of the deep-saline reference component and of a meteoric water component have been calculated. The compositions resulting from mixing of these proportions were then modelled with the PHREEQC geochemical code, assuming equilibrium with Fe(III)-oxyhydroxide and/or amorphous Fe-monosulphide, FeS, and with other minerals to estimate evolution of redox potential, Eh, Fe^{2+}, HS^-, pH and other parameters (Salas et al. 2010).

The modelled HS^- and Fe^{2+} concentrations for the periglacial period, derived with the methodology described above, are very similar to those for the initial temperate period (Salas et al. 2010, Fig 7-3, p 72). Effects of some other factors are discussed qualitatively in SR-Site: *i.e.* slowing down of microbial SO_4 reduction due to lower temperatures, and varying fluxes of DOC, methane and hydrogen that are microbial energy sources. SKB concludes that “the equilibrium solubility constraints applied cannot reflect the variability of sulphide concentrations that can be expected during periglacial conditions” (SKB 2011, p 514).

SKB expects that intrusion of glacial melt water would result in a ‘substantial decrease’ of HS^- due to dilution. Similarly, melt waters are expected to have low concentrations of SO_4 and of reductants such as DOC, CH_4 and H_2, and thus microbial SO_4 reduction during a glacial period should be more restricted than during other climatic conditions. On this basis, SKB argues that the assumption of HS^- contents in groundwaters during a glaciation being similar to those at the present day is pessimistic.

The possibility of transient increases of microbial HS^- production, during the expected short periods when the surface would be inundated with sea water which then infiltrated, is assumed to be analogous to the present condition in which Littorina sea water is present and is interpreted to have enhanced observed HS^- production (SKB 2011, p 363).

If deeper water were to be drawn upwards at some stage of ice sheet development then there could also be a transient period of higher SO_4 and potential for HS^- production although that would be constrained by supply of microbial nutrients.

Similar arguments are made by Tullborg et al. (2010, Table 6-1, p 61) concerning the likely evolution of HS^- contents through periglacial and glacial periods. Availability of DOC, CH_4 and H_2 “is not expected to increase substantially” during periglacial conditions, so HS^- concentrations will generally remain similar to or lower than those during the temperate climate period.

Tullborg et al. report only scant evidence for microbial SO_4 reduction beneath glaciers (Wadham et al. 2004; Hallbeck 2009), so discount this as a significant cause for enhancement of HS^-. Moreover they suggest that the influx of glacial melt waters with low SO_4, DOC, CH_4 and H_2 will tend to dilute pre-existing HS^-. It is suggested that HS^- might increase transiently only if and when the bedrock will be submerged beneath a transgression of sea water that would cause SO_4-containing relatively-dense brackish/saline water to infiltrate in a similar way to the infiltration of Littorina water.

Therefore SKB argues that the distribution of HS$^-$ during a glaciation would be adequately represented by the present-day concentrations and distribution (SKB 2011, p 520). This is regarded by SKB as a pessimistic assumption.

3.1.3. Sulphide contents used in the safety analysis

The data input and assumptions concerning HS$^-$ contents of groundwaters evolved slightly between the SR-Can interim safety assessment and SR-Site. Because a limited set of HS$^-$ measurements from the two sites was available for SR-Can, a “pessimistic distribution of sulphide concentrations” was assumed (SKB 2010a, p 185). In SR-Can, copper corrosion was evaluated using fixed groundwater concentrations of HS$^-$ that would either diffuse through the buffer to the canister or, in the eroded buffer variant, be transported advectively by groundwater flow. A cautious value for HS$^-$ of 10^{-4} mol/L was used for 10% of the deposition holes and 10^{-5} mol/L was used for the remaining 90%. The following paragraphs describe the data input, assumptions and simplifications concerning HS$^-$ contents that SKB has used in SR-Site.

Future HS$^-$ contents for the reference evolution

Concerning the evident uncertainties in present and future HS$^-$ concentrations, SKB state that “There is a large degree of uncertainty in the detailed distribution of dissolved sulphide in the groundwaters around the repository. Because no dependency has been found between sulphide and other groundwater geochemical or hydrogeological parameters, the observed distribution of concentrations shown in Figure 10-41 is propagated to the analysis of canister corrosion” (SKB 2011, p 367). Figure 10-41 in SKB (2011), which shows the depth dependence of the representative HS$^-$ concentrations selected by Tullborg et al. (2010) is reproduced below as Figure 9. The single highest value for HS$^-$ in the selected data is 1.2×10^{-4} mol/L (3.85 mg/L HS$^-$). All other HS$^-$ concentrations are $\leq 1.3 \times 10^{-5}$ mol/L.

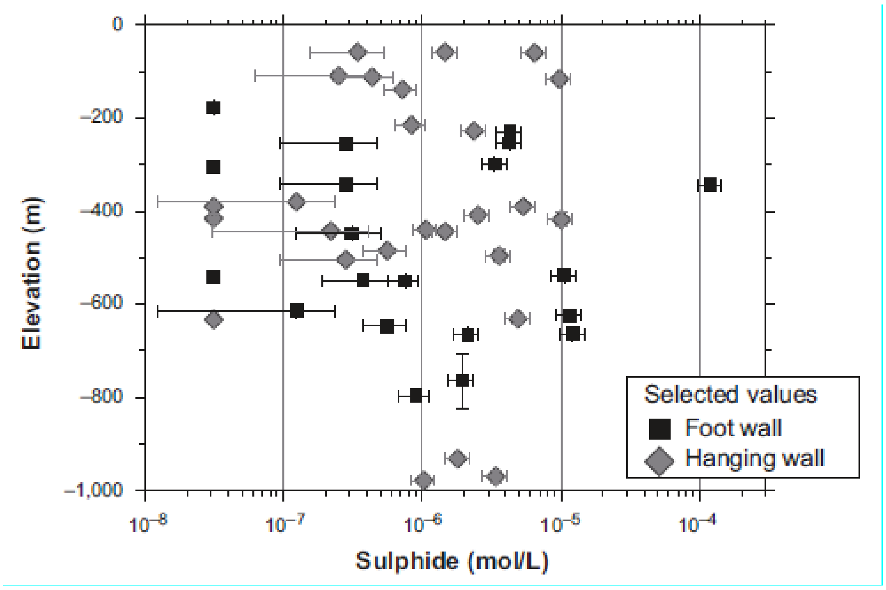

Figure 9. Selected HS$^-$ concentrations (see Tullborg et al. 2010) in present-day groundwaters used for the model of canister corrosion in the safety analysis (Figure 10-41 in SKB 2011). Data used in this diagram are essentially the same as those in Figure 4 of this report and in Table 4-1 and Figure 5-5a in Tullborg et al. (2010).

For corrosion calculations in the safety analysis of the reference evolution for Forsmark, SKB has assumed that the distribution of HS^- concentrations will be statistically similar to the observed present-day distribution, as shown in Figure 9, for both the temperate period and a subsequent glacial period (SKB 2011, p 603). Concentrations of HS^- at deposition hole positions in the repository have been assigned randomly from the distribution of present-day analyses in Table 4-1 of Tullborg et al. (2010) or have been assigned a fixed value corresponding to the 90-percentile in the ditribution. SKB has assumed that the assigned value at each position will be invariant over time and claims that this is pessimistic because it expects that HS^- contents will tend to be lowered as the groundwater compositions become more dilute over time.

Exactly how the data in Table 4-1 are represented in a statistical distribution for the Monte Carlo assignment of HS^- contents to deposition hole positions is not explained in the Main Report of SR-Site (SKB 2011, p 603). Nor is it explained in the Data Report for SR-Site which states that the modelling of copper corrosion is done "with a site-specific distribution of HS^- concentrations" (SKB 2010a, p 186). Some degree of clarification is provided in the Corrosion Calculations for SR-Site (SKB 2010b, pp 23-24), although the description of how HS^- values have been assigned for corrosion calculations is still rather unclear. Firstly it states that the "observed distribution of sulphide concentrations …… is used in the corrosion calculations" then it states that "in the corrosion calculations for an intact buffer, the 90% percentile of the distribution, $[HS^-] = 1 \times 10^{-5}$ mol/L, is used as a constant value over time and for all deposition positions" and "the extreme choice of using the highest measured value is included as an illustration" (SKB 2010b, p 24).

From those statements, I infer that the full distribution of HS^- values, as indicated by the first of these statements, is used in corrosion calculations for the case of partially eroded buffer and advective transport of HS^- to the canister surface in some deposition holes. The distribution of HS^- values from which Monte Carlo assignments are made is shown as a cumulative probability curve in Figure 4-4 in SKB (2010b) which is reproduced here as Figure 10. Note that HS^- concentrations are shown on a logarithmic scale, resulting in an approximately straight line probability curve. Presumably, HS^- values are assigned to deposition holes on the basis of random selection along the y-axis of Figure 10.

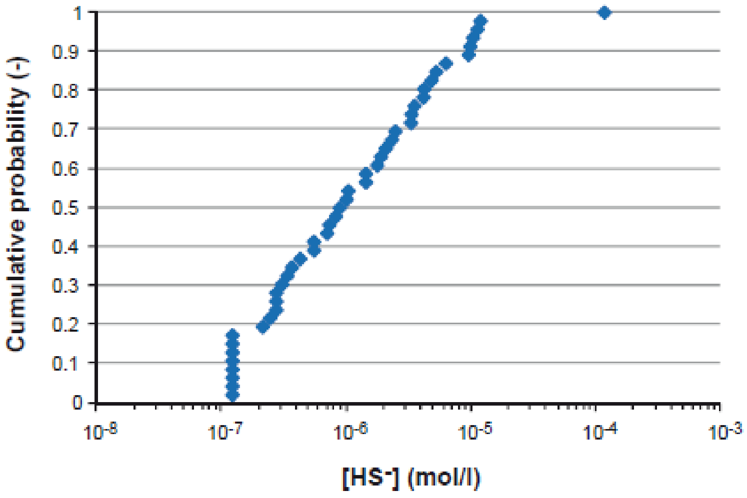

Figure 10. Cumulative probability distribution of HS^- concentrations in present-day groundwaters selected by Tullborg et al. (2010) and used for the assigning HS^- concentrations to deposition hole positions in the model of canister corrosion in the safety analysis. Data below detection limit of analyses, which is between 9×10^{-7} and 6×10^{-8} mol/L, are set to the lowest value in the distribution i.e. 1.2×10^{-7} mol/L.

Sensitivity to this assumed distribution of HS^- has been tested with a number of variant corrosion models: (i) the single highest value (3.85 mg/L = 1.2×10^{-4} mol/L) in analysed HS^- values is deleted from the distribution; (ii) a notional value of double the highest observed HS^- (i.e. 7.7 mg/L = 2.4×10^{-4} mol/L) is added to the distribution; (iii) all deposition hole positions are assigned a value which is the mean of the analysed HS^- values (i.e. 0.16 mg/L = 5×10^{-6} mol/L). The third variant effectively assumes that the future temporal variation at any deposition hole position will be the same as the present-day observed spatial variation. However a statement elsewhere challenges the validity of that assumption: "It cannot be concluded that the temporal variations will be sufficiently large that the time averaged concentration would correspond to the average of sulphide concentrations sampled at Forsmark today" (SKB 2011, p 362; also SKB 2010b, p 24). So SKB has sounded a note of caution about the simplification that is inherent in the third variant, whilst using it as an illustrative sensitivity test.

Future HS^- contents for modelling of corrosion in the buffer erosion scenario

For the variant evolution in which buffer might be partially eroded by dilute groundwater, SR-Site makes the same assumption that the distribution of HS^- concentrations in groundwaters around a repository at any time can be adequately represented by the analyses of present-day conditions. As in the reference evolution, a deposition position is assumed, pessimistically, to experience the same, randomly-sampled HS^- concentration throughout the assessment period (SKB 2011, p 607). Three sensitivity cases were defined to study the sensitivity to the properties of the HS^- distribution: (a) the mean HS^- value, 5×10^{-6} mol/L, of the site-specific distribution is assumed for all deposition positions; (b) omitting or doubling the highest HS^- value of 1.2×10^{-4} mol/L from the distribution; (c) assuming an unrealistic pessimistic geometry for corrosion of the canister.

The modelled probability distribution of corrosion rates for the base case semi-correlated hydrogeological DFN model with eroded buffer and advective conditions is shown in Figure 11. The fact that this modelling has been done using a single value for HS^-, 1×10^{-5} mol/L which is the 90-percentile value in Figure 10, suggests that the buffer erosion variant in the safety analysis has been modelled using this single value for HS^- and not a random selection for each deposition hole position from the distribution of HS^- values, as implied in the SR-Site Main Report and SR-Site Data Report, as discussed above.

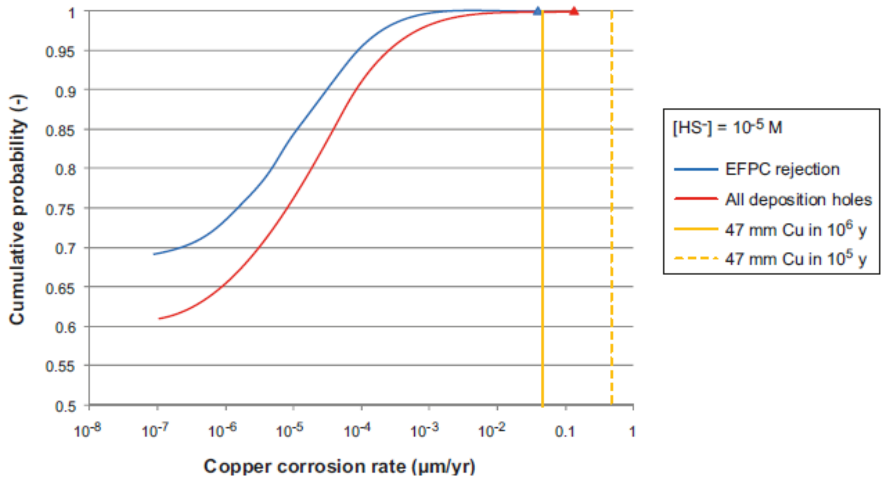

Figure 11. Cumulative probability distribution of corrosion rates for the base case semi-correlated hydrogeological DFN model with eroded buffer and advective conditions and HS^- concentration of $1x10^{-5}$ mol/L (Fig 10-158 in SKB 2011, p 532).

Modelling of the three sensitivity tests is the basis of SKB's statement that "on average less than one canister may fail due to dilute groundwater causing advective conditions in the deposition holes over the entire 10^6 year assessment period" (SKB 2011, p 533). Figure 12 shows the modelled results of the sensitivity testing of uncertainties in future HS^- contents.

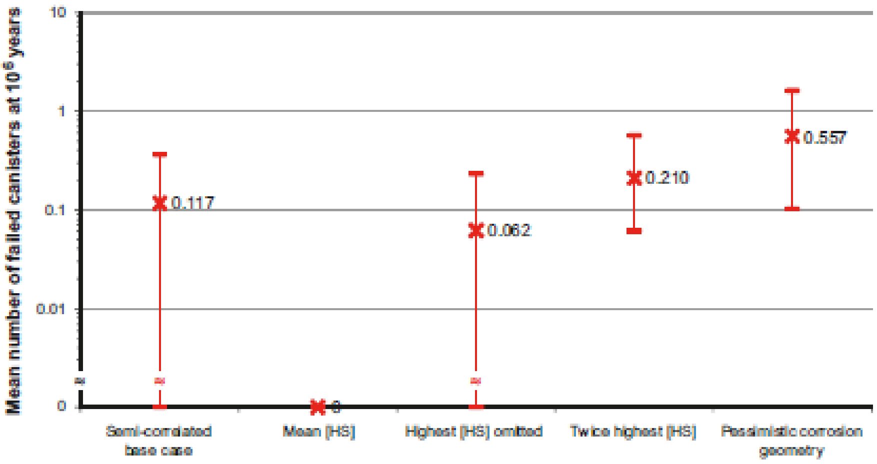

Figure 12. Results of modelling cases to test sensitivity to uncertainties in future HS^- contents. Mean values and variations of numbers of failed canisters for several realisations of the hydrogeological DFN model for different assumptions regarding HS^- values (Fig 12-17 in SKB 2011, p 608).

3.1.4. Plans for future monitoring

SKB's plans for detailed site investigations to be carried out during excavation of tunnels include "enhancing the confidence in calculations of future sulphide levels" (SKB 2011, p 48). SKB also identifies the need for more R&D to improve the basis for assessment on a number of issues including "better bounding of the expected evolution of sulphide at the Forsmark site, the role of microbial activity for maintaining a low and stable redox potential, for sulphide formation……" (SKB 2011, p 48).

3.2. Motivation of the assessment

3.2.1. Safety implications of future sulphide contents

As stated in the corresponding section of the first part of this report (Section 2.2.2), this assessment is motivated by the significance of HS^- as the main corrodant that could threaten the integrity of the copper canisters in the KBS-3 concept for deep geological disposal of spent fuel. The analysis of long-term safety of the proposed KBS-3 repository at Forsmark requires estimates of the amounts of HS^- that will come into contact with the copper canisters and will cause corrosion and thinning of the copper containment.

Characterisation of present-day contents of HS^- in groundwaters at the Forsmark site, and of the spatial variations of HS contents, is the basis of SKB's forecasting of the likely future contents of HS^-. Data for present-day contents of HS^- in groundwaters at Forsmark are assessed in the first part of this report.

Understanding what controls the present-day HS^- contents and describing the processes involved is the basis for modelling the future evolution of HS^- contents. Those processes, and modelling approaches to quantifying them, involve additional hydrochemical, biogeochemical and mineralogical data that also have been characterised. These data supporting the understanding and modelling of HS^- are concentrations of dissolved SO_4 and Fe^{2+}, mineral sources of sulphide, sulphate and iron, and populations of microorganisms that catalyse the redox transformations controlling sulphide. To the extent possible in a groundwater system that has a low level of organic activity, the energy and nutrient sources for microbial activity also need to be characterised.

During the long timescale of the safety analysis, the surficial environment will experience varying climate states. A long period, possibly many tens of thousands of years depending on the outcome of anthropogenic global warming, of temperate climate is predicted to be followed by a glacial climate stage during which periglacial conditions will be followed by glaciation. SKB's safety case has required the content of dissolved HS^- in groundwater entering the repository throughout that timescale to be forecast.

3.2.2. Uncertainties in future sulphide contents

The safety analysis of the reference evolution takes account of both 'typical' and pessimistic assumptions about the sources and contents of HS^- in the EBS-bedrock system. These calculations give an idea of the general tolerance of the system to variations of contents and properties of sulphide in the system – both in the EBS and in surrounding groundwaters. The extent of corrosion increases linearly and cumulatively with the amount of HS^- transported to the canister surface, so the key variables are the concentrations of HS^- in buffer pore water and in groundwater around deposition holes, and the durations for which any anomalously high concentrations might persist.

For diffusive transport of HS^- in groundwater from the rock-buffer interface to the canister surface, and assuming intact buffer, SKB calculates that it would cause maximum corrosion to 0.6 mm depth in 10^6 years. It assumes HS^- concentration of $1x10^{-5}$ mol/L, constant over time, for groundwater moving through fractures described by variants of the DFN model. My assessment is concerned with whether the assumed HS^- concentrations are reasonable forecasts for how groundwater conditions could evolve in response to future hydrogeological and climatic conditions. It is also concerned with whether there are pessimistic scenarios for HS^- concentrations that have not been considered.

The ‘worst case’ scenario for canister corrosion by HS^- in SKB’s safety analysis involves erosion and mass loss of buffer leading to advective transport of HS^- to the affected deposition hole positions. This scenario constrains the maximum possible rate of corrosion (SKB 2011). Groundwater flux in intersecting fractures and the HS^- concentration would be the critical parameters in that case, along with the timing at which buffer loss occurs and the variation of HS^- contents thereafter. SKB uses an illustrative calculation with the probabilistic DFN groundwater flow model to show that, if HS^- concentration is constant at $1x10^{-5}$ mol/L, there would be a low probability of a corrosion rate of up to 10^{-2} µm.a^{-1} after buffer loss had occurred (SKB 2011, Fig 10-158). Corrosion rate would be more likely to be at a maximum of about 10^{-4} µm.a^{-1}, according to the distribution of transmissive fractures and the success of rejecting deposition holes that would be intersected by such a fracture. These rates are equivalent to between 1 and 0.01 mm corrosion depth over 10^5 years. My assessment is concerned with whether this model of the ‘worst case’ scenario is adequate, given that it represents groundwater flow probabilistically but assumes simplistically that HS^- concentrations remain uniform both spatially and temporally.

For the full base case safety calculation, assuming that buffer remains intact, spatial variability of HS^- concentrations is taken into account (based on the present-day spatial variation, and assuming that the values and distribution remain constant through time). The distribution has a maximum HS^- concentration of $1.2x10^{-4}$ mol/L. SKB reports that the outcome of the coupled modelling of HS^- distribution and the DFN groundwater flow model is failure of less than one canister in 10^6 years (SKB 2011). The tolerance for uncertainties in HS^- contents of groundwaters therefore is high according to that modelling. My assessment is concerned with whether there is a realistic alternative scenario for HS^- concentrations that would challenge that degree of comfort in the safety analysis.

Estimations about the mass budgets of sulphur sources throughout the repository, engineered barriers and bedrock system are a simple but transparent way of scoping the maximum plausible HS^- contents if, for some unknown reason, the biogeochemical processes and controls did not operate in the expected way and allowed HS^- to exceed what is forecast with modelling. My assessment provides a number of such scoping calculations that have been done with ‘ballpark’ estimations of input parameters that may not be exactly consistent with SKB’s more precise data. Nevertheless they illustrate semi-quantitatively where the assumed conditions governing sulphide contents are more or less vulnerable.

3.3. The Consultant’s assessment

Future concentrations of HS^- in near-field groundwaters around deposition holes will depend on interplay of many biogeochemical properties and processes: influxes of SO_4, DOC, CH_4, Fe^{2+} and perhaps other redox-active solutes (including dissolved

O_2) in deep groundwater movements, quantities of locally 'introduced' organics and SO_4 originating from the repository itself (including buffer and backfill materials), microorganism populations, and natural sources of Fe^{II} and sulphide in local rock.

SKB has assumed that HS^- will not vary significantly outside the envelope of present-day values and has used the present-day distribution of HS^- for all stages of the assessment timescale. This assumption is justified by hydrodynamic modelling of mixing between reference waters and hydrogeochemical modelling of water-rock reactions through the long-term evolution of groundwaters. This indicates that the potential temporal variability of HS^- concentrations will be low relative to the range of observed present-day concentrations. Controls on the spatial variability of HS^- in relation to hydrochemical variations at any stage of the future evolution are not established.

On the basis of the insights provided by the modelling and the recognition of magnitudes of uncertainties, SKB has adopted a few gross simplifications about future HS^- contents. For the full reference evolution, i.e. with intact buffer, my understanding is that SKB has used a single ubiquitous and time invariant HS^- value of 1×10^{-5} mol/L, the 90-percentile value in the distribution of measured values. For the variant scenario of dilute water penetration to a deposition hole causing chemical erosion of buffer and subsequent advective transport of HS^- to the canister, SKB has used random selections of HS^- values for each deposition hole from the full distribution. That means that HS^- values are $\leq 10^{-5}$ mol/L for most deposition positions with a low probability that groundwaters surrounding some deposition holes will have HS^- concentrations as high as 1.2×10^{-4} mol/L (SKB 2011, p 363 & p 432). Values assigned to deposition holes are fixed for all modelled times, both for temperate and for glacial stages of the reference evolution. SKB has also assessed sensitivity to the particular limits of the HS^- distribution in a limited way by varying the upper limit of the distribution. Corresponding Fe^{2+} concentrations are expected to remain below 10^{-4} mol/L.

My assessment, therefore, considers the validity of these simplifications of how future HS^- contents are represented in the corrosion calculations for the safety analysis. I consider whether these are reasonable as well as pragmatic simplifications. I also consider what the ultimate constraints on HS^- contents are, in terms of the elemental S budget and the possibilities for production of HS^- from SO_4 and for control on HS^- concentrations by Fe^{2+} availability. The basic issue is whether processes, sources or other circumstances affecting sulphide contents can be envisaged that would create a significant possibility of future HS^- concentrations that would be significantly higher than the HS^- values assumed in SKB's safety analysis.

In the following two sections the processes of HS^- production and control in solution and scenarios for elevated HS^- concentrations are reviewed so that the robustness of SKB's approach can be assessed.

3.3.1. Biogeochemistry of sulphide production

Despite a substantial effort to obtain reliable samples for microbiological analysis, there is still a large degree of uncertainty about the interdependence of microbial populations and hydrochemical conditions. That is the present position for the relationship between sulphate reducing bacteria (SRB) and the contents of sulphide in groundwaters.

Some qualitative interpretations of SRB data in terms of the biogeochemistry of HS^- production have been reported by SKB, but it remains unproven whether groundwaters with low numbers of SRB have low or zero propensity for transformation of SO_4 to HS^- and, conversely, whether relatively high numbers of SRB indicate that SO_4 reduction is active. In theory, these are the expectations, but in my opinion these expectations are not yet confirmed with data. There are similar absences of clear evidence for the roles of dissolved organic carbon (DOC) and dissolved gases CH_4 and H_2 in biogeochemical production of HS^-. There are sparse or no data for dissolved acetate, and its role as an intermediate in microbial reduction of sulphate is also unclear with regard to the specific conditions at Forsmark.

Data for the identities and abundances of microorganisms in water samples taken from deep boreholes at Forsmark have been reported by SKB in the Site Descriptive Model (SKB 2008; Laaksoharju et al. 2008). Data for each metabolic group of microorganisms and the microbial model for Forsmark groundwaters are discussed in an overview report for SDM-Site (Hallbeck and Pedersen 2008a). These data for Forsmark, plus some data from Laxemar and from underground boreholes at the Äspö HRL, are also published and discussed in an overview paper (Hallbeck and Pedersen, 2008b).

Some microbiological data plus relevant chemical data for Forsmark are in Table 2. Reproducibility of microbial sampling and MPN analyses has been assessed, including a duplicate sampling of KFM06A/302m. In general, the 95% confidence range of MPN analyses is from 0.3 to 3x the obtained MPN value (Hallbeck and Pedersen, 2008a). This means that the order of magnitude contrasts between analysed microbial populations should be meaningful unless there are unrecognised artefacts of sampling.

My assessment of the microbial investigations is that, despite sampling and analyses being ‘state of art’ work, there is not yet a definitive conclusion about whether SO_4 reduction and production of HS^- are actively occurring in the unperturbed groundwater system at repository depth. Stable S isotope ratios for dissolved SO_4 indicate that some SO_4 content in the past had been reduced to HS^-. Spatial variations of present-day SO_4 contents, outside the ranges of contents that would result from simple mixing of reference waters, is further circumstantial evidence that SO_4 reduction has occurred and is probably still active. The only unequivocal evidence of active HS^- production is the occasional high HS^- analyses of time series samples from monitoring installations. I agree with SKB’s judgement that these are a transient and localised process that is caused by a perturbation of the biogeochemical system, although exactly what the cause is remains enigmatic.

Quantitative process modelling of biogeochemical conversion of SO_4 to HS^-, for microbial mobility and viability, and of transport of SO_4 and HS^- in the EBS has been developed by SKB (Liu 2006; Liu and Neretnieks 2004; Sidborn and Neretnieks 2006). The underlying concept assumes that microbially-mediated SO_4 reduction would take place in a rock fracture intersecting the rim of a deposition hole and would be kinetically fast, so that all supplied SO_4 is transformed effectively to HS^-. Modelled HS^- source concentrations at the diffusive outer boundary of the EBS are determined either by fluxes to that interface of SO_4 or of an energy source for SRB, *i.e.* DOC, acetate, hydrogen or possibly methane.

There are two generic formulae for the kinetics of microbially-mediated reactions: the Monod and the Michaelis-Menten formulae. Monod kinetics might apply if the utilisation of organic carbon (DOC) as energy source for SRB were directly the rate-determining process, whereas Michaelis-Menten kinetics might apply in the case where acetate, hydrogen or methane, rather than DOC, is the electron donor. Neither of these kinetic formulations would be appropriate if the rate of SO_4 reduction is controlled by the numbers of active SRB or by a threshold concentration of DOC, H_2 or CH_4.

Liu's model (Liu 2006; Liu and Neretnieks 2004) assumes that SO_4 reduction is instantaneous, whilst Sidborn's model (Sidborn and Neretnieks 2006) assumes a reduction rate of 10^{-3} $mol^{-1}.m^{-2}.a^{-1}$ (where the m^{-2} refers to rate per m^2 of a biofilm that is assumed to be the location of SRB activity at the rock-buffer interface) which is effectively instantaneous.

The observation of transient localised HS^- production associated with perturbations due to monitoring installations supports the assumptions in Liu's and Sidborn's modelling that SO_4 reduction at the fracture-buffer interface is rapid. Whether that is actually likely to occur probably depends in an unpredictable way on the prior perturbation of the deposition hole wall and the response of the biogeochemical system. Any such biogeochemical effect producing HS^- would be expected to diminish over time. My assessment overall is that SKB's modelling assumption that complete reduction of SO_4 would occur at the bedrock-buffer interface is conservative in terms of HS^- production. An argument supporting this is the persistence of at least some of the original SO_4 in deep groundwaters in spite of the redox conditions suggesting that it should be predominantly reduced to HS^-. In this respect, the contrast between SO_4 hydrochemistry at Forsmark and at Olkiluoto, Finland, is noteworthy (Geier et al. 2012). An explanation for the difference is not certain but may be related to the greater concentrations and inferred flux of dissolved methane at Olkiluoto, although doubt remains about the possibility of anaerobic oxidation of methane (AOM) being a direct cause of apparent SO_4 consumption.

SO_4 reduction and HS^- production in unperturbed groundwaters is an open question. The persistence of dissolved SO_4, predominantly derived from intrusion of Littorina seawater several thousands of years ago, is evidence that the process is, if anything, very slow. My judgement, based on the evident heterogeneity of HS^-, SO_4 and DOC concentrations and also of microbial populations and the relevant dissolved gases, H_2 and CH_4, is that the occurrence and rate of HS^- production is patchy. Whether it occurs, and the rate, presumably depends on whether fracture surfaces allow biofilms to develop and support microbial activity, and also on the availability of nutrients – DOC etc. That would be more likely where the groundwaters are dominantly of Littorina origin. This speculative model is more or less consistent with SKB's interpretation.

Therefore I conclude that SKB's interpretation of HS^- biogeochemistry in the general groundwater system is the most likely model. The most pessimistic extrapolation of the biogeochemical model into the future would be a scenario of increasing inputs of organic C as a form of DOC that would be available for microbial respiration and would promote rapid HS^- production from SO_4. In that case, the constraints on HS^- contents would be either a geochemical control on HS^- concentration *e.g.* by FeS equilibrium or, in the most pessimistic scenario, a mass budget control by SO_4 availability. These constraints are considered in the following sections.

3.3.2. Geochemical scenarios for raised sulphate contents

The potential effects of the long-term evolution of groundwater compositions on HS^- production and concentrations at repository depth are considered in the following paragraphs: (a) increasing meteoric water or glacial melt water infiltration and dilution, (b) regional hydraulic gradients that cause upwards flow of deep saline groundwater, and (c) transient salinization of infiltration due to 'freeze out' of salts during permafrost formation. The rate of biogeochemical production of HS^- is, as discussed above, dependent on three factors: the concentrations of potential electron donors (reductants), the concentrations of SO_4, and the population and activity of sulphate-reducing bacteria (SRB).

(a) Increasing dominance of fresh ('meteoric') water recharge and circulation as land rise continues, relative sea level declines and the Baltic shoreline recedes, so that groundwater at repository depth will become more dilute. Drawdown during the excavation and operational phases of a repository will tend to accentuate this effect transiently. SO_4 concentrations will be increasingly diluted as the influence of Littorina water diminishes. Glacial melt water infiltration would have a similar diluting effect. Changes affecting biogeochemical reactions such as SO_4 reduction could be (i) increasing or decreasing DOC concentrations, depending on soil conditions for biomass development and degradation, and (ii) associated changes of microbial populations including SRB. The condition for highest HS^- production is probably a groundwater regime that supplies DOC at higher fluxes/concentrations to repository depth. Future conditions under which that might occur, e.g. more organic-rich soils or peats at the surface than at present, are not expected so SKB's approach to this is reasonable. Glacial melt waters are likely to be less productive in terms of contents of DOC and other reductants.

(b) Increasing salinity and SO_4 contents if increasing regional hydraulic gradients push deep saline groundwater upwards. Salinity at repository depth might also increase transiently due to upconing during the excavation and operational periods when groundwater pressures are lowered. However deep saline groundwater below repository depth has low SO_4, probably close to zero below the maximum investigated depth of about 1000 m, so upconing would not increase SO_4 at repository depth (although SKB has asserted pessimistically that it would).

(c) Exclusion of salts from water during permafrost formation would make the underlying residual groundwater more saline. There are suggestions, based on interpretations of palaeohydrogeological evidence, that SO_4 salts might precipitate in residual 'freeze-out' solutions remaining when permafrost forms. As in the case of glacial infiltration, the changes in hydrochemistry that would be associated with permafrost thaw are uncertain, for example there is a possibility of higher DOC and microorganism inputs especially from peat. Periglacial climate and permafrost formation occupy a rather large timespan in the reference evolution, and in my opinion SKB's approach to potential hydrochemical effects is consistent with current evidence and understanding.

3.3.3. Geochemistry of dissolved iron

SKB's concept for HS^- concentrations in the reference evolution assumes that FeS precipitation and equilibrium with that phase or with more ordered minerals of iron monosulphide, e.g. mackinawite. Given an adequate supply of Fe^{2+}, it is extremely unlikely, if not inconceivable, that FeS or a similar iron sulphide solid will not precipitate but this may be a slow process. FeS precipitation may be inhibited by the slow supply of Fe^{2+} to the local water volumes where SO_4 is being reduced. Dissolution of Fe^{2+}-containing minerals is slow relative to SO_4 reduction.

In groundwaters at repository depth, dissolved Fe^{2+} derives from Fe-containing minerals, mainly biotite, chlorite and hematite/goethite. The latter two minerals are available in fractures. Dissolution of hematite has to be reductive because it contains Fe^{3+}. Persistence of hematite and chlorite that both have origins in previous fluid (hydrothermal?) conditions indicates that they dissolve very slowly. Kinetics of dissolution of chlorite has previously been considered in relation to attenuation of dissolved oxygen (see Guimera et al. 1999; Bath and Hermansson 2007). Slow release of Fe^{2+} or local absence of Fe^{2+} sources might allow HS^- concentrations to rise to anomalous levels locally and transiently. There are sufficient Fe^{2+} minerals in fractures generally in bedrock at Forsmark to provide a general control on maximum HS^- concentrations. Measured variations of Fe^{2+} concentrations support this.

3.3.4. Mass budgets of sulphide, sulphate and iron

Mass budgets of the key components in the biogeochemical cycle of sulphur are a robust approach to gaining confidence in what are possible variations in the HS^- contents of groundwaters.

Potential sources of HS^- in groundwaters in crystalline rock are:

- Biogeochemical reduction of dissolved sulphate, SO_4;
- Transformation of organically-bound S especially in soils;
- Dissolution of sulphide minerals, mainly FeS and pyrite FeS_2 but also potentially other sulphide minerals such as those of Cu and Zn;
- Deep ‘Shield’ saline groundwaters containing HS^- from an indeterminate and complex source related to the metamorphic history of bedrock;
- Mixing with deep-sourced hydrothermal fluids containing sulphide that are migrating into more shallow groundwaters due to thermal buoyancy;
- Leaching of fluid inclusions in minerals that have trapped hydrothermal solutions in past tectonic conditions.

The sources of dissolved sulphate, SO_4, occurring in groundwaters in crystalline rock, as discussed in the previous section, are:

- Sea water, infiltrated from a present-day marine source (in this case, Baltic Sea) or from a marine source in the past (*e.g.* from the Littorina stage of the palaeo-Baltic or much older seawater in the ‘geological’ past);
- Oxidation of pyrite mineral, FeS_2, or other sulphide minerals especially where these occur as secondary minerals in fractures; electron acceptors potentially causing oxidation are dissolved O_2, Fe^{III}, NO_3^-;
- Atmospheric sulphate dissolved in rain and snow that infiltrate to groundwater;
- Oxidation of organically-bound S in soils;
- Dissolution of anhydrite, gypsum or other trace sulphate minerals such as barite or mirabilite;
- Deep ‘Shield’ saline groundwaters containing sulphate from an indeterminate and complex source related to the metamorphic history of bedrock;
- Leaching of fluid inclusions in minerals that have trapped sulphate-containing solutions.

Illustrative mass budget calculations for the most potentially significant of these sulphide and sulphate sources are provided below. These are scoping calculations only and are intended merely to give an idea of the robustness of the arguments that sulphide and sulphate budgets are unlikely to change much in the future. They also provide semi-quantitative indications of the impacts of extreme processes, *e.g.* if all dissolved SO_4 were reduced instantaneously to HS^-, or if all pyrite in the rock were oxidised to dissolved SO_4. Parameters have either been abstracted from SKB sources or have been estimated by simplified geometry. It is emphasised that these are illustrative calculations only, containing various 'ball park' estimations and simplifications.

Reduction of SO_4 in groundwaters

Footprint of target area for repository = 8 km^2 approx
Total volume of rock between 300-500 m depth = 200 m x 8 km^2 = 1.6 x 10^9 m^3
Fracture porosity or kinematic porosity (SKB 2010a, Table 6-78) = 1 x 10^{-5}
Volume of groundwater in target rock volume = 1.6 x 10^9 x 1 x 10^{-5} = 1.6 x 10^4 m^3
Maximum concentration of SO_4 in groundwater at repository depth = 500 mg/L
Total mobile SO_4 in target rock volume = 1.6 x 10^7 x 500 x 10^{-3} = 8 x 10^6 g

Reduction of SO_4 in pore waters in rock matrix

Footprint of target area for repository = 8 km^2 approx
Total volume of rock between 300-500 m depth = 200 m x 8 km^2 = 1.6 x 10^9 m^3
Matrix porosity or diffusion-available porosity = 0.23 ± 0.11 % (for rock unit 101057)
Matrix porosity corrected for stress-release artefact (SKB 2010a, p 367) = 0.23 x 0.8
Volume of matrix pore water in target rock volume = 1.6 x 10^9 x 0.18 = 2.9 x 10^8 m^3
Concentration of SO_4 in pore water at repository depth is unknown
Assumed maximum value for SO_4 in pore water (based on SO_4/Cl in experimental solution; SKB Report P-12-18, Table 5-1) = 500-1500 mg/L
Estimated max immobile SO_4 in pore waters in target rock volume = 2.9 x 10^{11} x 1500 x 10^{-3} = 4.3 x 10^{11} g

This scoping calculation shows that mass budget of S in pore waters in rock matrix is potentially significant. SO_4 contents in pore waters are not known, but have been estimated in the above calculation. It is possible that the mass budget of S in pore waters is many orders of magnitude greater than that in fracture waters in the target rock volume. This reservoir of SO_4 in the long term will buffer the contents of SO_4 in fracture waters. However the diffusive exchange between pore waters and fracture waters is very slow.

Dissolution of pyrite in fractures and reduction of produced SO_4

There are two alternative scoping calculations, *A* and *B*. They use different assumptions and parameters to estimate the amount of pyrite in fractures in the target rock volume.

Footprint of target area for repository = 8 km^2 approx
Total volume of rock between 300-500 m depth = 200 m x 8 km^2 = 1.6 x 10^9 m^3
Intensity of open fractures in rock unit FFM01 (SKB 2010a, Table 6-32) = 0.6-1.7 m^2/m^3
A
Estimated fracture aperture (Selroos & Follin 2009, Eqn 2-5) = 1.4 x 10^{-6} m
Assumed thickness of fracture minerals in fracture = 20% of aperture = 0.2 x 1.4 x 10^{-6} m

Estimated max volume of fracture minerals in target rock volume
$= 1.6 \times 10^9 \times 1.7 \times 1.4 \times 10^{-6} \times 0.2\ m^3 = 7.6 \times 10^2\ m^3$
Estimated max proportion of pyrite in fracture minerals = 1%
Estimated max amount of fracture pyrite in target rock volume
$= 7.6\ m^3 = 5 \times 10^3 \times 7.6\ kg = 3.8 \times 10^4\ kg = 6.3 \times 10^5$ moles S
Volume of groundwater in target rock volume $= 1.6 \times 10^9 \times 1 \times 10^{-5} = 1.6 \times 10^4\ m^3$
Max concentration of SO_4 in groundwater if all fracture pyrite was oxidised in
static groundwater $= (6.3 \times 10^5)/(1.6 \times 10^7) = 3.9 \times 10^{-2}$ mol/L = 3.7 gSO_4/L
B
Average thickness of fracture pyrite (Löfgren & Sidborn 2010)
$= 7 \times 10^{-6}$ m
Estimated max amount of fracture pyrite in target rock volume
$= 1.6 \times 10^9 \times 1.7 \times 7 \times 10^{-6}\ m^3 = 1.9 \times 10^4\ m^3 = 5 \times 10^3 \times 1.9 \times 10^4$ kg
$= 9.5 \times 10^7\ kg = 3.4 \times 10^9$ moles S
Volume of groundwater in target rock volume $= 1.6 \times 10^9 \times 1 \times 10^{-5} = 1.6 \times 10^4\ m^3$
Max concentration of SO_4 if all fracture pyrite is oxidised in static groundwater
$= (3.4 \times 10^9)/(1.6 \times 10^7) = 2.1 \times 10^2$ mol/L = 20000 gSO_4/L

These two alternative scoping calculations arrive at very different estimates of the amount of pyrite in fractures. They are about 4 orders of magnitude apart. The lower of the two estimates indicates that there would be a significant increase of SO_4 concentration if all the pyrite were oxidised instantaneously. However that would not happen and any oxidation of pyrite will be spread over a period of time and the corresponding increase of SO_4 will be similarly dispersed in time. The higher of the two estimates indicates a very large relative amount of SO_4 being available for potential release if pyrite were to be oxidised. That amount might be very significant for the overall S budget available for reduction to HS^-, even if dispersed over a period of time.

Sources of Fe^{2+} in fractures

Proportions of total secondary minerals in open fractures (Gustafsson et al. 2008):
Chlorite: abundant, with large variations of FeO/MgO
Goethite FeOOH: sparse brownish precipitate
Hematite: small amounts common in fractures
Pyrite: in many open fractures
Calcite + quartz + pyrite <10 vol%, decreasing below 100 m depth
Chlorite + hematite 1-5 vol%, no depth trend; hematite <1 vol%
Footprint of target area for repository = 8 km^2
Total volume of rock between 300-500 m depth $= 200\ m \times 8\ km^2 = 1.6 \times 10^9\ m^3$
Intensity of open fractures in rock unit FFM01 (SKB 2010a, Table 6-32)
$= 0.6\text{-}1.7\ m^2/m^3$
Estimated fracture aperture (Selroos & Follin 2009, Eqn 2-5)
$= 1.4 \times 10^{-6}$ m
Assumed thickness of fracture minerals in fracture = 20% of aperture
$= 0.2 \times 1.4 \times 10^{-6}$ m
Estimated max volume of fracture minerals in target rock volume
$= 1.6 \times 10^9 \times 1.7 \times 1.4 \times 10^{-6} \times 0.2\ m^3 = 7.6 \times 10^2\ m^3$

Estimated max proportion of pyrite in fracture minerals = 1% (see case A above)
Estimated max amount of fracture pyrite in target rock volume
$= 7.6\ m^3 = 5 \times 10^3 \times 7.6\ kg = 3.8 \times 10^4\ kg = 3.2 \times 10^5$ moles Fe
Volume of groundwater in target rock volume $= 1.6 \times 10^9 \times 1 \times 10^{-5} = 1.6 \times 10^4\ m^3$
Max concentration of Fe^{2+} in groundwater if all fracture pyrite was oxidised in static

groundwater = $(3.2 \times 10^5)/(1.6 \times 10^7) = 2 \times 10^{-2}$ mol/L = 1.1 gFe^{2+}/L

Average thickness of fracture pyrite (Löfgren & Sidborn 2010)
= 7×10^{-6} m (see case B above)
Estimated max volume of fracture pyrite in target rock volume
= $1.6 \times 10^9 \times 1.7 \times 7 \times 10^{-6}\ m^3 = 1.9 \times 10^4\ m^3 = 5 \times 10^3 \times 1.9 \times 10^4$ kg
= 9.5×10^7 kg = 1.7×10^9 moles Fe
Volume of groundwater in target rock volume = $1.6 \times 10^9 \times 1 \times 10^{-5} = 1.6 \times 10^4\ m^3$
Max concentration of Fe^{2+} if all fracture pyrite is oxidised in static groundwater
= $(1.7 \times 10^9)/(1.6 \times 10^7) = 1 \times 10^2$ mol/L = 5600 gFe^{2+}/L

Average thickness of fracture chlorite (Löfgren & Sidborn 2010)
= 2×10^{-4} m
Estimated max volume of fracture chlorite in target rock volume
= $1.6 \times 10^9 \times 1.7 \times 2 \times 10^{-4}\ m^3 = 5.4 \times 10^5\ m^3 = 3 \times 10^3 \times 5.4 \times 10^5$ kg
= 1.6×10^9 kg = 2.8×10^9 moles chlorite
= 2.8×10^9 moles Fe (assuming Fe/Mg in chlorite =0.25)
Volume of groundwater in target rock volume = $1.6 \times 10^9 \times 1 \times 10^{-5} = 1.6 \times 10^4\ m^3$
Max concentration of Fe^{2+} if all Fe is released from fracture chlorite into static groundwater = $(2.8 \times 10^9)/(1.6 \times 10^7) = 1.8 \times 10^2$ mol/L = 9800 gFe^{2+}/L

Average thickness of fracture hematite (Löfgren & Sidborn 2010)
= 2×10^{-5} m
Estimated max volume of fracture hematite in target rock volume
= $1.6 \times 10^9 \times 1.7 \times 2 \times 10^{-5}\ m^3 = 5.4 \times 10^4\ m^3 = 5 \times 10^3 \times 5.4 \times 10^5$ kg
= 2.7×10^9 kg = 1.9×10^{10} moles hematite = 3.8×10^{10} moles Fe
Volume of groundwater in target rock volume = $1.6 \times 10^9 \times 1 \times 10^{-5} = 1.6 \times 10^4\ m^3$
Max concentration of Fe^{2+} if all Fe is released from fracture hematite into static groundwater = $(3.8 \times 10^{10})/(1.6 \times 10^7) = 2.4 \times 10^3$ mol/L = 134000 gFe^{2+}/L

These scoping calculations for Fe^{2+} budgets are similar to those above for S budgets. Two alternative scoping calculations have been done for Fe^{2+} budget from pyrite, but for the other Fe^{2+} source minerals only the second type of scoping calculation has been done. They show that there are potentially very large budgets of Fe^{2+} that could be released from pyrite, chlorite and hematite. Thus it is envisaged that in general there would be no limitation on FeS precipitation and equilibrium due to Fe^{2+} availability, assuming that these minerals are reactive in the groundwater system. Dissolution kinetics of these minerals are slow, so release of Fe^{2+} is also generally slow. Localised zones where these minerals are not available for dissolution into fracture waters might still be depleted in Fe^{2+}. Thus those zones of fracture waters might locally have enhanced HS^- concentrations, assuming some sort of control by FeS equilibrium, but these would disperse and average out, spatially and temporally, at lower HS^- contents.

SO_4 from soils and other sedimentary material

Footprint of target area for repository = 8 km^2 approx
Estimated amount of SO_4 added to shallow groundwater per year (by oxidation of pyrite in clays, till, marine sediments, also by atmospheric deposition, etc; Tröjbom et al. 2007, Table 6-9)
= 54750 kg SO_4 per year over footprint of target area
Net annual downwards flow of groundwater into bedrock (SKB 2008, p80)
= 3 mm out of total recharge 120 mm from unsaturated zone to surficial soils, clays, till and other sediments

Averaged concentration of SO_4 in total recharge water
= $(5.475 \times 10^6)/(120 \times 10^{-3} \times 8 \times 10^6)$ $g.m^{-3}$ = 5.7 $g.m^{-3}$ = 5.7 $mgSO_4/L$
Annual amount of SO_4 supplied from surface to target rock volume
= $5.7 \times 3 \times 10^{-3} \times 8 \times 10^6 = 1.4 \times 10^5$ g SO_4

This scoping calculation indicates that the contribution of soil-derived SO_4 to the overall budget of S in groundwaters is rather negligible in relation to other sources.

Sulphur compounds in introduced materials

Volume of repository (Hallbeck 2010) = 2×10^6 m^3
Amount of introduced organic C (Hallbeck 2010) = 5×10^6 kg (backfill) + 3.9×10^5 kg (buffer) + 8.5×10^3 (other materials) kg org C
Proportion of S in introduced materials: no data in Hallbeck (2010)
Total volume of water in repository after closure and resaturation (Hallbeck 2010)
= 3.7×10^5 m^3 (deposition tunnels) + 1.95×10^5 m^3 (main & transport tunnels) + 1.3×10^5 m^3 (central area, shafts & ramps) = 7×10^5 m^3 total
Theoretical amount of HS^- from reduction of SO_4 by H_2 from corrosion of introduced steel (395 tons, Hallbeck 2010)
= 0.65×10^3 to 1.6×10^6 mol (depending on extent of corrosion)
Resulting concentration of HS^- in water in saturated repository = 0.067 to 140 mg/L
Theoretical concentration of HS^- produced by reduction of SO_4 in biofilms on rock surfaces (Hallbeck 2010) = 0.78 to 5.8 mg/L in different areas of repository

This scoping calculation indicates that the amount of HS^- that could be produced within the repository due to reduction of groundwater SO_4 (plus any introduced sulphate) is potentially significant. It emphasises the importance of controlling introduced materials that would contribute to the reduction capacity, *i.e.* steel, organic materials.

Iron in introduced materials

Volume of repository (Hallbeck 2010) = 2×10^6 m^3
Amount of introduced iron (Hallbeck 2010) = 395 tons steel = 4×10^5 kg Fe
Total volume of water in repository after closure and resaturation (Hallbeck 2010)
= 3.7×10^5 m^3 (deposition tunnels) + 1.95×10^5 m^3 (main & transport tunnels) + 1.3×10^5 m^3 (central area, shafts & ramps) = 7×10^5 m^3 total
Theoretical max amount of Fe^{III} from total corrosion of steel = 4×10^5 kg
= 7.1×10^6 moles Fe^{III}
Resulting concentration of Fe^{2+} in water in saturated repository if all Fe^{III} is reduced to Fe^{2+} = $(7.1 \times 10^6 \times 56 \times 10^3)/(7 \times 10^5 \times 10^3)$ mg/L = 570 mg/L

This scoping calculation indicates the maximum concentration of dissolved Fe^{2+} in water within the repository that would occur if all the introduced construction steel were corroded and dissolved instantaneously. Of course that will not happen, but it shows that the produced concentration of Fe^{2+} is comparable with that of HS^-, so it can be concluded that HS^- concentrations would be controlled by FeS equilibrium.

3.3.5. Sulphide contents during glacial climate

Some clarification of the assumptions and simplifications involved in the modelling of sulphide evolution during periglacial and glacial conditions is required. The validity of SKB's approach and the resulting range and spatial distribution of HS^-

concentrations might need to be considered further in the light of those clarifications. However the fundamental principle that SKB have used to constrain the range of values for HS^- in the base case seems to be that it comprises mixing of equilibrated HS^- in the marine and deep saline groundwater components and then dilution of HS^- as the meteoric component increases over time. This biases the range of HS^- towards low values, $<10^{-5}$ mol/L. The variant case involves mixing and then control of HS^- by equilibrium with $FeS_{(am)}$ and indicates a narrower range of HS^-, between 10^{-5} and 10^{-4} mol/L. This hydrodynamic and hydrogeochemical modelling underpins the simplified parameterisation of HS^- that has been used by SKB in safety analysis for the whole duration of the reference evolution.

A process that could theoretically influence the rate at which SO_4 would be reduced to HS^- during or after a glacial period is the episodic release of methane (CH_4) that had been trapped in ice or permafrost as methane hydrate. An episode of higher CH_4 availability would tend to promote microbial activity and specifically that of SRB.

In the deep boreholes at Forsmark and Laxemar, dissolved CH_4 concentrations are low: typically <1 mL/L (= 0.04 mmol/L) whilst at Olkiluoto they are significantly higher and close to or at saturation, up to 800 mL/L (= 36 mmol/L) below 800 m depth. If this natural CH_4 flux were trapped as hydrate or in some other way during a period of permafrost, then CH_4 concentrations should be expected to rise transiently when the permafrost thaws. At the same time as CH_4 would be released, DOC and microbial activity might also increase in shallow groundwaters. Enhanced CH_4 concentrations would promote SO_4 reduction, as is possibly happening at Olkiluoto, but the production of HS^- would be limited by SO_4 concentration and the concentration of HS^- would probably be limited by sulphide precipitation if Fe^{2+} is sufficient. However, no evidence has been found to suggest that coupled permafrost-CH_4-HS^- biogeochemical processes have been significant during glacial cycles in the past. Another argument against this is that released CH_4 would migrate upwards from the location of hydrate, and would probably not affect groundwaters at repository depth.

4. The Consultant's overall assessment

4.1. SKB's approach to sampling and data selection

Water samples for analyses of sulphide (HS^-) contents have been collected from surface-based boreholes at the Forsmark site. Appropriate control measures and monitoring of sample quality have been used to check that selected samples are as close as possible to being representative of *in situ* groundwaters. The methods of sampling and analyses and the rationale for data selection are well documented by SKB. Analyses for HS^- and associated data have been carried out, as far as I know, by appropriate methods. For HS^- analysis, contents of water samples were stabilised by adding zinc acetate to precipitate zinc sulphide on site prior to transport to the laboratories. Two laboratories were used to check accuracy and reproducibility.

Various perturbations invariably affect water samples collected in deep surface-based boreholes. For example, introduction of oxygen during sampling, could oxidise HS^- and thereby reduce the analysed content. For some, but not all, samples used for HS^- analysis, redox (Eh) has been monitored and is an additional indicator of the sample not being perturbed. HS^- is known to be difficult to sample and analyse reliably and, as has become evident, repeat samplings from existing monitoring installations are prone to perturbations.

Two types of sampling arrangement have been used to collect samples for HS^- analysis. Both methods samples from specific intervals, isolated between packers. Complete chemical characterisation (CCC) samples have been collected using a downhole testing tool soon after drilling. Monitoring systems have subsequently been installed and samples extracted by pumping from piezometer tubing; Eh has not been monitored in these cases. My assessment of SKB's technology and procedures for sampling for HS^- is that they are at the state-of-art for obtaining water from deep boreholes in low permeability fractured rock that optimises preservation of *in situ* conditions.

Early samples in some time series from monitoring installations have shown anomalously high HS^- contents which have declined over the course of water extraction. The pattern of these HS^- contents have been interpreted as indicating that the transient high HS^- contents have been an artefact of perturbations to the biogeochemical system in the monitoring installation prior to sampling. The phenomenon of transient HS^- contents in these conditions is still not fully understood and I agree with SKB that this is a source of uncertainty in representative values for *in situ* HS^- concentrations in groundwaters. Whilst the existence of these transient high anomalies obscures the upper limit of the spatial distribution of unperturbed *in situ* HS^-, it is justified to discount the higher values from the selected range. The uncertainty therefore arises in where expert judgement distinguishes between natural maxima and perturbed maxima, i.e. the range of HS^- contents is rather arbitrarily truncated at about 3.9 mg/L. The rather small number of samples and the low level of understanding of the perturbations underlie the uncertainty and weaken the statistical validity of the selected range.

The scale of uncertainty is probably an order of magnitude or so on top of an apparent range of spatial variability of about 3 orders of magnitude. In my opinion this degree of uncertainty due to an artefact of sampling is acceptably managed by SKB's approach which is to apply expert judgement to data from repeat samplings and time series samplings in selecting a single sample as being representative of unperturbed *in situ* composition for each borehole interval. The way that this has been done has been documented transparently by SKB. The highest anomalies are evidently the most transient and therefore have been discounted. Individual sample selections from the remaining set of HS^- data give a broad and regular distribution of values that is not biased to lower values. My overall assessment is that, despite these issues, it is unlikely that HS^- varies substantially outside the existing data range. SKB's decision to use the 90-percentile HS^- value from the distribution of selected data is a sensible and reasonable choice for a simplification that is most likely to be appropriate for 'typical' or average long-term HS^- contents.

Samples for related data that are required to support the interpretations of SO_4 reduction, *i.e.* dissolved organic carbon (DOC), dissolved gases (CH_4 and H_2), and microbial populations have been collected using similar expertise and state-of-art technology and appropriate precautions against contamination. There is a limited amount of replicate sampling which suggests reasonable reproducibility. There should be more effort to understand how representative samples and analyses are of *in situ* microbial numbers. At present, the large variations in microbial numbers between samples from different locations at repository depth range are not well understood. This suggests that there may be greater degrees of uncertainty in how representative samples and analyses are than is so far realised. If microbial analyses will be part of the underground monitoring programme during construction, then there needs to be a more robust and quantitative interpretation of their significance.

SKB should continue its efforts to understand the causes of the transient HS^- anomalies in monitoring samples. Localised HS^- production in monitoring installations and in other perturbations of the natural biogeochemical system could be problematic in future sampling during underground construction. Monitoring methods will need to be fit for purpose. It will be necessary to understand the impacts of construction perturbations on microbial populations, DOC, and other biogeochemical agents, as well as HS^-, on the chemical environment in rock around tunnels.

4.2. SKB's approach to evolution of dissolved sulphide

4.2.1. Processes affecting evolution of sulphide contents

SKB's conceptual model for the processes affecting future contents of HS^- in groundwaters is broadly well-founded and consistent with general understanding of redox biogeochemistry, SO_4 reduction, and FeS precipitation. This is the basis and justification for their assumptions and simplifications of HS^- contents for use in corrosion calculations for safety analysis throughout the reference evolution. SKB's site data and research has some remaining gaps which restrict the level of confidence in site-specific understanding of the processes and factors influencing them in the future.

It is reasonably evident that SO_4 reduction and production of HS^- is actively occurring in groundwaters at repository depth at Forsmark. Overall, however, the microbiological and geochemical data do not offer a clear and consistent picture of the biogeochemical processes affecting the spatial and temporal distribution of HS^-. Biogeochemical HS^- production is more likely to occur in groundwaters that are dominated by the Littorina component, mainly because this is the dominant source of dissolved SO_4 and also because it would be expected to contain DOC originating from seabed sediments, but there is no compelling evidence of such a simple correlation. The data do not indicate that SO_4 reduction occurs preferentially in some depth interval or in a particular water type.

It is likely that the Fe system is the basis of long-term buffering of redox in the Forsmark groundwater system. The redox conversion of SO_4 to HS^- may be coupled to Fe^{2+}/Fe^{3+} depending on the kinetics of the relevant reactions, *i.e.* the reduction of SO_4 and the release of Fe^{2+} from Fe-containing minerals. Those and other redox reactions, *i.e.*, DOC/CO_2 and CH_4/CO_2, may be involved to a greater or lesser degree in HS^- production depending on the viability of microbial mediation of the reactions.

SKB has done rather little characterisation and research into DOC as the potential driver for redox, and also does not have data for acetate in repository-depth groundwaters despite its importance as an intermediate in microbial SO_4 reduction (including the AOM pathway). I support SKB's general position and conclusion concerning the nature and availability of DOC, but more data coupled with DOC characterisation in different parts of the groundwater system would give greater confidence. The relationship between DOC and its component compounds including acetate is an issue that justifies more research by SKB, although I appreciate the analytical and sampling challenges. Better understanding about organic C availability for microbial activity/growth will also be necessary as background for understanding potential impacts, *e.g.* on HS^- production, of introduced organic materials in the near field. SKB's response to SSM's request for complementary information on these issues (see Appendix 2 of this report) is a reasonably comprehensive and balanced account of what is known and what can be hypothesised.

Overall, the evidence suggests that, even in crystalline rock groundwaters that are generally 'carbon-poor', sulphur geochemistry is closely interdependent on carbon and iron geochemistry. In the long-term, unless reactive Fe becomes highly depleted in the groundwater system and the biogeochemical productivity of the system is enhanced by influx of reactive carbon, it is concluded that HS^- concentrations will be controlled at low levels similar to those observed in the present systems.

The overall uncertainties and significance of high variability in microbial population numbers are, in my opinion, not well understood and, accepting that data are 'state-of-art' and representative, interpretations of the relative significance for SO_4 reduction of population densities of SRB and other types remain vague. I agree, overall, that the balance of evidence including energetics calculations points to AOM not being currently active at Forsmark. The argument that it could not occur in the future is less secure.

It can be expected that, whatever the exact process, SO_4 in deep groundwaters at Forsmark will continue to be progressively reduced to HS^-. Groundwaters at proposed repository depth have varying SO_4 contents up to a maximum of ~500 mg/L, indicating the potential for production over a period of time of a large amount of HS^-. Considerations of the experimental evidence for microbially-mediated reduction of SO_4 suggest that reduction of most or all of this SO_4 could occur within a relatively short timescale of about 50 years. Therefore HS^- production would be constrained by SO_4 flux and concentration and not by reduction kinetics. This hypothetical model calculation has to be considered against the inference that SO_4 persists in the Forsmark groundwater system for more than 50 years. The bulk of the dissolved SO_4 originates from Littorina seawater and has therefore been in the rock for about 5000 years.

Scoping calculations of mass budgets of SO_4 in groundwaters and rock matrix pore waters, using estimates for pore waters because analyses are not available, indicate that the mass budget of SO_4 in pore waters is probably many orders of magnitude greater than in fracture waters. So the pore waters will be a long term buffer of SO_4 in fracture waters though diffusive exchange between the two water reservoirs is very slow. Similarly, mass budget estimation of total S available in the form of secondary pyrite for conversion to SO_4 suggests that the amount, though it has large uncertainty, could be significant for available SO_4 in the long term. However this source of SO_4 would be dispersed over time and anyway would be dependent on large scale oxidation of pyrite which is not expected in the future and for which there is no evidence of it occurring in the past evolution.

4.2.2. Sulphide evolution through temperate and glacial periods

Biogeochemical production of HS^- around deposition holes in the early period immediately after waste emplacements will potentially be susceptible to microbial activity being stimulated by introduced DOC, nutrients and the formation of biofilm at the buffer-canister interface, and then accelerated by the thermal field. SKB will need to have procedures to monitor these processes and to control the inventory of introduced materials. Understanding of possible microbial and organic perturbations in borehole installations would be a contribution to better understanding of potential impacts of these much greater perturbations.

SKB has used hydrodynamic mixing and hydrogeochemical modelling to forecast potential evolution of HS^- through both the temperate and glacial/periglacial periods. The timescale that has been modelled (7000 y) is short relative to the potential longevity of a temperate period extended due to global warming. HS^- evolution is simulated according to mixing between changing proportions of reference waters, of which only the marine and deep saline waters are assigned HS^- contents which are buffered by FeS or FeS_2 equilibrium. These data seem to be inconsistent with the statement in the SR-Site Main Report that only two reference waters, marine and deep-saline, were assumed to contain HS^-. The hydrogeochemical modelling report states that the two most significant reference waters in terms of HS^- contents are the marine (Littorina) and glacial waters. These apparent inconsistencies need to be clarified as the basis for modelling future HS^- concentrations. SKB also reason that HS^- concentrations might be lower during influx of glacial melt water, and thus argue that the assumptions for HS^- evolution through a glacial period are pessimistic.

Fe^{2+} contents, which are necessary for predicting the scale of potential FeS precipitation and the effect on controlling HS^- concentrations, are modelled in terms of alternative reactions: dissolution of Fe from chlorite or biotite, precipitation of FeS and redox equilibrium. Control of Fe^{2+} concentrations in this model of mixing between reference waters and varying equilibria is complex and is not clearly described. Resulting HS^- contents have wide ranges, 2 or more orders of magnitude depending on the particular model assumptions. It is uncertain whether this range of variability has a similar cause as the spatial variations in currently observed HS^- concentrations. My conclusion from the hydrogeological modelling is that it usefully explores the scale of variability of HS^- for the various conceptual models for S-Fe hydrogeochemistry. Inevitably these conceptual models involve assumptions and simplifications that mean that long-term modelling of temporal and spatial variations would be uncertain though the maximum HS^- contents are highly likely to remain controlled by the fundamental FeS equilibrium.

Nevertheless, SKB has decided not to use these modelled HS^- contents in the safety analysis. The geochemical modelling output that they have discounted is interesting and is probably the most robust way of studying potential variability, but there is little if any evidence to support the multiple hydrogeochemical concepts that underlie the modelled variability. SKB's reasoning for not using the modelled HS^- values is that they do not compare with the measured data in the present-day system; the data ranges are pessimistically high. Instead SKB use the present-day HS^- contents for the entire reference evolution through temperate and periglacial/glacial periods.

My judgement is that SKB's approach with uniform HS^- is straightforward and has been implemented in the safety analysis with a limited set of sensitivity analyses to show the potential impacts of alternative scenarios for HS^- contents. However SKB's range of sulphide values for sensitivity testing does not include the higher values calculated for equilibrium with FeS. SKB discount this process because it would indicate maximum HS^- contents an order or so higher than are observed presently, but in my opinion sensitivity analysis should have considered this possibility at least as an illustration of the most pessimistic condition. The undersaturation is probably due to the slowness of SO_4 reduction and Fe^{2+} release from minerals. There is also uncertainty over the exact nature of the FeS phase and its thermodynamic properties.

4.3. General conclusions

Sulphide is a labile trace solute in groundwaters. It is characteristic of chemically reducing environments in which S-reducing microbes facilitate its production from sulphate. In shallow groundwaters, especially in sediments, sulphide production is usually correlated with large amounts of organic material. In deep groundwaters in crystalline rock, such as at Forsmark, sulphide production is much slower or may be negligible because organic carbon is sparse and non-reactive and microbiological activity is correspondingly muted.

In most natural environments, dissolved sulphide is controlled at low concentrations by reaction with dissolved iron to precipitate iron sulphide mineral. Slow production of sulphide in crystalline rock groundwaters makes it more likely that sulphide will be consistently constrained by solution-mineral equilibrium as long as there is a corresponding source of dissolved iron.

These are the basic principles of sulphide hydrogeochemistry on which SKB base their argument that groundwater sulphide contents at Forsmark will remain low and reasonably predictable and therefore that corrosion of the copper canisters in a geological repository will also occur at a very low rate in the long-term future. In my opinion that argument is well-founded and reasonably robust. There are, nevertheless, some aspects of SKB's case where lack of knowledge and of ability to quantify processes could be interpreted to challenge that opinion and to limit the degree of confidence.

My judgement is that these issues could not be resolved at this stage of the programme and that any refinement of science on these issues would not affect substantially the implications for long-term safety. However focussed investigations and monitoring underground during the construction phase offer a chance to evaluate the probabilities of delirious conditions at the present-day and to improve quantitative understanding of processes so that there is greater confidence in the limits of future evolution.

Sampling and analyses for groundwater sulphide in deep surface-based boreholes have, as could be expected, been challenging. It is a similar case, and perhaps more difficult, for microbial sampling. The uncertainties in understanding the causes of variability in microbial analyses make it even more problematic to interpret and quantify their significance for repository performance.

Future method development for use in underground investigations should address these data reliability issues for sulphide and related biogeochemical and microbial information. That would include appropriate data acquisition for parameters such as DOC, acetate, hydrogen and methane and also analyses of indicators of microbial growth such as ATP. Appendix 2 discusses in more detail the present state of data and knowledge for DOC in terms of bioavailability and also the challenge of understanding the *in situ* process responsible for producing sulphide in this environment.

SKB's approach to forecasting and modelling the evolution of sulphide concentrations has necessarily involved expert judgements on which the rationale is to some extent questionable and which result in potentially significant uncertainties. An example is the discounting of values of sulphide contents obtained by hydrogeochemical modelling through future prolonged temperate, periglacial and glacial periods, in favour of sulphide contents as seen now. Although in my judgement SKB's approach is defensible, the simple strategic decision is rather lost amongst model descriptions and discussions that are eventually rejected.

There is additional simplicity in using a random spatial distribution of sulphide values, based on measured data, for nodes in the groundwater flow-transport model in the modelling of corrosion in the safety analysis.

These simplifications, in place of trying to represent all possible scenarios for future evolution, are obviously contentious but in my judgement they do not bias the safety analysis away from any probable or sensibly pessimistic outcome.

Future research and monitoring during construction and operation will hopefully improve SKB's understanding of processes and the robustness of their position. However in my opinion the impact of the growing knowledge base on the safety analysis is very probably to change little if at all.

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APPENDIX 1

Coverage of SKB reports

Table 4: SKB reports that have been accessed and reviewed in the course of this assessment.

Reviewed report	Reviewed sections	Comments
TR-11-01. Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main report of the SR-Site project. 3 volumes.	Section 4.8 (Groundwater) Section 6.2 (Climate evolution) Section 8.3 (Safety functions for containment) Sections 10.2.5, 10.3.7, 10.4.7 (Chemical evolution) Section 13.5 (Canister corrosion)	These sections reviewed with regard only to groundwater sulphide contents and selection of data for canister corrosion model.
TR-10-39. SR-Site – sulphide content in the groundwater at Forsmark. (Authors: E-L.Tullborg et al).	All sections	This is the key report in terms of sulphide sampling, analyses and data selection, also in terms of sulphide interpretations and biogeochemistry of sulphate reduction
TR-10-58. SR-Site – hydrogeochemical evolution of the Forsmark site. (Authors: J.Salas et al).	Section 6.2 (Fe and S modelling for temperate period) Sections 7.3 & 7.6.3 (Fe & S for ref glacial cycle) Sections 8.2 to 8.5 (DOC, acetate, methane, H_2)	
TR-10-52. Data report for the safety assessment SR-Site.	Section 6.1 (Groundwater chemical composition)	Only in terms of sulphide and related parameters
TR-10-66. Corrosion calculations report for the safety assessment SR-Site.	Sections 3 & 5.3	Used as source of more definitive information about HS^- values used in corrosion calculations for the safety analysis
TR-08-05. Site description of Forsmark at completion of the site investigation phase.	Section 9 (Bedrock hydrogeochemistry) Section 11.7 (Groundwater composition and evolution)	Reviewed for background information on hydrogeochemical site description

APPENDIX 2

Comments on SKB’s response to SSM’s request for complementary information, nr. SSM2011-2426-82

‘The significance of microbial sulphate reduction through dissolved organic carbon (DOC)’, SKB doc id 1396704 (compiled by B Kalinowski, translated into English by SSM).

SSM requested additional information about SKB’s assertion (SKB doc id 1346686) that microbial SO_4 reduction due to reaction with DOC or dissolved H_2 would not contribute substantially to corrosion by sulphide of copper canisters. SKB, whilst ‘not ruling that out’, argues that SO_4 reduction takes place generally in the bedrock and not preferentially in deposition holes and that resulting HS^- is controlled by FeS precipitation. SSM points out that SKB’s data show that DOC concentrations in groundwaters at Forsmark are generally higher than those of HS^- and that extensive HS^- production would be possible ‘in principle’ in some bedrock locations if a greater proportion of DOC were available to participate in microbial SO_4 reduction. SSM also points out that HS^- production might be intermittent rather than continuous and therefore might occur in the future at times when environmental conditions are more beneficial for microbial activity than at present.

SSM has requested (i) SKB to account for forms of DOC occurring in Forsmark groundwaters and for the availability of these forms for microbial SO_4 reduction; and (ii) SKB to provide literature supporting the hypothesis that microbial SO_4 reduction by CH_4 (=AOM, anaerobic oxidation of methane) cannot be shown to occur in Forsmark bedrock.

On the first issue, DOC, SKB makes several observations and interpretations:

- Measureable DOC remains in groundwaters that are up to 10,000 years old, therefore at least this fraction of original DOC has low reactivity. One analysis of ^{14}C in DOC in Forsmark groundwater indicates residence of at least 5000 years.

- Measureable DOC coexists with ‘relatively high’ SO_4 in groundwaters to repository depth at Forsmark. ‘High’ DOC in groundwaters at Äspö/Laxemar coexists with SO_4 that increases with depth.

- The role of DOC in SO_4 reduction is ‘difficult to assess’.

- Methods are available to characterise DOC to a limited extent, *e.g.* 40% of DOC in groundwaters from Finnish bedrock (*e.g.* ONKALO at Olkiluoto) is humic/fulvic acids.

- Past studies at Äspö have confirmed the stability of humic compounds.

- DOC in natural waters consists of thousands of different compounds with varying molecular sizes. Enzymes capable of catalysing microbial breakdown of DOC are likely to be even more sparse because of their complexity. Together these properties imply low reactivity of DOC.

- SKB refers to only one characterisation of DOC in Forsmark groundwaters. The Göteborg microbiology lab report that the largest part of DOC comprises molecules of molecular weight <1000D.

- SKB gives a brief overview of text book information and make inferences about future microbial SO_4 reduction in a repository. Microbes thrive in chemical gradients, thus enhanced HS^- production will be likely during construction and operation. Key electron donors for SO_4 reduction are H_2 and acetate, and these need to be present at concentrations able to produce enough energy and ATP for cell growth. SRB and SO_4 occurrence will not necessarily produce HS^-.

- Calculation of available energy from measured SO_4, H_2 and acetate at Forsmark indicates that SO_4 occurs (for 48 mg/L SO_4) when H_2 is >0.1 µM or 10 nM<acetate<10 µM. At these conditions, free energy production by the reaction is <-30 kJ/mol.

- Measured levels of SO_4, H_2 and acetate are likely to limit production of HS^- to micromolar concentrations. This aspect of SO_4 reduction reduces the relevance of identifying DOC components (which would require method development).

On the second issue, AOM, SKB refers mostly to general literature and makes various inferences from sparse site-specific information:

- AOM occurs where methane-oxidising microbes produce H_2 or acetate as an intermediate which can then be used by SRB.

- AOM by this route is common in marine sediments in which both methanogens and methane-oxidising microbes are active (to produce and consume methane respectively) and, by implication, is also the route for HS^- production there.

- Energy production by AOM is at the limit for microbial viability. It is more favourable as methane and SO_4 concentrations rise. Methane contents in Forsmark groundwaters probably are too low for AOM. Energetics modelling indicates that SO_4 reduction and methane oxidation would only be concerted optimally for a low H_2 concentration, about 10^{-9} mol/L. Higher H_2 content would favour direct SO_4 reduction on its own.

- For AOM to occur, there has to be a feasible pathway for electron transfer between SRB and methane oxidisers. That could involve H_2 or acetate as intermediates.

- AOM in marine sediments tends to be optimised at the base of the SO_4 reduction zone where CH_4 diffuses upwards from the methanogenic zone.

- CH_4 in crystalline rock groundwaters in Finland is of both biogenic and abiogenic origins. At Olkiluoto, SO_4 contents decrease at 300 m depth, below which CH_4 contents increase. At 740 m depth, CH_4 contents have increased by more than x1000.

- CH_4 occurs in relatively much lower concentrations in crystalline rock groundwaters at Laxemar. It has a biogenic origin bur methanogenic bacteria are very sparse. $^{13}C/^{12}C$ isotope ratios of some fracture calcites (mainly between 350650 m depth) are very low, indicating strongly that AOM occurred here in the past. $^{18}O/^{16}O$ ratios of these calcites suggest that AOM was stimulated by ingress of SO_4-rich sea water in the past. Present SO_4 contents are too low for AOM to occur.

- CH_4 is also low in Forsmark groundwaters and is thought to have mixed biogenic-abiogenic origins. Methanogens are sparse but SRB and acetogens occur widely. $^{13}C/^{12}C$ in groundwaters does not show evidence of ongoing AOM. $^{13}C/^{12}C$ has been analysed in recent fracture calcites much less frequently than at Laxemar; none of the data indicate AOM in the past. Older fracture calcites (?Palaeozoic age) do show some evidence of AOM and are associated with traces of organic C as asphaltite which is inferred to have derived from overlying shale at that period.

- Possibility of AOM at Forsmark in the future cannot be ruled out but there is ‘no indication of it’ at present and evidence of it in the past is rare. AOM ‘should not be viewed as a common phenomenon in crystalline rock’.

SKB’s response to SSM’s request for complementary information is, in my opinion, a reasonably comprehensive and balanced account of what is known and what can be hypothesised about the roles of DOC and AOM in Forsmark groundwaters. It presents interpretations of data indicating the present state of the system and of data that are proxies for past processes. The interpretations are used to complement inferences based on generic and theoretical knowledge about the relevant biogeochemical reactions. Of particular significance are the thermodynamic calculations of the energetics of the half-reactions in relation to dissolved H_2 or acetate as the energy source. The energy that becomes available for microbial consortia as a function of H_2 concentrations is an indication of the viability of biogeochemical reactions. These calculations provide the most rigorous and compelling insight of the viabilities of sulphate reduction and AOM.

My comments on some aspects of detail in SKB’s response are:

- SKB relies to a large extent on Posiva’s characterisation of DOC in Olkiluoto groundwaters. SKB’s only site-specific information for DOC at Forsmark is the data for molecular size (*i.e.* mostly <1000D). As SKB admit, the significance of this for reactivity is not evident. Similarly, Posiva’s work indicating ~40% of DOC is humics and fulvics is not interpretable in terms of DOC reactivity. In the context of the importance of DOC, even in trace amounts, as the potential driver for redox in groundwaters at Forsmark, SKB have done remarkably little characterisation and research. SKB comment on the analytical development effort that would be required, but this is not a reason for doing so little about this significant issue.

- The single ^{14}C measurement in DOC from Forsmark is strong evidence of the low or zero reactivity. However SKB have not considered the suggestion that the humic fraction of DOC could facilitate SO_4 reduction by transferring electrons from otherwise-refractory organics (Lovely et al. 1996), as discussed in my assessment of biogeochemistry of sulphate reduction in Section 2.3.4 of this report.

- Despite the apparent importance of acetate as an intermediate in microbial SO_4 reduction (including the AOM pathway), SKB has not obtained reliable data for its occurrence in repository-depth groundwaters. Acetate is more effective than H_2 (as shown in SKB's Figure 1).

- The basis for SKB's semi-quantitative assertion that 'measured levels of SO_4, H_2 and acetate are likely to limit production of HS^- to micromolar concentrations' is not evident. Additionally, SKB have not measured acetate, as far as I know, and if they have done, the data are not included in their technical note. Therefore the rationale for the additional statement that 'this aspect of SO_4 reduction reduces the relevance of identifying DOC components' is also not evident. In my opinion, the relationship between DOC, its component compounds, and concentrations of acetate is an issue that justifies more research by SKB, although I appreciate the analytical and sampling challenges. It seems to be a worthwhile geoscientific research target with an existing background of relevant generic knowledge and methodologies.

- The other aspect of the discussions of SO_4 reduction including AOM that remains rather unsatisfactory is the interpretation of microbial data. In this case, SKB has acquired abundant data. In my opinion, the overall uncertainties in microbial population numbers are not well understood although I note that a few replicate analyses and other tests have been done. However, accepting that data are 'state-of-art' and representative, interpretations of the relative significance of lower or greater population densities of SRB or acetogens etc remain vague. What do the substantial variations of SRB populations throughout the Forsmark system and especially around repository depth indicate in terms SO_4 reduction? Can SRB numbers be interpreted quantitatively and do they indicate any meaningful variations of the propensity for SO_4 reduction? The only clues about this come from the observation of relatively higher SRB numbers at the interface between SO_4 and CH_4 domains in groundwaters at around 300 m depth at Olkiluoto.

- I agree, overall, that the balance of evidence points to AOM not being currently active at Forsmark. The most compelling evidence to support this conclusion comes from the energetics calculations in SKB's Figure 2. However SKB does not provide a full argument for why AOM should not be active in the observed Cl-SO_4 brackish water, derived from Littorina seawater. Clarity about that would help to constrain the probability of AOM in any similar marine influx in the future.

- Discussion of AOM tends to be blurred with regard to biogeochemistry of methanogenesis and methane oxidation. They are complementary in the sense that, if CH_4 is biogenetic, methane has to be produced before it is oxidised. However they involve contrasting microbial populations and redox conditions. SKB have not attempted to interpret variabilities of these two microbial populations and have not considered the potential significance of redox heterogeneity especially at repository depth.

In summary, my judgements about these issues are:

- I support SKB's general position and conclusion concerning the nature and availability of DOC. The ^{14}C(DOC) evidence is compelling but more data coupled with DOC characterisation in different parts of the groundwater system would give greater confidence. I consider that more could have been done to characterise the components of DOC and its availability to SRB. A large effort has been put into geomicrobiological characterisation and a similar research effort is also needed in understanding organic C (including acetate) geochemistry to confirm whether or not organic C variability is the key variable that facilitates or inhibits SO_4 reduction, and whether interaction of DOC with mineral-sourced Fe is another factor in the C-S-Fe biogeochemical cycle. Better understanding about organic C availability for microbial activity/growth will also be necessary as background for understanding potential impacts, *e.g.* on HS^- production, of introduced organic materials in the near field.

- I agree with SKB's conclusion about AOM, even though most of the evidence is circumstantial. As for normal SO_4 reduction, the energetics calculations are key to understanding reactivities and they rather side-line the immediate usefulness of microbial data. Significant uncertainty about AOM remains even for Olkiluoto groundwaters in which CH_4 concentrations are orders of magnitude higher, so the conclusion that AOM is at least insignificant at Forsmark, even if cannot be proven to be absent, is the most defensible. AOM in crystalline rock, *i.e.* in environments with such low DOC and low microbial activity, is a little-researched topic, so there is little more that SKB could do to clarify matters in the short term. Nevertheless further site-specific information about DOC, as above, and related sources of microbial energy, H_2 and especially acetate, would add to the knowledge base especially if carried out as a concerted comparison between Forsmark and Olkiluoto. Consideration of future evolution could be framed in terms of scenarios for these specific factors rather than in terms of a general process.

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