State of Science Review of Sulfide Production in Deep Geological Repositories for Used Nuclear Fuel

NWMO-TR-2021-18

November 2021

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ABSTRACT

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Abstract

The NWMO is planning to construct a Deep Geological Repository (DGR) for used nuclear fuel in stable crystalline or sedimentary host rock. The used nuclear fuel would be contained in copper-coated used fuel containers (UFCs) surrounded by highly compacted bentonite (HCB). While the copper-coating and bentonite are engineered to provide robust protection against many corrosion processes anticipated in the DGR, it is possible that sulfide produced by sulfate-reducing bacteria at the host rock-bentonite interface may transport through the bentonite and corrode the UFCs during the DGR design life (i.e., one million years), depending on the site. The objective of this document to provide an extensive review on sulfur cycle in deep subsurface and describe the geochemical and microbial processes that could impact the production and consumption of sulfide. The ultimate goal is to obtain an accurate sulfide flux to copper-coated container by incorporating the understanding of these processes to information from site-specific data as they become available.

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1. INTRODUCTION

The copper-coated used fuel container (UFC) is an important safety feature in the Canadian Deep Geological Repository (DGR) concept, owing to its stability against corrosion in the deoxygenated water that is expected to comprise the DGR environment. Within this system, reduced sulfide species such as bisulfide can interact with copper to cause corrosion. Equation (1-1) illustrates this reaction for bisulfide.

 $2Cu + HS^{-} + H_2O \to Cu_2S + H_2 + OH^{-}$ (1-1)

As per Equation (1-1), bisulfide is the predominant fully reduced groundwater sulfur species, but the more general term, "sulfide" is used throughout this text to account for the presence of all reduced sulfide species.

Although the sulfur atom itself does not undergo a redox reaction, it does catalyze the reduction of hydrogen and oxidation of copper, as the cuprous sulfide that forms (irreversibly) is a very stable species. The reaction of sulfide with copper is kinetically fast, and the rate of the reaction is dependent on the sulfide concentration and its flux toward the copper-coated container. At repository level, the amount of sulfide that can reach the container surface is known to result from various sources in the host rock, the backfill and the buffer. Sulfide is effectively immobilised by iron (Fe) to form insoluble iron sulfide compounds and, therefore, dissolved sulfide levels in a reducing environment are expected to be generally low. In zones favourable for sulfate reducing bacteria (SRB) activity, more elevated sulfide concentrations may be possible, often on a temporary basis. Therefore, the sulfate reduction and subsequent iron sulfide precipitation processes depend on geochemical conditions, microbial activity and mass transfer of the reactants, and are site- and design-specific. The overall objective of this document is to provide a thorough background of the sulfur cycle in a Canadian DGR system.

At this point, the Canadian program has yet to select a DGR site; thus the prediction of systemdependent processes affecting sulfide fluxes cannot be based on site-specific data. It's ideal to constrain sulfide fluxes from the groundwater and backfill porewater to the buffer and container in the emplacement rooms of a DGR. Alternatively, an attempt should be made to accurately estimate sulfide fluxes potentially generated by SRB from the sulfate inventories in the buffer materials. Previously, the NWMO supported the development of a 3D COMSOL Multiphysics model to predict the rate of sulfide diffusion from the host rock interface to the container and the resulting extent of corrosion (Briggs and Krol 2018). This model used the very conservative assumption of a constant 3 ppm sulfide concentration at the host rock interface, which needs to be refined on a site- and design-specific basis. Continued development and optimization of this model should include both microbial and geochemical processes. The purpose of this document is to provide additional information with regard to the sulfur cycle that can be incorporated in the transport models.

2. BACKGROUND: THE CANADIAN DEEP GEOLOGICAL REPOSITORY

Many countries using nuclear power for production of electricity, including Canada, are currently considering long-term disposal of their used nuclear fuel in a deep repository located in a suitable geological formation, such as crystalline rock or sedimentary rock. Geological disposal also relies on an engineered barrier system (EBS) to contain and isolate the radioactive wastes for a long period of time (i.e., one million years). In a Canadian DGR, the EBS includes coppercoated used fuel containers (UFC) surrounded by highly compacted bentonite (HCB) clay, that will be placed in emplacement rooms approximately 500 m underground in a low-permeability host rock formation that meets the technical and safety requirements for a DGR. The current NWMO UFC design has around 3 mm copper corrosion barrier directly bonded onto a strong inner container made of steel. Each UFC will be encased in a HCB clay buffer box, Figure 2-1. Once an emplacement room is full of loaded buffer boxes, remaining voids will be filled and sealed with a gap fill material (GFM) composed of granulated HCB. Bentonite is a lowpermeability clay that will swell when come to contact with groundwater, making it an excellent sealing material. The HCB and GFM are anticipated to be emplaced at around 1.7 and 1.4 a/cm³ dry density, respectively, and have been designed to fulfill several important functions (Dixon 2019). These functions include: i) limiting the rate of liquid movement to diffusion, ii) providing mechanical support to the container, iii) retaining radionuclides in the event of container failure, iv) providing a thermally conductive medium to transmit heat to the surrounding host rock, and v) protecting the container from microbiologically influenced corrosion (MIC) by inhibiting microbial activity. Before closure of the repository, all tunnels and shafts will be filled with similar backfills and sealants, isolating the repository from the environment. The performance of the repository will be monitored during placement operations and during an extended post-closure period.

Since 2010, the NWMO has been remain engaged in a multi-year, community-driven, site selection process to identify a site where Canada's used nuclear fuel can be safely contained and isolated in a DGR. The site selection process has a phased approach, which narrows the list of potential host communities based on a series of multidisciplinary studies that assess geoscientific suitability, engineering, transportation, environment, and safety, as well as social, economic, and cultural considerations. As of 2021, two Ontario communities remained in the siting process, Figure 2-2, one with a crystalline rock geology and the other with a sedimentary rock geology.

Since the NWMO does not presently have a single site, a set of nominal reference groundwaters has been developed that represent plausible site conditions. These reference groundwaters are representative compositions derived from a range of measurements and modified for internal composition consistency. The groundwaters also cover the two potential host rock types that are of interest: crystalline rock, largely found on the Canadian Shield, and sedimentary rocks, such as those found in the Michigan basin in the southern Ontario.



Figure 2-1: Conceptual illustration of multi barrier system in a deep geological repository in crystalline geosphere.



Figure 2-2: A map that shows the two remaining communities in the NWMO siting process.

3. THE GEOCHEMISTRY OF THE CANADIAN DEEP GROUNDWATER SYSTEM

3.1 INTRODUCTION

The geochemistry of deep groundwater is determined mainly by two factors, i.e., the origin of the groundwater and the in-situ water-rock interactions that follow.

In crystalline rocks, the primary fluids exsolved from their parent magmas were lost mostly during cooling except minute amounts that were retained in fluid inclusions in minerals. Secondary hydrothermal fluids associated with later tectonic activities possibly could have been sealed in hydrothermal minerals such as calcite (Bottomley 1987), precipitated in some fracture systems. Subsequently, these fracture systems could have been reactivated/opened by more recent seismic activities related to the release of stress built up over time. These hydrothermal fluids (if any were preserved) could have been highly diluted by subsequent surface water ingress (Bottomley and Veizer 1992). As a result, the current groundwater in crystalline rocks is mainly secondary, and was mostly generated from ancient meteoric water, which infiltrated into the rocks along faults and fractures (Frape et al. 1984).

In sedimentary rocks, particularly those formed in paleo-ocean basins, ancient seawater could have been trapped in the pore spaces and contribute to the current groundwater (Skuce et al. 2015). In addition, the sedimentary groundwater system could have been affected by hydrothermal fluids associated with later local or regional tectonic activities (if there were any). The geochemical features of the current groundwaters in these two types of lithologies are discussed below.

3.2 TOTAL DISSOLVED SOLIDS

In crystalline rocks, the total dissolved solids (TDS) concentration in initial infiltration water would have been low. However, subsequent fluid-rock interaction would have leached cations and anions from the host rocks into the water and consequently increased the TDS (Frape et al. 1984). The magnitude of the TDS increase is dependent on the reaction time and lithology (Frape et al. 2004). The residence time of the groundwaters in the Precambrian cratons can vary from hundreds of thousands of years to hundreds of millions of years, e.g., in the Witwatersrand Basin in South Africa (Heard et al. 2018; Lippmann et al. 2003), and even to billions of years, e.g., in the Canadian Shield (Holland et al. 2013; Warr et al. 2018). Water-rock interaction over such long time periods would have extracted significant amounts of cations and anions from rock-constituting minerals to the groundwater. More specifically, in granitic rocks, Ca²⁺, Na⁺, K⁺, and Cl⁻ can be progressively enriched in groundwater as observed in leaching experiments (Chae et al. 2006). This process will elevate the TDS of the groundwater continuously until saturation is reached eventually, if time allows.

In sedimentary rock systems such as limestones, the groundwater and the limestone are likely in chemical equilibrium if the groundwater originated from ancient (evaporated) seawater from which the limestone was precipitated. Further fluid-rock interaction may not change the geochemical signature significantly. However, if the groundwater originated from sources other than seawater, such as later hydrothermal fluid and/or meteoric water, interaction with the limestone can somewhat shift the original geochemical signature of the water. For example, dissolution of carbonate minerals and syn-deposited salts in limestone can increase the Ca²⁺,

 Mg^{2+} , Na^+ , K^+ , as well as SO_4^{2-} and HCO_3^- concentrations in groundwater (Lamar and Shorde 1953).

The TDS in groundwaters can vary significantly with depth in both crystalline and sedimentary rocks. A general trend that has been observed repeatedly is that the groundwaters at shallow depths are mostly fresh water, but subsequently evolve to brackish water and to saline to hypersaline waters with greater depths (Hobbs et al. 2011). This is because the groundwaters in the deep subsurface have been isolated for long times, whereas those at shallow depths have received recharge from surface fresh water more recently.

Reference groundwater compositions have been developed by the NWMO for crystalline and sedimentary systems in advance of site-specific information. For crystalline groundwater the primary reference groundwater is CR-10, which has been used for many investigations, and was the reference for the most recent safety assessment of a generic crystalline site (NWMO 2017). The situation for sedimentary groundwater is more complex. The reference groundwater known as SR-270 was used for the most recent generic sedimentary site safety assessment (NWMO 2018a) Table 3-1 provides a comparison of the major cations and anions between CR-10 and SR-270 reference waters and seawater.

The TDS data of the reference crystalline rock groundwater, CR-10, which was based on the composition of groundwater from a depth of 500 m in granitic rocks of the Canadian Shield, is ~11 g/L (Table 3-1). This number is significantly higher than the value in surface fresh water. The ratios of major cations (Table 3-1) over chloride in the CR-10 groundwater exclude diluted seawater as a source. The relatively high TDS number of CR-10 is more likely a result of groundwater-granite interaction over a considerable time period, although the possible influence of later hydrothermal fluids cannot be excluded completely.

The TDS of the reference sedimentary rock groundwater, SR-270, which was based on the composition of groundwater from a depth of 500 m in limestone of the Ordovician Cobourg Formation at the Bruce nuclear site in Ontario, is ~276 g/L (Table 3-1). This value is toward the upper end of the TDS range of 150 - 360 g/L for the groundwaters recovered from a number of OPG DGR boreholes in the Cobourg limestone (NWMO 2011).

More recently a revised reference composition known as SR-290 was developed based on subsequent data. Chemical differences between SR-270 and SR-290 are generally small. However, notable for the present report is the range in Fe concentrations – about 30 mg/L in SR-270 and 5 mg/L in SR-290. While analyses in this report are based on SR-270, some discussion is provided about the range. Upon selection of a single site, which is expected to occur within this decade, a site-specific groundwater condition will be defined, and some information contained within this report may require updating.

	CR-10	SR-270	Modern Seawater
рН	7.0	6.3	8.2
Eh (mV)	-200	-200	~+400
Ionic strength (mol/kgw)	5.78	5.88	
Na (mg/L)	1900	50,025	10,556
K (mg/L)	15	12,486	280
Ca (mg/L)	2130	32,494	400
Mg (mg/L)	60	8,173	1,272
Fe (mg/L)	1	30	< 0.03
CI (mg/L)	6100	168,058	18,980
SO ₄ (mg/L)	1000	1,784	2,700
HCO ₃ (mg/L)	70	135	
TDS (mg/L)	11300	276,184	
Na/CI (x10)	3.1	3.0	5.6
K/CI (x100)	0.2	7.4	14.8
Ca/Cl (x10)	3.5	1.9	0.2
Mg/CI (x100)	0.98	4.9	6.7
Fe/Cl (x10 ⁶)	163	179	<2
SO ₄ /Cl (x10)	1.6	0.1	1.4

Table 3-1 Comparison of major cations and anions between the two reference groundwaters and seawater (NWMO 2018b, 2016).

The major cations and anions on a Piper diagram (Figure 3-1) indicate that the CR-10 groundwater is a Na-Ca-SO₄-Cl type water. This is consistent with the occurrence of intensive water-rock interaction (Velde and Meunier 2008). Within granitic host rocks, Na and Ca can be enriched from dissolution of plagioclase; Cl can be enriched from dissolution of biotite and apatite (Nordstrom et al. 1989); and sulfate can be derived from oxidation of sulfide minerals (Nordstrom 2011). The pH has not been lowered significantly by sulfide oxidation, which would have produced pronounced amounts of H⁺ (see Equations 3-1 in section 3.4). This may be attributed to a balanced consumption of H⁺ by weathering of granite to precipitate clay minerals such as kaolinite (Velde and Meunier 2008; Papoulis et al. 2004).

The SR-270 groundwater is also Na-Ca-SO₄-Cl type groundwater (Figure 3-1). The lower end of the TDS range of groundwaters in limestone appears very similar to that of seawater. However, seawater (or diluted seawater) solely cannot account for the geochemical properties of the SR-270 groundwater. If the groundwater was sourced purely from ancient seawater (or diluted seawater), the Na/Cl and K/Cl rations, which would not be influenced significantly by interaction with the host limestone, should be similar to the seawater values. In fact, these two ratios in SR-270 groundwater are about half of those of seawater (Table 3-1), suggesting that the SR-270 groundwater contains significant contributions from a source that is more enriched in Cl but more depleted in Na and K. A compilation of δ^2 H and δ^{18} O values in the porewater from the same level in a number of other boreholes in the Geosynthesis (NWMO 2011) shows that the porewaters in the Cobourg Formation display obvious ¹⁸O depletion (-8‰ to -3‰) relative to seawater (~0‰), which also indicates that a second water source has contributed to the groundwater in the Cobourg limestones. This is supported further by Sr isotope evidence, i.e., more radiogenic Sr in the groundwater than in seawater (NWMO 2011). Interestingly, based on analysis of O and Sr isotopes and fluid inclusions of the host limestone, Tortola et al. (2020)

found that the Silurian and Devonian carbonate rocks above the Cobourg limestone had been affected by different types of later diagenetic fluid, including some fluids characterized by negative δ^{18} O and more radiogenic Sr. If the Ordovician carbonate also experienced such later diagenetic fluids, they could account for the second water component in the SR-270 groundwater.



Figure 3-1: Piper diagram showing that CR-10 and SR-270 groundwaters are both Na-Ca-SO₄-CI type.

3.3 pH, AND REDOX CONDITIONS

The pH and redox conditions of groundwaters also can be influenced strongly by several types of water-rock interactions. With respect to the pH, oxidation of sulfide can produce hydrogen ions and decrease the pH significantly; whereas radiolysis of water, carbon dioxide reduction, sulfate reduction by sulfate-reducing bacteria, and alteration of silicate minerals (e.g., feldspars) in granite to clay minerals (e.g., kaolinite) all consume hydrogen ions and thus increase the pH.

In terms of redox conditions, reactions such as oxidative weathering of sulfide minerals, radiolysis of water, reaction of water with Fe(II)-bearing minerals, and decomposition of organic matter by microorganisms, can either consume oxygen or produce hydrogen, and thus promote reducing conditions. In contrast, reduction of some components in the groundwater, such as carbon dioxide, nitrate and sulfate (by microorganisms) can consume hydrogen and thus decrease the reducing capacity of the groundwater. In most cases, water-rock interactions tend to push the redox condition of groundwater to more reducing conditions. Only rocks containing abundant strong oxidants, such as hematite, may be able to maintain oxic conditions in their groundwater over long time periods through water-rock interaction.

The redox conditions of the reference groundwaters CR-10 and SR-270 are both reducing, indicating effective removal of original oxygen in these systems, which in turn implies insufficient recharge of surface oxic water and/or fast consumption of oxygen by microorganisms and relatively long residence times in these groundwaters. The pH of groundwater CR-10 is near neutral (Table 3-1), which is consistent with a rainwater origin (pH = 5-8) with or without slight modification by water-rock interactions. The pH of groundwater SR-270 is also near neutral, at 6.3. This value is lower than the expected original value of ~8.3 for a groundwater that is in equilibrium with limestone and air, and it is also at the lower end of the carbonate buffer system. Two possibilities could have caused a pH shift. The first is that the second water component in SR-270 had a low pH value. However, if this low-pH fluid was introduced into the Cobourg Formation episodically hundreds of million years ago, the subsequent long-time interaction with limestone should have been able to consume the hydrogen ions and elevate the pH to the equilibrium value around 8. Alternatively, another explanation is that some *in situ* process(es) can produce hydrogen ions continuously and at a sufficiently high rate to maintain the pH at a disequilibrium level.

Oxidation of sulfide minerals has been postulated as the most likely process to account for this. Oxidation of sulfide minerals can occur even under anaerobic conditions (Li et al. 2016). Interestingly, the sulfate in the SR-270 water (Table 3-1) does not appear to be enriched as expected. Even taking into account the fact that the Paleozoic seawater sulfate could be half of the modern seawater sulfate (Algeo et al. 2015), the SO₄/CI ratio is only slightly higher than the expected value (Table 3-1). This may suggest that sulfate reduction (by microorganisms) also is occurring in the system, indicating a complicated sulfur cycle in the Cobourg Formation. Because of the neutral to slightly acidic conditions of these waters, the reduced sulfur species in these waters are dominated by H_2S and HS^- according to Henry's Law (Figure 3-2 and Figure 3-3).

3.4 DISSOLVED GASES

The gas components in deep groundwater also are dependent on water source(s) and fluid-rock interactions. In addition, microbial activity also may play an important role in gas production in deep groundwater systems. When the groundwater was first formed by infiltration of surface water (either ancient meteoric water or seawater), the major gas components should have been dominated by air (e.g., N₂, O₂, Ar, CO₂). Once the groundwater was isolated from air, a variety of chemical, geological and biological processes might have occurred that consumed some of the active gas components (e.g., O_2 , CO_2) and produce new gases (e.g., H_2 , CH_4 , other alkanes and noble gases) (Strobel et al. 2020; Diomidis et al. 2016). These processes are reviewed below:

(1) Oxidative weathering of sulfide

In the presence of O_2 , sulfide minerals can be oxidized into sulfate, at the expense of O_2 . Taking pyrite as an example, the oxidation reaction can be described by the following equations (Jacques et al. 2016):

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
 (3-1)

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \to Fe^{3+} + \frac{1}{2}H_2O$$
 (3-2)

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

Oxidative weathering of sulfide minerals may or may not involve microbes. In general, the microbial oxidation of sulfide is believed to be much faster than abiotic sulfide oxidation (Gleisner et al. 2006); although the net reactions shown above as Equations (3-1) - (3-3) would be the same.

(2) Radioactive decay

The decay chains of several radionuclides in rocks, such as 235 U, 238 U and 232 Th, include several steps of α decays. As a result, helium gas can be an important gas component in the deep subsurface groundwater systems. Radioactive decay of elements in the host rocks also produces other noble gases, such as Ar, Ne, Xe, Kr (Warr et al. 2018). These noble gases, although in trace amounts in most cases, are important components that can provide key information about sources and residence time of the groundwater, particularly when isotopic analysis is used.

(3) Radiolysis of water

The high energy particles released from the decay of radionuclides in rocks (e.g., 235 U, 238 U, 232 Th and 40 K) can induce radiolysis of water which produces H[•] and OH[•] radicals. The H[•] radicals can combine together to form H₂ (Lin et al. 2005; Sherwood Lollar et al. 2014; Li et al. 2016), while the oxidizing OH[•] radicals may form O₂. Both can be consumed by other redox reactions, such as oxidation of sulfide (see Equation 5.1 in section 5.1) and other reducing components (e.g., H₂, Fe²⁺, CH₄, organics) dissolved in the reducing groundwaters.

(4) Serpentinization

Minerals in mafic and ultramafic rocks are not stable at low pressure and lowtemperature conditions in the shallow crust. When groundwater is in contact with mafic and ultramafic rocks, reactions can occur between H_2O and the Fe^{2+} and Mg^{2+} -rich minerals (such as olivine and orthopyroxenes) to produce a variety of secondary minerals, among which an ubiquitous one is serpentine. During this serpentinization process, ferrous iron in these minerals can react with H_2O to produce H_2 , which contributes the majority part of the H_2 observed in the global Precambrian cratons (Sherwood Lollar et al. 2014).

(5) Abiotic synthesis of hydrocarbons

The strong reducing reagents (e.g., H_2 , Fe^{2+}) in the groundwater system can reduce CO_2 (or HCO_3^- , CO_3^{2-}) into CH_4 . This reaction can be driven by water-rock interactions in the deep subsurface groundwater system (Sherwood Lollar et al. 1993b), and enhanced by the presence of radiolytically produced strong reducers (i.e. radicals). Further reaction between CH_4 molecules can synthesize higher-carbon-number alkanes, such as ethane, propane, butane, propane (Sherwood Lollar et al. 2002). In shallower groundwaters, CO_2 reduction to CH_4 is carried out by microorganisms (methanogens-see below).

(6) Microbial methanogenesis

Some microorganisms can use dissolved inorganic carbon or small organic compounds for their metabolism to produce methane as a byproduct. There are two major pathways for microbial methanogenesis. One is through CO₂ reduction with

hydrogen (Equation 3-4) and the other is through fermentation of organic compounds (e.g., acetic acid, formate; Equation 3-5).

$$CO_2 + 2H_2 \to CH_4 + 2H_2O$$
 (3-4)

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{3-5}$$

Sherwood Lollar et al. (1993a, b) have reported both biotic and abiotic hydrocarbons in the subsurface groundwaters in the Canadian Shield. The relative contributions from biotic and abiotic processes in groundwaters are also depth-dependent. At shallower depths where the groundwaters are less saline and microbial activity is abundant, hydrocarbons from a biotic origin are dominant; whereas in the deeper, more saline, and lower-energy groundwaters where microbial biomass is low, hydrocarbons from an abiotic origin are dominant (Sherwood Lollar et al. 1993a, b).

(7) Thermal decomposition of organic matter and minerals in rock

Sedimentary rocks often contain some organic matter, particularly shale beds and igneous rocks often contain some secondary minerals formed by low-temperature alteration over their evolution history. This organic matter and these secondary minerals contain abundant volatile elements, such as carbon, nitrogen, and sulfur. Upon burial and heating of these rocks as a result of tectonic activity over their evolution history, the organic matter and low-temperature secondary minerals can decompose and release gases such as N_2/NH_3 , CO_2/CH_4 , depending on the redox conditions of the system.

(8) Methanotrophic reaction

Microorganisms that use methane for their metabolisms also can occur in deep subsurface groundwater systems (Bowman et al. 1993). These microorganisms use either oxygen (if available) or form consortia by coupling with nitrate-reducing bacteria and/or SRB. The effect of these microbial activities on the gaseous components is to reduce the contents of CH_4 (and O_2) but increase the contents of CO_2 and N_2/N_2O or sometimes H_2S . The reactions of these pathways can be described by the following equations:

$$CH_4 + 2O_2 \to CO_2 + 2H_2O$$
 (3-6)

$$CH_4 + SO_4^{2-} \to CO_2 + HS^- + OH^- + H_2O$$

(3-7)

(9) H₂S dissolution/degassing

 H_2S gas is often a minor component in the gas phase in equilibrium with deep groundwaters. While to our knowledge, no significant H_2S gas contents have been reported for deep groundwater systems, it is an important component in the study of the sulfur cycle in such systems (Section 5.1 and Figure 5-1).

 H_2S levels in the gas phase can be affected by several factors. Figure 3-2 illustrates Henry's law constant for dissolution of H_2S in water. It shows that, in the temperature range of 0-50 °C, which most of the groundwaters for this study would fall into, the partition of H_2S into the gas phase increases with elevated temperature and salinity (as expressed by the ion strength of the water; Figure 3-2). In groundwater, aqueous

 H_2S is a weak acid and can be dissociated into HS^- and S^{2-} ions according to Equations 3-8 and 3-9, which constrains its ability to degas:

$$H_2S(aq) \rightleftharpoons HS^- + H^+$$

$$HS^- \leftrightarrows S^{2-} + H^+$$
(3-8)
(3-9)

The dissociation constants of these two reactions depend strongly on water pH, and can be affected by temperature as well (Barbero et al. 1982; Phillips and Phillips 2000). Based on the temperature-dependent dissociation constants for H₂S (Barbero et al. 1982; Phillips and Phillips 2000) and H₂O (Marshall and Franck 1981), the fraction of aqueous H₂S over the sum of the total dissolved sulfide species (H₂S + HS⁻ + S²⁻) is illustrated in Figure 3-3. This diagram shows that the fraction of dissolved H₂S cannot be ignored until pH > 9.

The relative contributions of these individual processes to the gas composition in subsurface groundwaters may vary significantly in different systems, depending on their detailed lithological and geochemical properties. For example, the concentrations of radioactive elements are relatively higher in granitic rocks than in limestones. Consequently, processes 2 (radioactive decay) and 3 (radiolysis of water) may play more important roles in a granitic system than a limestone system. In addition, granitic rocks contain some minerals (e.g., biotite) that have ferrous iron in their mineral structures, which can cause reduction reactions to proceed, whereas limestone generally does not contain high Fe²⁺ concentrations, unless pyrite and/or siderite are present. In contrast, limestones may contain organic matter, and thus decomposition processes may play a more important role in controlling the gas composition in equilibrium with the groundwater in limestones. The sulfide oxidation process depends strongly on the redox condition and the concentration of sulfide minerals in the host rocks, which can vary significantly in both granites and limestones. The microbial processes are more unpredictable depending on the presence/absence of relevant microbes in the groundwater systems. In general, the serpentinization process is not facilitated in either granites or limestones due to the lack of Fe- and Mg-rich silicate minerals in these rocks. However, if maficultramafic rocks exist in a close location, H₂ produced in those rocks by the serpentinization process possibly can migrate along faults and/or permeable zones to the groundwaters in granites or limestones, depending on the permeability and the occurrence of faults/fractures in the host rocks.

Sherwood Lollar et al. (1994) studied the gases in the groundwaters in Southwestern Ontario at a regional scale in an area around the Bruce nuclear site. Their results showed that the gases were dominated by hydrocarbons (>90%) with >5% N₂ and a small amount of CO₂, and very low H₂ content. Carbon and hydrogen isotope compositions of these hydrocarbons indicated that the gases were mainly thermogenic in origin at a regional scale (Sherwood Lollar et al. 1994).



Figure 3-2: The Henry's law constant between gaseous H_2S (unit: bar) and aqueous H_2S (unit: molarity) at temperatures from 0-50 °C for waters with various salinity. The salinity of water is expressed by the ionic strength μ ; pure water $\mu = 0$. Data source: (Suleimenov and Krupp 1994).



Figure 3-3: Fraction of H₂S in total dissolved reduced sulfur species (H₂S + HS⁻ + S²⁻) relative to pH values at temperatures from 10-50 °C. The numbers on the dashed lines labels the temperature of each line. The read solid line highlights the case of 25 °C. The ion product constants Ka1 (Equation 3-8) and Ka2 for H₂S dissociation (Equation 3-8) and Kw of water used for the calculations at these temperatures were from Barbero et al. (1982); Phillips and Phillips (2000); Marshall and Franck (1981).

4. MICROBIOLOGY IN DEEP TERRESTRIAL SUBSURFACE GROUNDWATER SYSTEMS

4.1 INTRODUCTION

Microorganisms have been reported in numerous studies to exist widely in continental subsurface groundwaters. A recent compilation of global data (Magnabosco et al. 2018) indicated that, although no obvious dependence of cell abundance on lithology, ionic strength, pH or dissolved organic carbon was observed, cell concentrations generally decrease with an increase in depth. However, Magnabosco et al. (2018) found that the composition of subsurface microbial communities showed statistically significant correlations with lithology. At individual sites, microbial community composition is more affected by environmental parameters (e.g., temperature, redox condition).

There are many terrestrial underground sites around the planet that have been explored in the general scientific study of subsurface microbiology, i.e., boreholes, mines, caves and tunnels. In addition, researchers with a focus on geologic disposal of nuclear waste have taken advantage of dedicated Underground Research Laboratories (URLs) in their study of subterranean microbiology and its potential effect on the performance of a DGR. A table with a summary of those URLs dedicated to research for the development of radioactive waste disposal, where microbiological studies have been carried out, can be found in Appendix A1 of this report. This table includes information on the observation of sulfide producing microorganisms in various URLs.

Microbial processes comprise the decomposition and production of organic molecules with various electron donors, energy sources, and electron acceptors. Organic carbon, including methane, and reduced inorganic molecules, including H_2 , are possible electron donors and energy sources for microbial processes in deep groundwater systems. During the microbial oxidation of these energy sources, microorganisms preferentially reduce electron acceptors in a particular order. First oxygen, and thereafter nitrate, manganese, iron, sulfate, sulfur, and carbon dioxide are reduced. Simultaneously, fermentative processes supply the metabolizing microorganisms with, for example, H₂ and short-chain organic acids such as acetate. As the solubility of oxygen in water is low, and because oxygen is the preferred electron acceptor of many bacteria that utilize organic compounds in shallow groundwater, anaerobic environments and processes usually dominate at depth in the subterranean environment. The reduction of microbial electron acceptors may alter the groundwater composition significantly and influence fracture minerals. Dissolved nitrate is reduced to dinitrogen and nitrogen dioxide, both of which dissolve in groundwater, solid manganese and iron oxides in fracture minerals are reduced to dissolved species, and the sulfur in sulfate is reduced to sulfide. In addition, the metabolic processes of some autotrophic microorganisms produce organic carbon, such as acetate, from the inorganic gases carbon dioxide and H₂, while other microorganisms produce methane from these gases. All microbial processes generally lower the redox potential.

4.2 GROWTH

Growth is defined as a microbial process in which a coordinated increase in the mass of essential cell components leads to cell division and an increase in the number of cells. The content of solid and dissolved organic material can be influenced by growing microbes because, during growth, microorganisms oxidize various organic and inorganic energy sources. The harvested energy is used to synthesize new cell components, such as cell walls, proteins, fat, carbohydrates, and nucleic acids. The microorganisms produce organic molecules that can be expelled to the environment, for example, as chelating agents for trace elements needed for growth and as polymers enhancing attachment and biofilm formation. During growth, many microorganisms excrete waste products such as alcohols, organic acids, and carbon dioxide.

4.3 RESPIRATION

Respiration must proceed in all active microorganisms, except those running a fermentative metabolism. Respiration is a membrane-bound process in which electrons from metabolic, dissimilatory, oxidative processes are expelled from the cell via the reduction of various electron acceptors. The electron donors to the metabolic processes can be either organic compounds or inorganic, reduced molecules. Respiration may influence the groundwater composition, gas composition, and fracture minerals. This is because the process of respiration changes the oxidation state of the electron acceptor. Microorganisms will contribute to the removal of oxygen that intrudes with groundwater and the process of oxygen respiration in shallow groundwater explains why most deep groundwater systems are anaerobic.

In anaerobic systems, nitrate is the preferred electron acceptor in microbial respiration. The main sustainable source of nitrate in groundwater originates from surface ecosystems, in particular, from soil fertilizers. Oxygen is rapidly removed by microbial respiration processes in shallow, infiltrating groundwater. When oxygen is used up, nitrate will be reduced. Most deep groundwater systems are consequently depleted not only in oxygen but also in nitrate.

Solids containing iron(III) and manganese(IV) oxides, such as some fracture minerals, can serve as electron acceptors in microbial respiratory processes. In this process, the state of aggregation is changed from solid to dissolved, and fracture minerals and groundwater composition can be influenced. Microorganisms can dissolve solid fracture metal oxides either by direct contact or by remotely operating chelating agents and nanowires.

In many oxygen- and nitrate-depleted systems, sulfate becomes the preferred electron acceptor for microbial respiration. Sulfate is a dissolved species that is reduced to the gas hydrogen sulfide. This gas dissolves readily in water with a significant dependence on pH. The reductant can be organic carbon, H₂ or methane. Sulfate reduction mainly affects redox potential. Several types of microorganisms can reduce elemental sulfur to sulfide. The biological nature of sulfate reduction in natural and engineered systems has been investigated thoroughly and the process is ubiquitous in most anaerobic aquatic systems with temperatures below 110 °C.

4.4 AEROBES AND FACULTATIVE AEROBES

Aerobes live on O_2 , and facultative aerobes favor O_2 but can live without O_2 . These groups mostly thrive in relatively shallow fresh groundwaters where the water is oxic and O_2 is readily available. Since O_2 is a strong oxidant and an energy-effective electron acceptor for microbial

metabolism, the near-surface shallow groundwater environment provides favorable conditions for a variety of microorganisms that rely on energy from aerobic oxidation of organic and inorganic substances in groundwater as well as minerals in host rocks. During future construction and operation of a DGR, the initially reducing environment of the host rock would be disturbed and it will take time after repository closure for the DGR environment to return to its rock-buffered anaerobic state (McKelvie et al. 2016). A case study in the Swedish Äspö Hard Rock Laboratory (Banwart et al. 1996) suggested that, when a deep groundwater system is disturbed by intrusion of shallow water from new openings (e.g., created by natural pressure release or by drilling), aerobes can invade and thrive. These aerobes promote the consumption of O₂ and accelerate the process for the deep groundwater to return to its reducing state.

Obligate aerobic and facultative aerobic microbial communities may include:

- (1) Anaerobic fermenters: in the absence of O₂, organic compounds in groundwater can be used by facultative anaerobes via fermentation processes that produce intermediate products (such as short-chin fatty acids) that maybe broken down further by other microorganisms.
- (2) Methanotrophs: the presence of methane in the groundwater, either produced *in situ* or migrated in from deeper groundwater, facilitates the thriving of methane-oxidizing bacteria, which oxidize methane into CO_2 with O_2 (see Equation 3-6).
- (3) Nitrifying bacteria: these bacteria can use ammonia/ammonium (i.e., ammoniaoxidizing bacteria) or use nitrite (i.e., nitrite-oxidizing bacteria) in the water to produce nitrate.
- (4) Sulfide-oxidizing bacteria: these bacteria can oxidize either dissolved sulfide in water (chemotrophic) or sulfide minerals in the host rock (thus chemolithotrophic) to produce sulfate (e.g., see Equation 3-1). The existence of sulfide oxidizing bacteria (if there are any) can, therefore, limit the accumulation of dissolved sulfide in the groundwater.
- (5) Iron-oxidizing bacteria: in most near-surface oxic environments, iron is a limiting electron acceptor, and thus iron-oxidizing bacteria are not abundant. However, iron content can be rich in subsurface groundwaters (Chapter 5, section 5.4). Once O₂ is introduced into these ferrous iron-rich systems, iron-oxidizing bacteria can proliferate and oxidize ferrous iron into ferric iron; the latter has a much lower solubility in neutral to alkaline water and would be precipitated as Fe(OH)₃. The metabolisms of these microbes can have significant impact on the chemical compositions of both dissolved and gaseous components.

4.5 ANAEROBES, SULFATE REDUCING BACTERIA AND METHANOGENS

Anaerobes reduce inorganic substances (other than O₂) for energy, such as nitrate, iron, manganese, sulfate and CO₂ (in descending order of energy yield).

Sulfate reducing bacteria (SRB) contain a wide range of genera that can be present but inactive in aerobic but more significant in anaerobic environments. Sulfate reduction can in fact occur in both bacteria and archaea. The sulfate reduction pathways fall into two main categories: assimilatory and dissimilatory. Assimilatory sulfate reduction uses sulfate to produce cysteine as an end product, whereas dissimilatory sulfate reduction can use a large portion of sulfate to produce sulfide as an end product. Dissimilatory sulfate reduction occurs widely in subsurface reducing groundwaters and can involve the oxidation of a variety of inorganic and organic components. In long-isolated deep subsurface groundwaters, reducing gases such as H₂ and

CH₄ are often present (Sherwood Lollar et al. 2002, 2014). Thus, H₂ is generally preferentially used as an energy-efficient electron donor.

$$SO_4^{2-} + 4H_2 \to HS^- + 0H^- + 3H_2O$$
 (4-1)

In the absence of H₂ but in the presence of CH₄, SRB can use CH₄ as the main electron donor. These SRB commonly live closely together with anaerobic methanotrophic archaea to form a syntrophic consortium (Hinrichs et al. 1999), and react according to Equation (3-7). A variety of organic compounds also can support the metabolism of SRB. These organic compounds are mostly short-chain organic molecules, such as alcohols (methanol, ethanol, propanol) and organic acids (e.g., acetate, formate, lactate, propanoate) (Simkus et al. 2016; Kieft et al. 2018).

During the sulfate reduction process, microorganisms preferentially use the lighter sulfur isotopes. This is known as kinetic isotopic fractionation and the magnitude of this process can be affected by both metabolic pathways and sulfate availability. For example, assimilatory sulfate reduction generally shows a small isotopic fractionation of less than 5‰ (Patron et al. 2008), whereas dissimilatory sulfate reduction shows much more variable and larger isotope fractionation, up to 70‰ (Stroes-Gascoyne et al. 2011b). Habicht et al. also found that sulfate content could play an important role in regulating sulfur isotope fractionation associated with SRB (Habicht et al. 2002). When the sulfate content in the water is less than 100 μ M, the magnitude of sulfur isotope fractionation could be diminished significantly (Detmers et al. 2001).

Methanogens comprise a large group of archaea. They are widespread in anaerobic environments with large ranges in temperature, pH and salinity conditions. Methanogens can use H₂ and a number of relatively simple organic compounds (e.g., acetate, formate, alcohol) for their metabolism. Depending on the compounds a methanogen uses, the metabolic pathway is different. When H₂ is used as electron donor, dissolved inorganic carbon (CO₂/HCO₃^{-/}CO₃²⁻) would be the electron acceptor, a process referred to as the CO₂ reduction pathway (Equation 3-4); when an organic compound is used, the process is referred to as the fermentation pathway (see Equation 3-5). Although both pathways are mediated by microorganisms, each generates different isotopic features in the carbon and hydrogen, and thus gives distinct isotopic signatures in the end product methane. As a result, the combined isotopic analysis of the carbon and hydrogen in methane can be used as a robust tool to distinguish between methane produced from these two pathways (Whiticar et al. 1986). For example, some samples of ground- and porewater from sedimentary rock in the Michigan basin show evidence of methane with mixed biogenic and thermogenic ¹³C signatures (Jautzy et al. 2021; Clark et al. 2015)

4.6 FUNGI

Information on fungi in terrestrial deep subsurface groundwaters is relatively scarce. An older and some recent studies have discovered fungi in the terrestrial subsurface, particularly in fracture waters in crystalline rocks (Ekendahl et al. 2003b; Sohlberg et al. 2015; Drake et al. 2017). These studies identified a large number of fungal classes and the ubiquitous presence and large diversity of fungi in the deep subsurface was somewhat unexpected. A better understanding of fungal behavior in terrestrial deep subsurface groundwaters is only now emerging. The recent study by Drake et al. showed that fungi can be active in anaerobic environments, using carbohydrates for their metabolism to produce H₂, CO₂ and organic compounds (e.g., acetate, formate, lactate) as waste (Drake et al. 2017). Fungi also can form consortia with SRB and/or methanogenic archaea.

One notable consequence of fungal activity in highly fractured regions of deep subsurface environments is extensive weathering of clay minerals in crystalline rocks (Drake et al. 2017). This observation was accompanied by the presence of pyrite, which was assumed to be due to an enhancement of SRB activity within this fractured rock region. In principle, the coupling of the anaerobic fungi respiration (which produces H₂) and the sulfate reduction (which consumes H₂) could create an environment in the far-field that enhances the concentration of sulfide. It was speculated that such an environment could cause increased corrosion of the copper canisters in a DGR (Drake et al. 2017); although the authors did not speculate the level to which this process could be enhanced. Within NWMO microbiology studies no fungal signatures in bentonite has been detected to date. The ongoing work will keep targeting fungi more explicitly by using metagenomic and targeted PCR analysis of subsurface samples from the two potential siting areas. Should they be detected, complementary data including DNA and PLFDA will be obtained to decide whether fungi are significant members of the overall community.

4.7 ENVIRONMENTAL FACTORS CONTROLLING MICROBIAL ACTIVITY

There are several environmental factors that control microbial activity in the deep subsurface.

4.7.1 Temperature

Environmental temperature profoundly affects bacteria, like all other microorganisms. Bacteria are particularly susceptible because they are unicellular and poikilotherm – their temperature varies with that of the external environment. The growth rate of bacteria has been estimated to roughly double for every 10 °C rise in temperature (Ratkowsky et al. 1982). However, beyond a species-specific upper temperature limit, a further increase in temperature will damage the cells by denaturing enzymes, transport carriers and other proteins and finally growth is inhibited because the damages occur faster than they can be repaired. Each bacterium has a minimum, optimum and maximum temperature that defines its temperature range. Except for a very few species of extremophiles, bacterial growth occurs at temperatures extending from -15 °C to around 120 °C (Brock and Darland 1970), and the growth temperature range for a typical bacterium species usually spans about 30 °C. Further, survival of vegetative cells is possible below the minimum temperature for growth, but not above the maximum temperature for growth temperatures above the maximum growth temperature.

During the high temperature period it is likely that most or all microbial life will be killed, including thermophiles. This is because thermophiles need to be metabolically active when exposed to high temperatures. The metabolism is needed to repair heat damaged cell components. Such metabolic processes will require a continuous supply of energy in the form of reduced organic or inorganic compounds, which, for instance, is how thermophiles survive in hot spring environments. However, such flow of reduced compounds is not likely in a DGR environment. But, once the DGR has cooled down, SRB may invade from cooler parts of the DGR far-field environment.

4.7.2 Energy

Microorganisms can survive for long time periods under nutrient limitations, without showing any signs of metabolic activity. However, all life has a basic need for renewable energy sources, both for maintaining a basic standby metabolism under nutrient limitations and energy for growth and propagation. The large majority of microorganisms found in deep groundwater are either chemoorganotrophic heterotrophs or chemolithotrophic autotrophs. The heterotrophs obtain all carbon and energy needed for growth from organic carbon compounds. The lithotrophs on the other hand, obtain energy for growth from inorganic reduced elements and carbon for cell synthesis from carbon dioxide.

The sources and contents of organic matter in the deep subsurface groundwater were recently reviewed by Marshall and Simpson (2014a). Two major organic sources have been considered. One consists of anthropogenic organics introduced by drilling and installing operations. This source is relatively easy to control and cannot sustain microbial activity over a long period of time. The other source consists of the natural organic matter produced *in situ* in the deep subsurface groundwater. A data complication from several sites suggests that the content of natural organics in groundwaters as deep as 500 meters is likely at a low level (e.g., <15 ppm) (Marshall and Simpson 2014a). The sources/sinks and producing/consuming mechanisms of those natural organic compounds are key information for understanding whether this natural organic matter can sustain long-term microbial sulfate reduction activities in deep subsurface groundwaters but is not well understood yet. This then implies that geological sources of H₂ and methane, and possibly also low molecular hydrocarbon gases, will be the only possible long-term sustainable source of energy for the deep biosphere (Stevens 1997).

The reference groundwaters CR-10 and SR-270 do not include organic carbon or reduced gases. Investigations of the Canadian Shield and other Precambrian rock sites do report the presence of abiotic H₂, methane, and low molecular hydrocarbon gases (Sherwood-Lollar et al. 1993; Sherwood-Lollar et al. 2008). More recently, it has been demonstrated that these gases can be found not only in groundwater but also in the crystalline rock matrix pore water (Eichinger et al. 2011). Methane, H₂, ethane, propane and butane concentrations in matrix pore water generally were higher than those in fracture groundwater suggesting that the rock pore water is a reservoir of reduced gases.

4.7.3 Salinity

The most limiting condition for microbial growth seems to be availability of water (Potts 1994). As far as is known, bacteria cannot grow within solid ice or in steam. In solutions, or on surfaces, a substantial amount of water is needed for bacteria to be active and grow. Prokaryotes are influenced by changes in osmotic pressure. Many prokaryotes keep the osmotic concentration of their interior protoplasm above that of their habitat by using various compatible solutes. A few halophilic archaea such as *Halobacterium salinarium* raise their osmotic concentration with potassium ions and have enzymes that require high salt concentrations.

With respect to microbial growth, potential DGR sites are in low permeability and water-poor rocks. One major difference between the two hypothetical DGR environments, in crystalline and sedimentary rock, is the difference in TDS. While the reference crystalline groundwater has approximately 1% salinity, the sedimentary porewater has 27%. In other words, the crystalline rock groundwater is brackish while the sedimentary rock porewater is hypersaline (15 - 30%)

salinity). Most SRB can grow in brackish water; their need for sulfate and other respirable sulfur compounds makes them more fit for growth in water with dissolved solids compared to freshwater. However, many SRB also can grow also in environments with a low TDS content, including reduceable sulfur compounds. In contrast, very few microorganisms can grow in hypersaline environments. They belong to the Archaean family of Halobacteriaceae (Oren 2001).

The hypersaline environment in the hypothetical sedimentary DGR is anaerobic and reducing. It is, therefore, not an environment in which extreme halophiles can be active, but they may survive. The expected very high salinity will, consequently, keep the groundwater free from actively metabolizing microorganisms including SRB. The brackish environment in the hypothetical crystalline rock DGR can be inhabited by a large array of different prokaryotes including SRB, provided there are metabolizable energy sources available.

4.7.4 Macro- and Trace-Elements

Over 95% of a bacterial cell's dry weight is made up of a few elements, i.e., carbon, oxygen, hydrogen, nitrogen, sulfur, phosphorus, potassium, calcium, magnesium and iron. These are called macro-elements because they are required by bacteria in relatively large amounts. All bacteria require several trace elements besides the macro-elements. The elements manganese, zinc, cobalt, molybdenum, nickel and copper are needed by most cells in concentrations so low that contaminants in water, glass or chemicals often are adequate for dense growth in the laboratory. Besides these common elements, bacteria have particular requirements that reflect the special nature of their physiology and the environment where they live.

All needed macro-elements are present in the hypothetical contact waters (Table 3-1). Sources of carbon can be organic or inorganic. Probably all prokaryotes can use CO_2 , to incorporate carbon into organic molecules. However, by definition, only autotrophs can live with CO_2 as their sole source of carbon. Most prokaryotes are heterotrophs that use reduced complex organic molecules as carbon sources, and some can use methane. In deep aquifers, the supply of readily utilizable carbon sources may be extremely low. Organic carbon, therefore, probably is the most limiting nutrient for heterotrophic prokaryotes in environments considered for DGRs for spent nuclear fuel. Nitrogen is available as nitrate in the contact waters. In addition, many anaerobic prokaryotes can fix N₂ dissolved in groundwater into organic molecules, such as amino acids. Although the amount of phosphorus is low or below detection in deep groundwater, it can still be enough for a standing population of bacteria. Phosphorus in minerals can be available in apatite [Ca₅(PO₄)₃(F, Cl, OH)]. Phosphorus is not consumed, oxidized or reduced in microbial metabolism. As long as there exists a pool of phosphorus, in equilibrium with solid phosphorus minerals, this element will not be limiting.

It is obvious that oxidized sulfur compounds must be available for SRB to produce sulfide. Both reference groundwaters (C-10 and SR-270) contain sulfate to allow SRB to be active. There is no information about trace elements in the reference waters. However, deep groundwater contacts large areas of rock minerals and the tiny amounts of trace elements needed for bacterial life are most likely available.

4.7.5 The Controlling Effect of Phages

A range of total number of cells from 10³ to 10⁶ cells mL⁻¹ is typical of many deep groundwater samples around the world (Bomberg et al. 2016; Hallbeck and Pedersen 2012; Ino et al. 2016; Leupin et al. 2017). Microbial populations in deep groundwater systems do not appear to grow to numbers above 10⁶ cells mL⁻¹ despite the presence of electron donors and acceptors and organic carbon, while in laboratory cultures, the bacterial total cell count can easily reach 10⁹ cells mL⁻¹ or even higher. It has been suggested (Kyle et al. 2008b) that viruses attack, kill, and disintegrate microbial cells and, thereby, regulate total cell counts to numbers at or below 10⁶ cells mL⁻¹ in many non-polluted water systems, and it has been shown that such viruses (bacteriophages or phages), are present in large numbers and diversity in deep groundwater (Kyle et al. 2008a). In addition, the controlling effect of phages on the population size of SRB in deep groundwater was demonstrated (Eydal et al. 2009). It appears likely that such viruses move residue material from microorganisms into particulate and dissolved organic matter and that the chemical composition of this matter can differ from that of the microorganisms from which it was derived. Highly labile materials, such as amino acids and nucleic acids, tend to be recycled quickly by microorganisms whereas more recalcitrant carbon-rich material, such as that found in cell walls, probably contributes to the pool of total and dissolved organic carbon in groundwater. Thus, although the observed numbers of microorganisms remain approximately constant over time, the populations can be active and growing at a rate approximately similar to the phage killing rate. Autotrophic microorganisms (e.g., homoacetogens and methanogens) fix carbon dioxide into organic compounds using H₂ as a reductant. Microbial oxidation of thermocatalytic methane will also add organic carbon in the form of microbial cells and possibly also dissolved organic carbon via phagal attack.

4.7.6 Main Constraining Factors on Microbial Activity

The main lasting constraining factors for sulfide production by SRB, provided oxidized sulfur compounds are available, and for activity of bacteria other than SRB, are salinity and energy availability. The very high salinity (27.6 % w/w TDS) and absence of O₂ in the sedimentary rock case will prevent growth and activity of all known Prokaryotes. For the crystalline rock environment, growth and activity by SRB and other prokaryotes will be possible in the long run if there is a continuous supply of organic carbon, and/or reduced gases such as H₂ and possibly methane. Observations of bacterial and archaeal diversity and biomass in various subterranean environments suggests that this generally is the case (Magnabosco et al. 2018).

5. SULFUR CYCLE IN THE DEEP GROUNDWATER SYSTEM

5.1 INTRODUCTION

The sulfur cycle in deep subsurface groundwater is illustrated in Figure 5-1. The sulfur species in groundwater are likely dominated by dissolved sulfate (SO_4^{2-}) and/or sulfide (S^{2-}), although some other sulfur species, such as thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}), elemental sulfur (S_0), and organic sulfur compounds, may also exist. Many of the species are weak bases, so they will exist in a protonated form within the environment, or as acid/base equilibria. The transformation among these sulfur species, particularly between dissolved sulfate and sulfide, constitutes the major framework of the sulfur cycle in deep subsurface groundwater.



Figure 5-1: Sketch diagram showing the sourced and sinks of dissolved sulfate and sulfide, as well as the processes that drive the sulfur cycle in the deep subsurface groundwater.

5.2 SOURCES AND ABIOTIC PRODUCTION OF SULFATE IN DEEP GROUNDWATERS

Sulfate in terrestrial deep subsurface groundwater may come from several sources and processes, including the following:

- (1) The sulfate inherited from source water. If the source water originated from ancient seawater, the abundant sulfate dissolved in seawater would have contributed a considerable amount of sulfate to the groundwater. If the water originated from meteoric water, sulfate could have accumulated in the groundwater to a higher concentration than that in fresh water by oxidative weathering of sulfide along the flow path in the fracture system of the rock, because Precambrian cratonic rocks contain abundant sulfide minerals. Therefore, regardless of the water source, subsurface groundwater is expected to have a one-time sulfate supply from its source water.
- (2) Episodic recharge from surface water or hydrothermal fluids. Once the groundwater is isolated from the surface, surface supply would be cut off. However, driven by tectonic activities, the groundwater could receive episodic input of sulfate from recharge of surface water along newly generated faults, or from hydrothermal fluids associated with tectonic activity. However, this secondary sulfate supply can be

highly variable among different groundwater systems and is difficult to model quantitatively.

- (3) Leaching of sulfate minerals in host rocks. Sedimentary rocks may contain some evaporite minerals, including sulfate minerals such as anhydrite, gypsum, and barite. In addition, carbonate minerals commonly contain some carbonate-associated sulfate (CAS). These sulfate minerals, if existing in host rocks, can be a large reservoir that supplies sulfate to the groundwater continuously. Some studies (Lin et al. 2006) found that fluid inclusions in minerals also can contain some sulfate and contribute to groundwater through fluid-rock interaction. However, the sulfate budget in fluid inclusions is very small given the small volume of those fluid inclusions in minerals and thus may not be a major contributor to the groundwater sulfate budget.
- (4) In situ oxidation of dissolved sulfide and other sulfur-containing minerals in host rocks. The oxidation of sulfur species can be driven by either biological (e.g., sulfide-oxidizing bacteria) or abiotic processes. Oxidation would not only occur at the early stage of groundwater evolution, when the post-infiltration water was still oxic, but could also continue for a long time after any free oxygen was consumed and the groundwater had turned into a reducing environment. In the latter case, Li et al. (2016) found that oxygen radicals, released from water radiolysis induced by decay of radioactive elements (e.g., ²³⁵U, ²³⁸U, ²³²Th and ⁴⁰K) in the host rocks, can oxidize sulfide minerals (mostly pyrite, FeS₂) in contact with water. This process, called indirect radiolytic oxidation of sulfide (IROP) to distinguish it from direct radioactive bombardment of sulfide minerals, can be described by Equation 5-1:

$$FeS_2 + 40H^{\bullet} \rightarrow Fe^{2+} + S^0 + SO_4^{2-} + 2H_2$$
 (5-1)

Because the half-lives of the major radioactive elements (²³⁵U, ²³⁸U, ²³²Th, ⁴⁰K) in rocks are in the order of a billion years, the IROP process driven by radioactive decay can persistently generate sulfate over geological time scales as long as sulfide minerals in the host rocks are not consumed completely. Although it is not as efficient as oxidative sulfide weathering, the IROP process can supply enough sulfate to support a long-standing ecosystem dominated by SRB in deep subsurface groundwater (Li et al. 2016; Lin et al. 2006), over a billion-year time period.

5.3 MICROBIAL PROCESSES INVOLVED IN SULFIDE PRODUCTION

In the low-energy anaerobic environment of deep subsurface groundwater in Precambrian cratons, sulfate generally serves as the major electron acceptor for microbial metabolism (Li et al. 2016). This is because other electron acceptors (e.g., nitrate and ferric iron) with higher oxidation potentials are less available. Microbial sulfide productivity in deep subsurface groundwater would depend on several controlling parameters (i.e., temperature, salinity and the availability of energy and macro- and trace-elements, as discussed in Chapter 4 and the sulfur inventory in the groundwater. The sulfur species in groundwater are likely dominated by dissolved sulfate ($SO_4^{2^-}$) and/or sulfide (S^{2^-}), although some other sulfur species, such as thiosulfate ($S_2O_3^{2^-}$), sulfite ($SO_3^{2^-}$), elemental sulfur (S_0), and organic sulfur compounds, may also exist in the system.

The anaerobic part of the microbial sulfur cycle is mediated by many different sulfur-related microorganisms of which several have been detected in sequence libraries from URLs (see URL table in Appendix). The families/genera involved with sulfate reduction to sulfide use a variety of electron donors and carbon sources. Microbial sulfur utilization includes assimilatory processes where sulfur is incorporated into cell constituents, and dissimilatory processes where energy is generated through the oxidation or reduction of sulfur compounds. In dissimilatory sulfate reduction $SO_4^{2^-}$ is used as an electron acceptor and HS⁻ is produced. This process can take place only under anaerobic conditions. Sulfate-reducing microorganisms have been found abundantly in anaerobic deep groundwater environments. At the temperatures and pressures prevailing in the deep groundwater environment $SO_4^{2^-}$ reduction is exclusively a microbiological process.

Some $SO_4^{2^-}$ reducing microbial consortia may oxidize CH_4 as a source of energy and produce dissolved sulfide (this process is called anaerobic oxidation of methane (AOM), (Weber et al. 2017; Ino et al. 2018a). Electron donors in $SO_4^{2^-}$ reduction may also be organic compounds or H_2 . Many microbial metabolic groups compete for the organic matter used for $SO_4^{2^-}$ reduction, including those utilizing more energetically favorable processes such as NO_3^- , Fe(III) or Mn(IV) reduction.

Microorganisms can, in addition, obtain energy from sulfur compounds by oxidation or disproportionation reactions. For instance, under anaerobic conditions, some Epsilonproteobacteria are known to oxidize reduced sulfur compounds such as S⁰ and S₂O₃²⁻ with NO₃⁻ as an electron acceptor (Grote et al. 2012). Such sulfur-oxidizing Epsilonproteobacteria were found in deep subsurface groundwater from the Fennoscandian Shield (Bell et al. 2020; Miettinen et al. 2015b). During disproportionation processes, a compound is simultaneously reduced and oxidized to form two different products. Disproportionation of S⁰ or S₂O₃²⁻ (or SO₃²⁻) simultaneously forms both SO₄²⁻ and HS⁻ (Böttcher et al. 2001). Microorganisms catalyzing such disproportionation processes belong to the sulfate-reducing Deltaproteobacteria and Clostridia. In addition, the oxidation of HS⁻ with dissimilatory reduction of NO₃⁻ and NO₂⁻ to NH₄⁺ has been shown recently for *Desulfurivibrio alkaliphilus* (Thorup et al. 2017). The oxidation pathway included reductive-type *dsr*AB genes that are normally used as functional genetic markers for sulfate reduction.

The amount of dissolved sulfide in groundwater can be mitigated by microbial anaerobic oxidation of reduced sulfur species. This can be mediated by for instance HS⁻ and S⁰ oxidizing *Thiobacillus* as well as by *Sulfurimonas* and *Sulfuricurvum*. As further discussed in Section 5.4, precipitation may also reduce sulfide concentration, as demonstrated by the inverse relationship of Fe²⁺ and HS⁻ concentrations in Fennoscandian groundwater samples (Pedersen 2008), because of iron sulfide precipitation... The relationship is clear regardless of HS⁻ concentration, which suggests an active role of solid iron sulfide phases in controlling the concentration of dissolved sulfide in the groundwater systems studied (Wersin et al. 2014a). Iron-reducing bacteria (IRB) produce Fe²⁺ from Fe(III) and Fe²⁺ reacts readily with HS⁻, forming iron sulfide that precipitates out of solution.

Iron(III) minerals can serve as electron acceptors for IRB, as was illustrated with the bacterium *Shewanella oneidensis* MR-1, that was shown to conserve energy from the reduction of Fe(III) in biotite and chlorite (Brookshaw et al. 2014). The Fe²⁺ produced in the reduction of iron minerals can contribute to the mitigation of dissolved sulfide concentrations. It is also possible that dissolved sulfide produced by SRB reacts directly with Fe(III) in minerals resulting in the formation of Fe²⁺, S⁰, according to Equation 5-3.

$$HS^{-} + 2Fe(III) \rightarrow 2Fe^{2+} + S^{0} + H^{+}$$
 (5-3)

A so-called cryptic sulfur cycle has been detected in marine oxygen-minimum zones and in sediment environments (Canfield et al. 2010). Its occurrence in deep crystalline bedrock groundwater environment is also possible. In a cryptic sulfur cycle, the HS⁻ formed during $SO_4^{2^-}$ reduction oxidizes rapidly back to $SO_4^{2^-}$ or to less oxidized sulfur compounds such as S⁰, or $S_2O_3^{2^-}$ (Canfield et al. 2010; Holmkvist et al. 2011; Reese et al. 2014) and the HS⁻ formed is thus not measurable. A cryptic sulfur cycle may be driven by biological or geochemical means but it may also be a combination of biologically and geochemically driven cycles, if after biological $SO_4^{2^-}$ reduction the HS⁻ formed reacts with insoluble Fe(III) in minerals, reducing it to soluble Fe²⁺ and eventually precipitating as pyrite. In a cryptic sulfur cycle, the occurring reactions cannot be measured from the concentrations of different sulfur species in the water phase. Eventually most of the sulfide produced would end up as iron sulfide as long as ferric iron is available to react with the biogenic sulfide and sulfur. In the long-term, the FeS formed can react with S⁰ and become pyrite, FeS₂, which is poorly soluble and acts as an final sink for sulfide (Rickard and Luther 2007b).

5.4 DISSOLVED IRON AND SULFIDE IN THE GROUNDWATER

Sulfide is soluble in water only in the presence of ammonia, or alkali or alkaline earth metal cations such as sodium or calcium. With all other metal cations, sulfide will precipitate. This applies to this includes metal cation components in the groundwater, such as Fe²⁺, Cu²⁺, Zn²⁺ and Pb²⁺ that can combine with sulfide to precipitate sulfide minerals such as FeS/FeS₂, CuS, ZnS, and PbS. Among these metals, Fe²⁺ generally has the highest concentration in deep subsurface (particularly reducing) groundwater.

Despite the possibility of hydrothermal input in some cases, dissolved iron in groundwater is believed to be mostly derived from host rocks by water-rock interaction. Iron occurs widely in natural minerals. In crystalline rocks, Fe in the form of Fe(II) occurs as a major element in a variety of silicate minerals (e.g., olivine, pyroxene, biotite) that range from ultramafic-mafic rocks to felsic rocks (e.g., granite). Magnetite, in which Fe occurs in a higher valence state, commonly is also seen in granitic rocks. In sedimentary rocks, Fe occurs in more variable valence states and is a major element in magnetite, goethite, lepidocrocite, hematite, siderite, ankerite, and some clay minerals. Fe can be enriched significantly if sedimentary rocks. Over long periods of water-rock interaction, the Fe(II) in silicate carbonate and pyrite can be leached out. Higher valence Fe can be reduced to Fe²⁺ by H₂ produced from H₂O radiolysis and/or by organic compounds in the groundwater system. All this Fe²⁺ would accumulate in the groundwater and have a significant impact on the dissolved sulfide concentration of the groundwater.

As described in the summary by Raven et al, (Raven et al. 2011), the Fe concentration in pore water of the Cobourg Formation shows an increasing trend, i.e., from <0.05 mmol/kg at the top to > 0.2 mmol/kg at the bottom of the formation. These high Fe concentrations throughout the Cobourg Formation would limit sulfide concentrations in the groundwater to very low level. As already noted above, other metals, such as lead, zinc and copper, may also limit the sulfide concentrations in groundwater. In general, these metals may not be enriched as much as Fe in groundwater, but these metals are much more efficient than Fe in removing dissolved sulfide from groundwater. This is because of the low solubility product constants (Ksp) of the

corresponding sulfides of these metals (i.e., orders of magnitude lower than the Ksp of FeS). Therefore, the effects of these metals may need to be assessed as well.

5.5 THE EFFECTS OF REDOX CONDITIONS AND PH ON SULFIDE CONCENTRATIONS

Redox and pH conditions may have strong controls on sulfide concentrations in deep subsurface groundwaters because both Fe and S have several valence states and the solubility of Fe-S minerals is affected by the pH of groundwater.

Figure 5-2 illustrates the stability fields of different Fe and S species at 25 °C on an Eh-pH diagram. Surface waters in contact with atmospheric O₂ (i.e., rain-, river and lake-water and shallow seawater) generally have a relatively high Eh value of 0 to +0.8 V and a variable pH ranging from 3-10 (Becking et al. 1960) which dictates that the Fe and S species in these source waters should be dominated by Fe³⁺ and sulfate. With progressive water-rock interaction underground, the Eh and pH would evolve to values that are buffered by the host rocks. The Eh of both reference groundwaters CR-10 and SR-270 is about -0.2 V with pH values of 6.3 and 7.1, respectively (Table 3-1), which puts both groundwaters in the pyrite stability field. In other words, thermodynamically, the concentrations of dissolved Fe²⁺ and sulfide would be controlled by the solubility product constant of pyrite (Ksp = $10^{-26.89}$ at 25 °C). Therefore, since the Fe²⁺ content in reducing groundwaters can be enriched to ppm levels, it is unlikely that these groundwaters contain a significant quantity of dissolved sulfide species (King 2013).



Figure 5-2: Eh-pH diagram of Fe²⁺ - HS⁻ - H₂O system at 25 °C. The diagram was produced using the Geochemist's Workbench (Bethke and Yeakel 2016).

6. REPRESENTATIVE SULFIDE CONCENTRATIONS IN DEEP SUBSURFACE ENVIRONMENTS AND STATE-OF-THE-ART ANALYTICAL METHODS

This chapter presents discussions on representative sulfide concentrations in groundwater and rock in crystalline (CR) and sedimentary (SR) geospheres.

6.1 SULFIDE CONCENTRATIONS IN DEEP GROUNDWATERS

Sulfide concentrations in deep groundwaters are a function of multiple factors as outlined in previous chapters. In the sedimentary system, the limestone host rock contains sulfide minerals as well as various evaporitic sulfate minerals, such as anhydrite, gypsum and celestine (Zhang 2019), which could all contribute sulfate to the groundwater. Predominant biogenic hydrocarbons in the dissolved gas in the Cobourg Formation (NWMO 2011) indicate the existence of an active ecosystem. In subsurface reducing environments, an active ecosystem likely contains sulfate reducers, which can produce sulfide. However, the occurrence of relatively high dissolved Fe concentrations (e.g., 30 mg/L in SR-270 water; Table 3-1) suggests that the dissolved sulfide concentration in the SR-270 groundwater will be very low, due to an efficient removal of HS⁻ by pyrite deposition. A complicated sulfur cycle including sulfide oxidation, sulfate reduction, and secondary pyrite precipitation has been illustrated clearly by morphology studies of pyrite in the pyrite minerals and δ^{34} S studies in the dissolved sulfate in the drill cores of the Cobourg formation (Zhang 2019).

Appendix A2 presents the research undertaken by nuclear waste management agencies and other research institutions on the topic of sulfide content in deep groundwater. Research undertaken by nuclear waste management agencies in Canada (AECL/NWMO), Finland (Posiva), Sweden (SKB), Switzerland (Nagra), and Japan (JNC/JAEA) are included in an annotated bibliography, as well as a list of journal articles that discuss this topic. For each source, information on the location, lithology and depths of the site studied is included, as well as the exact species of sulfide that was targeted. A range (minimum, maximum, and average) of the measured sulfide content is outlined. Each source also has additional notes on the right-most column detailing the fidelity of the data, method of analysis, and/or borehole number, as available.

6.2 SULFIDE SOURCES IN ROCK

Sulfide salt concentrations in rocks could vary from place to place. Even in a specific rock body, the amount of sulfide salts can change both horizontally and vertically. Therefore, prediction of sulfide concentrations will be more accurate by core characterizations within different locations of a specific rock body.

Tworo (1985) reported Mississippi-Valley type lead-zinc sulfide mineralization in the middle Silurian dolomites in the Bruce District to the north of the Algonquin Arch on the eastern margin of the Michigan Basin. Based on a study of lead isotopes in the sulfide minerals of the Niagara Escarpment, Farquhar et al. (1987) speculated that the sulfide mineralization occurred hundreds of million years after the sedimentary strata were deposited, and that the metal source could have been remobilized from rock units in the Appalachian Basin.

Another factor that may affect sulfide concentrations in rock is the process of microbial sulfate reduction. In particular, microbial sulfate reduction could have supplied significant amounts of
sulfide, which subsequently would have been precipitated as pyrite in the presence of high Fe²⁺ concentrations. Such secondary sulfide precipitation has been observed throughout the limestone in the Cobourg Formation (Jautzy et al. 2017) as well as in the shale cap rocks below the Bruce nuclear site (NWMO 2011).

Section 7.2 describes the sources of sulfide production within the rock and presents preliminary calculations to obtain rate of sulfide production.

6.3 STATE-OF-THE-ART METHODS FOR MEASURING SULFIDE/SULFATE CONCENTRATIONS IN GROUNDWATERS

In deep subsurface groundwaters, the major dissolved sulfur species are sulfide and/or sulfate, although a variety of sulfur species with valence state ranging from -2 (sulfide) to +6 (sulfate) may exist, particularly in those groundwaters with active microbial communities. While field kits are available to give a rough range of the sulfur content on site, the precise analysis of dissolved sulfide and sulfate contents is time consuming and requires careful handling of samples over the course of preparation, sampling, shipping, and storage to laboratory analysis. One major challenge for precise analysis of the concentration of each sulfur species in a groundwater sample is the instability of dissolved sulfide, which can be oxidized quickly by atmospheric O₂ after sampling, unless the dissolved sulfide is fixed immediately upon sampling. For this purpose, zinc acetate has been added commonly to the sample bottle prior to or during the sampling process to fix dissolved sulfide as ZnS. However, Li et al. (2016) indicated that the addition of zinc acetate to the samples may promote microbial activity that in turn can affect the sulfate and/or sulfide concentrations in the samples. A better alternative is the addition of CdCl₂ that can fix the dissolved sulfide as CdS while the excess Cd²⁺ in the solution can inhibit microbial activity. To decrease microbial activity after sampling as much as possible. Li et al. (2016) also suggested that the groundwater samples should be filtered through 0.2 micron filter paper, frozen onsite, covered by dry ice during shipping, and stored at -80 °C until laboratory analysis.

Groundwaters generally will form a yellow CdS precipitate if they contain dissolved sulfide. In the laboratory, this CdS can be filtered out and quantified by gravimetry to calculate the concentration of dissolved sulfide. However, in some groundwaters, other components may coprecipitate with CdS, e.g., a white precipitate of CdCO₃ may form if the water contains abundant CO₃²⁻. As a result, the filtered solids are a mixture of precipitates rather than pure CdS. An additional laboratory analysis would be required using techniques for solid sulfide analysis (see below) to achieve the dissolved sulfide concentrations. After the filtration of CdS (and any other precipitates), the water sample can be recollected and sulfate can be precipitated as BaSO₄ by adding BaCl₂, following the protocols by Burdett et al. (1989) and Kampschulte et al. (2001). The resulting BaSO₄ subsequently can be quantified by gravimetry to calculate the concentration of dissolved sulfate in the groundwater sample.

6.4 STATE-OF-THE-ART METHODS FOR MEASURING SULFIDE CONCENTRATIONS IN ROCK

Driven by mineral exploration, analytical methods for sulfide concentrations in rocks were developed a long time ago (Thode et al. 1949). The technique most commonly used involves converting sulfur-bearing minerals in rock powders into SO₂ gas by combustion in a furnace at

high temperatures (> 1000 °C). The SO₂ gas thus produced can then be quantified by a variety of methods. Initially this was done by titration (Coller and Leininger 1955), which then evolved to analysis by infrared spectroscopy (Gibson and Moore 1973) and mass spectrometry (Studley et al. 2002). A number of oxidants have been developed over the years for efficient combustion, such as O₂ (Thode et al. 1949), Cu_xO (Fritz et al. 1974), V₂O₅ (Ueda and Krouse 1986), and WO₃ (Grassineau et al. 2001). The details of these methods have been reviewed by de Groot (2004). The currently widely used method of elemental analyzer mass spectrometer (EA-MS) is a representative of such techniques. The strength of the combustion-based technique is a quick turnaround time and a reasonably low detection limit at the ppm level. However, this technique has notable limitations – it gives bulk sulfur concentrations only. It cannot distinguish spatial variations nor discriminate between several types of microbially precipitated sulfur- or sulfidebarial minerals, particularly in those rocks that contain both sulfate and sulfide minerals.

For rocks that contain multiple sulfur phases (e.g., different sulfate and sulfide minerals), X-ray diffraction (XRD) on fine rock powders is a well suited technique that can distinguish between mineral phases. Monecke et al. (2001) showed that by careful sample preparation and refinement of the Rietveld method, XRD can be used to determine quantitatively the mineral compositions of complicated rocks such as hydrothermal alteration haloes. The XRD method is quick and harmless to the material. However, it requires relatively large amounts of sample (tens of milligrams to grams) and a high sulfide content (at the percent level) to yield precise results.

X-ray fluorescence also has been employed extensively for analysis of sulfur concentrations (Williams et al. 1957), but mostly for bulk sulfur analysis. Recently, a quantitative analysis method for sulfide as well as coexisting other sulfur species (e.g., sulfate) in rock has been developed using wavelength-dispersive X-ray fluorescence (Uhlig et al. 2016; Chubarov et al. 2016). This method uses high-resolution measurements to easily detect the wavelength difference between sulfide and sulfate. The samples can be loaded as either pressed powder pellets or flux-fused borate beads (see Chubarov et al. (2016) and references therein). The signal is then calibrated to standard material. Again, this method is more applicable to a large amount of sample material (tens of milligrams to grams) and a high sulfide content (at the percent level).

In some cases, sulfide may be distributed relatively homogeneously as micro-crystalline or amorphous forms in rocks or melts, but at a very low content (e.g., at the ppm level). In such cases high-resolution *in-situ* analysis can be employed to determine the sulfide concentration from a representative small area of the sample. Electron probe microanalyzer (EPMA), laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), and secondary ion mass spectrometry (SIMS) are all well established methods. These methods use high-energy beams to collect samples directly from polished rock chips for measurement. It should be noted that the EPMA method may not be suitable for silicate containing materials as they might be altered by the electron beam. The size of the sampling point can be as small as 1 micron by EPMA to as large as ~100 micron by laser ablation. The rapid analysis of these methods allows systematic sulfide mapping (at the ppm level) of selected areas of a sample, which can enhance the understanding of hidden sulfide in rocks and melts significantly.

7. MODELLING OF SULFIDE AND SULFATE CONCENTRATIONS IN DEEP GROUNDWATER

7.1 OVERVIEW OF MODELLING APPROACH

Figure 5.1 illustrates that multiple sources and sinks may affect the concentration of dissolved sulfide in deep groundwaters. The dissolved sulfide mainly originates from two major sources: dissolution of sulfide mineral in wall rocks and reduction of dissolved sulfate in the water. The dissolved sulfate in the deep groundwater mainly comes from the primary sulfate in the original water source, and secondary sulfate produced by leaching of sulfate minerals and/or oxidation of sulfide minerals in wall rocks. The sinks of dissolved sulfate in deep groundwater include H_2S degassing, sulfide precipitation, and/or oxidation.

In addition, some microorganisms can obtain energy from sulfur compounds (e.g., S^0 , $S_2O_3^{2^-}$, $SO_3^{2^-}$) by oxidation or disproportionation reactions. Microorganisms that oxidize reduced sulfur compounds such as S^0 and $S_2O_3^{2^-}$ with NO_3^- were found in deep subsurface groundwater from the Fennoscandian Shield (Miettinen et al. 2015a; Wu et al. 2015). Disproportionation of S^0 and $S_2O_3^{2^-}$ (or $SO_3^{2^-}$) simultaneously forms both $SO_4^{2^-}$ and HS^- (Böttcher and Thamdrup 2001).

The CR-10 and SR-270 reference groundwaters have pH values from 6-7 (Table 3-1), which suggest that around half or more of the dissolved sulfide in the groundwater exists in form of dissolved H_2S (Figure 3-3). Given the relatively high Henry's law constant for H_2S (Figure 3-2), degassing of H_2S from the groundwater may occur. However, the extent of H_2S degassing is dependent on several conditions including water temperature, air pressure, and volume of the gaseous phase.

The CR-10 and SR-270 groundwaters also contain Fe (1-30 ppm; Table 3-1), which could have been built up in the reducing aqueous environments through long-term water-rock interactions. These relatively high Fe concentrations have a strong impact on the concentrations of dissolved sulfide in these groundwaters due to the low solubility of iron sulfide minerals. Even conservatively assuming that FeS (with higher solubility constant (Ksp)) is the precipitated sulfide mineral (Rickard 2006), the dissolved sulfide concentration is expected to be around 0.001 ppm under the range of Fe concentrations (1-30 ppm). This is consistent with the analytical results of dissolved sulfide in the groundwaters that were assessed to develop the CR and SR references, which all had sulfide values below the detection limit of 0.5 mg/L. Therefore, when a steady state is reached after long-term water-rock interactions with the CR and SR groundwaters, the sulfide concentrations in these deep groundwaters should be buffered by the Fe concentrations to remain at a very low level (see also section 9.3).

This steady state will be temporarily disturbed by the construction of a DGR. When exposed to oxic conditions, the dissolved Fe²⁺ in the deep groundwater can be oxidized rapidly (which may or may not involve microbes) into Fe³⁺, and subsequently would be removed from the groundwater due to its low solubility. As a result, dissolved sulfide may slowly accumulate in the groundwaters by sulfate reduction. Direct dissolution of sulfide is not considered to play a major role in increasing sulfide concentration here because (i) the water pH is not highly acidic, and thus the dissolution rate is likely very low; (2) under oxic conditions, oxidative sulfide weathering is a more efficient pathway for sulfur recycling.

The calculations below aim to estimate the maximum sulfate production in a range of sites upon exposure of these systems to oxic conditions. A bounding-case scenario is considered with the

assumption that all the sulfate produced from the wall rocks will be reduced to sulfide through microbial reactions.

7.2 GEOCHEMICAL BASE AND VARIANT CASES

For this analysis, two hypothetical sites were considered, one in crystalline rock (CR) and one in sedimentary rock (SR). The crystalline site is assumed to be dominated by biotite-granodiorite-tonalite, with small amounts of sulfide minerals (mainly pyrite). The groundwater chemistry is described by CR-10. The sedimentary rock is assumed to be Cobourg limestone from southern Ontario, with groundwater chemistry as described by SR-270. Assumptions and uncertainties involved in this analysis are listed in Section 7.4.

In the CR site, any sulfate that could be generated from minerals in the wall rocks is through the process of sulfide oxidation. Sulfide oxidation can proceed via two mechanisms.

Mechanism one is the "indirect radiolytic oxidation of pyrite" (IROP; section 5.2) (Li et al. 2016), in which pyrite is oxidized into sulfate by oxidants generated from the pyrolysis of water, induced by the energy from the decay of radioactive isotopes such as ²³⁸U, ²³⁵U, ²³²Th and ⁴⁰K in the rocks. This is a long-standing process that is not affected by redox conditions.

Mechanism two is the direct oxidation of sulfide by dissolved O_2 and/or Fe^{3+} , a process favored under oxic conditions. To distinguish this process from the indirect mechanism, the term "oxidative pyrite weathering" is used to refer to this process. Although both dissolved O_2 and dissolved Fe^{3+} can oxidize sulfide under oxic conditions, oxidation by Fe^{3+} occurs mostly at low pH (Williamson and Rimstidt 1994a). The groundwater from the CR site has a near neutral pH, in which the concentration of dissolved Fe^{3+} is very low. Therefore, only oxidation by dissolved O_2 is considered here.

7.2.1 Input Parameters

(1) Indirect radiolytic oxidation of pyrite (IROP)

The sulfate production rate from IROP can be calculated by Equation 7-1 below (Li et al. 2016):

$$P_{(M)Sulfate} = D_{Total}^{abs} \times G \tag{7-1}$$

in which G is the unit sulfate yield, which was determined by laboratory experiments to be 2.1×10^{-9} mol m⁻² Gy⁻¹ (Lefticariu et al. 2010); D_{Total}^{abs} is the absorbed dose rate, which is a function of the water/rock ratio, and the radiation dose rate:

$$D_{Total}^{abs} = \frac{D_{Total}^{App} \times W \times S}{1 + W + S}$$
(7-2)

in which W is the water/rock weight ratio, S is the stopping power constant, and D_{Total}^{App} is the total apparent dose rate from the radioactive decay of ²³⁸U, ²³⁵U, ²³²Th and ⁴⁰K in the rocks:

$$D_{Total}^{App} = \sum_{i=235} U_{,238} U_{,232} Th_{,40} K_{,i} \frac{C_{i} \times E_{i} \times \lambda_{i} \times N_{A}}{M_{i} \times R}$$
(7-3)

in which C is the concentration of each radionuclide, E is the energy released per decay, λ is the decay constant, N_A is the Avogadro's constant, M is the atomic mass of each radionuclide, R is a unit conversion factor.

The input parameters of water and wall rocks in modeling are given below:

The hypothetical crystalline site:

- (i) The water:
 - a) Density:
 A density of 1.01 g ⋅ cm⁻³ is used (NWMO 2016).
- (ii) The rock:
 - a) Density:
 - A common number of 2.7 g \cdot cm⁻³ is used for the biotite granodiorite-tonalite and biotite tonalite wall rocks.
 - b) Porosity: Porosity and permeability in the crystalline rocks is dominated by fractures. A number of 0.25% was used for the calculation (Drury, 1981).
 - c) Concentrations of ²³⁸U, ²³⁵U, ²³²Th and ⁴⁰K: These can be calculated from the concentrations of U, Th, and K. The assumed concentration ranges from < 5 ppm to 14.8 ppm for U, from 0.6 ppm to 13.5 ppm for Th, and from 0.89 ppm to 5.71 ppm for K. The average values of 1.74 ppm, 5.72 ppm, and 2.45 ppm were used for U, Th, and K, respectively, in the modeling.
 - d) Sulfur concentration: The sulfur concentration of the tonalities in the CR site is assumed to range from 20 ppm to 200 ppm. Other features that may be present like felsic dykes could higher sulfide concentration, but their volume is assumed small, and thus not considered to influence the results.

The hypothetical sedimentary site:

- (i) The water:
 - a) Density: water in the Cobourg limestone has a density of ~1.168 g·cm⁻³ (Raven et al. 2011)
- (ii) The rock:
 - a) Density: 2.7 g \cdot cm⁻³ (Selvadurai 2017).
 - b) Porosity: the measurements of rocks from the Cobourg Formation yielded a porosity about 1.5% (Selvadurai and Głowacki 2018)
 - c) Concentrations of U, Th and K: based on the geochemical data of 4 drill cores at the Bruce nuclear site (Wigston and Jackson 2010a, b; Jackson and Murphy 2011), the average contents are 1.2 ppm for U, 2.5 ppm for Th and 0.9 ppm for K₂O in the Cobourg Formation.

 d) Sulfide mineral concentration: the pyrite content in the Cobourg Formation varies from 0-3% (Raven et al. 2011). An average of 1.5% is used for modeling.

(2) Oxidative pyrite weathering

The rate of sulfide oxidation (r) by dissolved oxygen has been studied extensively. Experimental studies (Williamson and Rimstidt 1994a) have given the pyrite oxidation rate as a function of the amounts of dissolved O_2 and H^+ (m_{DO} and m_{H+}) for the pH range of 2-10:

$$r = 10^{-8.19} \times \frac{m_{DO}^{0.5}}{m_{H^+}^{0.11}} \tag{7-4}$$

The hypothetical crystalline site:

- (i) The water:
 - a) pH:

The measured pH is about 7 for the reference groundwater CR-10 (Table 3-1; NWMO (2016)).

b) Dissolved O₂:

Dissolved O_2 in groundwater can be calculated by Henry's Law assuming dissolved O_2 is equilibrated with atmospheric O_2 at the operation site. The solubility of O_2 in groundwater is dependent on temperature, pH and aqueous chemistry. Employing the pH (~7) and aqueous chemistry (Table 3-1; NWMO (2016), the dissolved O_2 was calculated by the USGS PHREEQC software package (Charlton and Parkhurst 2011), which gave values of 2.78 x 10⁻⁴ mol \cdot kg⁻¹ at 20 °C and 1.85 x 10⁻⁴ mol \cdot kg⁻¹ at 50 °C, respectively.

(ii) The rock:

Same as for the CR site (IROP process)

The hypothetical sedimentary site:

- (i) The water:
 - a) pH:

The pH is about 6.3 for the groundwater from the reference groundwater SR-270 (Table 3-1; (Gobien et al. 2018)

- b) Dissolved O₂: same as for the CR site (see above)
- (ii) The rock:

Same as for the SR site (IROP process).

(3) Sulfate dissolution

The measurements on drill core samples from the Cobourg Formation yielded a sulfate concentration of 0.4-0.5% in the Cobourg limestone (Raven et al. 2011). As a result, the dissolution of sulfate minerals (gypsum, anhydrite) in the pore water may become an important process. (Dotson et al. 1999) gave the $CaSO_4$ solubility in brine water as:

at 25 °C,
$$[Ca^{2+}] = 0.000249 \times [SO_4^{2-}]^{2.579}$$
 (7-5)
at 75 °C. $[Ca^{2+}] = 0.000276 \times [SO_4^{2-}]^{2.444}$

7.3 RESULTS AND DISCUSSION

7.3.1 The hypothetical crystalline site

Using the parameters for the <u>hypothetical</u> crystalline site, the modeling yielded a unit sulfate productivity from IROP of $1.1 \times 10^{-11} \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$. From pyrite oxidation by dissolved O₂, the sulfate productivity would be $4.0 \times 10^{-2} \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ at 20 °C or $3.2 \times 10^{-2} \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ at 50 °C. By comparing these two oxidations processes it is clear that pyrite oxidation by dissolved O₂ is much more important (i.e., 8 orders of magnitude higher) than the background pyrite oxidation by radiolysis of water.

To translate these unit sulfate productivity values into sulfate concentrations in the groundwaters, other parameters, such as bulk rock density, porosity, sulfur concentration, and the surface area of pyrite in rock also play a role. Among these, the surface area of pyrite in rock is difficult to determine, and thus bears the major uncertainty. Assuming a range of surface area from $0.12 \text{ m}^2 \cdot \text{kg}^{-1}$ (equivalent to a cubic pyrite grain with a side length of ~1 cm) to $1.2 \text{ m}^2 \cdot \text{kg}^{-1}$ (equivalent to a cubic pyrite grain with a side length of ~1 cm).

- (1) the sulfate accumulation rate from IROP in groundwater would be 5 x 10⁻¹² to 5 x 10⁻¹¹ mg.L⁻¹·yr⁻¹ for a bulk-rock sulfur concentration of 20 ppm (where ppm expresses the sulfate-water mass ratio), and 5 x 10⁻¹¹ to 5 x 10⁻¹⁰ mg.L⁻¹·yr⁻¹ for a bulk-rock sulfur concentration of 200 ppm. This slow sulfate production rate would not generate notable sulfide in the deep groundwater on a time scale of thousands of years.
- (2) The sulfate accumulation rate from pyrite oxidation by dissolved O₂ in groundwater would be 0.017 to 0.17 mg.L⁻¹·yr⁻¹ for a bulk-rock sulfur concentration of 20 ppm and 0.17 to 1.7 mg.L⁻¹·yr⁻¹ for a bulk-rock sulfur concentration of 200 ppm at 20 °C, or 0.014 to 0.14 mg.L⁻¹·yr⁻¹ for a bulk-rock sulfur concentration of 20 ppm and 0.14 to 1.4 mg.L⁻¹·yr⁻¹ for a bulk-rock sulfur concentration of 200 ppm at 50 °C. If the fracture waters in the host rocks are well connected to the groundwater system, this sulfate would eventually be mixed into the groundwater. If this sulfate can be reduced rapidly to sulfide, a significant amount of sulfide would be accumulated in the deep groundwater. However, this assumes that the amount of atmospheric O₂ in the placement chambers is unlimited. In a closed system (i.e. once the chambers and tunnels are sealed off), atmospheric O₂ levels in the chambers would decrease with the progression of pyrite oxidation and eventually would be consumed completely. In this scenario, the total sulfide that can be built up in the deep groundwater would depend on the quantity of O₂ in the chambers at the time of sealing.

It should also be noted that aerobic microorganisms likely also would use a portion of the O_2 , which would reduce the O_2 concentration in the emplacement room even faster.

7.3.2 The hypothetical sedimentary site

Using the parameters for the hypothetical_sedimentary site, the modeling calculations yielded a sulfate production rate from IROP of $2.2 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$. Again, IROP contributes only very minor amounts of sulfate ($1.8 \times 10^{-9} \text{ mol} \cdot \text{yr}^{-1}$) to the pore water in the Cobourg limestone.

Similarly, the sulfate production rate from oxidative weathering of pyrite (2.7-3.3 mol·m⁻²·yr⁻¹ at 20-50 °C) is also much more efficient in the SR site. Assuming the surface area for pyrite is in the range of 0.12-1.2 m²·kg⁻¹, weathering of pyrite would contribute sulfate at a rate of 0.99-12.3 mg.L⁻¹.yr⁻¹ to the pore water in the Cobourg limestone. However, it is unlikely that such a high rate would be reached because that requires full oxidation of the pore water. Currently, the water system in the Cobourg Formation is highly reducing. During operation, penetration of O₂ into the pore waters would occur mostly likely via diffusion, which is very slow and, therefore, it would be difficult to fully oxidize the entire pore water system in the Cobourg limestones over the relatively short operational period.

The sulfate concentration in the pore water of the Cobourg limestone is also strongly dependent on the Ca²⁺ content in water. Given the system is limestone buffered, high Ca²⁺ content is expected. Assuming the measured Ca²⁺ content of the groundwater (Table 3-1) as the lower limit in the pore water, calculations using Equations 7-5 and 7-6 gave a sulfate content of 0.11 mol/L at 25 °C and 0.10 mol/L at 75 °C. These contents are much higher than the current sulfate content (~0.02 mol/L; Table 3-1) in the SR-270 groundwater. It should be noted that, if oxidative weathering of pyrite occurs, the accumulated sulfate in the pore water also would be regulated by the Ca²⁺ content. Given that Ca²⁺ is highly available in this limestone buffered system, the estimated sulfate contents likely represent the upper level of sulfate that can be accumulate in the pore water. Depending on the permeability of the limestone, pyrite- and sulfate-containing minerals in host rocks may contribute sulfate to the groundwater water by pyrite oxidation or sulfate dissolution to various extents. However, as along as the Ca²⁺ content in the groundwater can be maintained at high levels, sulfate would not be much enriched in the SR site groundwater.

7.4 ASSUMPTIONS AND UNCERTAINTIES

It should be noted here that several parameters and conditions employed in the calculations above were assumed based on general information, and that site-specific calculations cannot be performed at this point. As such any changes in these parameters and assumption could alter the modeling results. These parameters include:

(1) Porosity and permeability of the rocks:

The calculation assumes that oxidation of sulfide minerals occurs on the contact surfaces between sulfide minerals and water, that are distributed in the pore spaces inside the rocks. The distribution of water inside the rocks is dependent on the rock's porosity and permeability, and the water may, therefore, not be in contact with sulfide minerals. Furthermore, to simplify the calculation, the fractures in the rocks are assumed to be all well-connected and distributed homogeneously inside the rocks. In a real case scenario, the fracture network in the crystalline rocks and the pore distribution in the sedimentary rocks can be very heterogeneous. Some of the pore spaces and fractures in the rocks may not be well-connected but instead may be isolated from the groundwater system, and thus do not contribute to the sulfate concentration in groundwater.

(2) Oxidation state of the fracture water system:

The undisturbed deep groundwaters at the CR and SR sites are highly reducing as a result of water-rock interaction over geological time scale. This calculation assumes that the groundwaters at these sites will become fully oxidizing instantaneously during operation, and that this oxidizing state also will be extended instantaneously to the entire fracture and pore water systems. In a real case scenario, it will take time for oxygen to be transported to the fracture and pore water systems which are not in direct contact with air. The length of the transport time can vary significantly, depending on the detailed oxygen transfer mechanism. If the water inside the rocks remains static, oxygen will be transferred mainly via diffusion, which would be very slow. If the fracture water is over-pressurized and is draining out of the rocks, the natural flow may act as a barrier against O_2 penetration into the fracture waters inside the rocks. If water circulation and/or infiltration of oxidizing water into the rocks does occur, the water circulation pathway and the amount of oxidizing water involved, which are both controlled by the detailed fracture network, will determine the spatial and temporal scales of the oxidation process in the fracture water system.

(3) Oxygen availability:

The calculation assumes that the amount of oxygen in groundwater available to support the oxidation of sulfide minerals is infinite. However, each operation may introduce a limited amount of atmospheric O₂ into the system, which is then consumed by multiple processes, such as microbial respiration, abiotic oxidation of dissolved reductants in groundwater, oxidation of minerals (such as sulfide, biotite) and corrosion reactions. Regarding corrosion: most assessments of corrosion damage conservatively presume that oxygen will be consumed entirely by corrosion reactions (Hall et al. 2021; Scully and Edwards 2013). Consumption of oxygen by corrosion would make it unavailable to liberate sulfide via the mechanism noted above. Conversely, if oxygen were consumed according to the above mechanism, the total corrosion damage assessment could or should be reduced. It is noted that microbial respiration and oxidation of dissolved reduced components can consume O_2 at much higher rates (lonescu et al. 2015; Leonte et al. 2017) than the abiotic oxidation of minerals (Williamson and Rimstidt 1994a). Thus, oxygen that can be used for sulfide oxidation will not be infinite relative to the amount of sulfide in the rocks.

(4) Water availability:

Water in contact with sulfide and/or sulfate is a premise for sulfide oxidation and sulfate dissolution. In the calculations, either fracture water or pore water is assumed to remain constant or circulate in a closed system, such that the sulfate produced can accumulate in the water. However, if the fracture water keeps draining out from a limited water reservoir, the water-mineral contact area will diminish, which will reduce the sulfate production rate.

(5) Sulfide mineral surface area:

Sulfide oxidation will occur on the surface of sulfide minerals in direct contact with water. In the calculations, a range of surface areas of cubic grains with side lengths of 0.1-1 cm is used for simplicity. In addition, by applying the experimentally determined sulfide oxidation rate (Williamson and Rimstidt 1994a) in the calculation, the requirement that water is in contact with the entire grain surface, is automatically embedded in the assumptions. In a real case scenario, the sulfide minerals in the rocks may cluster in various shapes (e.g., platy, round) of much larger sizes, which could result in a much smaller surface area per unit mass. In addition, it remains unknown whether the surface areas of sulfide grains/accumulates are fully or partially hydrated. These uncertainties also impact the calculation results.

(6) Oxidation rate:

The sulfide oxidation rate constant employed in the calculation was determined in well-controlled laboratory experiments, which ensured efficient oxidation of sulfide minerals and little disturbance from secondary minerals. In a real case scenario, sulfide oxidation is always associated with the oxidation of Fe(II) in the sulfide minerals, which would precipitate quickly as a secondary mineral due to the low solubility of ferric iron. The precipitation of secondary minerals can reduce the surface area of sulfide in contact with water and O_2 progressively, and thus slow down the sulfide oxidation process.

More detailed characterization of these parameters in the future will help to better constrain the boundary conditions for the calculations and refine the results obtained from the modelling.

8. ASSESSMENT OF SULFIDE PRODUCTION AND SULFIDE CONCENTRATIONS IN BUFFER MATERIALS

The general objective of this chapter is to estimate the sulfide concentration in buffer material. Sulfide concentrations and sulfide production will be affected by complex coupling of difficult to quantify hydraulic, geochemical and microbial processes. The approach adopted is to provide reasonable bounds for fluxes and dissolved concentrations of sulfide occurring in the buffer and within the buffer/rock boundary.

8.1 DESIGN AND MATERIAL PROPERTIES OF BUFFER

Based on the current DGR design, the UFCs will be surrounded by clay-based sealing materials in the form a highly compacted bentonite (HCB) buffer box. Remaining voids will be filled with gap-fill materials (GFM) or other HCB components such as spacer blocks and floor-levelling tiles (Dixon 2019), Figure 8-1. The current reference material selected for the sealing system in a Canadian DGR concept is Wyoming MX-80 bentonite which is mostly composed of montmorillonite. Typical accessory minerals present in bentonites are other clay minerals, quartz, feldspars, gypsum, calcite, pyrite and various iron oxides/hydroxides (Karnland 2010), as shown in Table 8-1.





Table 8-1: Results from the XRD analyses of five consignments of the Wyoming MX-	-80
material. Only the mean value is shown here (Karnland 2010).	

Minerals	Mean Content %
Montmorillonite	81.4
Illite	0.8
Calcite	0.2
Cristobalite	0.9
Gypsum	0.9
Muscovite	3.4
Plagioclase	3.5
Pyrite	0.6
Quartz	3.0
Tridymite	3.8

Among the minerals in bentonite, gypsum, anhydrite, pyrite and iron oxides play an important role in the availability of sulfide and the potential production of sulfide from sulfate by indigenous bacteria, including SRB, in the bentonite (Haynes et al. 2018; Lopez-Fernandez et al. 2015; Masurat et al. 2010a). The survival, viability and activity of the indigenous microbial population in buffer and backfill will depend on several variables, partially related to the type of clay, including porosity and pore space, organic matter content and composition, the degree of water saturation and the swelling pressure at water saturation. High density bentonite clay will have sufficiently small pore sizes to discourage microbial activity in the buffer matrix (Stroes-Gascoyne 2010; Stroes-Gascoyne et al. 2010b). Past and ongoing studies have indicated that sufficient swelling pressure (> 2 MPa) could suppress microbial activity. The natural organic matter (NOM) content of MX-80 has been measured to be around 1% (Marshall and Simpson 2014a), and it has been determined that this NOM occurs in a highly degraded state and is composed mainly of long-chain aliphatic carbon molecules with minimal side branching and aromatic carbon molecules. The NOM is predominantly recalcitrant and, therefore, not a labile carbon source for microbes (Marshall et al. 2015; Marshall and Simpson 2014b).

8.2 VARIABLES AFFECTING MICROBIAL ACTIVITY IN BUFFER

8.2.1 pH and Temperature

The pH of most bentonite clays is slightly alkaline but still well within the range of what most microbes can tolerate.

In the Canadian nuclear waste disposal repository concept, the maximum surface temperature of the used fuel containers will not exceed 100°C and is unlikely to exceed 90 °C (Guo 2015).

It was found previously that heat treatment of MX-80 bentonite at 120 °C for 15 h (Masurat et al. 2010b) or 110 °C for 170 h (Bengtsson and Pedersen 2017) failed to kill all indigenous bacteria in the bentonite; in particular, a large number of culturable SRB were observed in the heat-treated MX-80 (Masurat et al. 2010; Bengtsson and Pedersen 2017). The resistance of SRB to high temperatures in bentonite was recently corroborated by (Haynes et al. 2018).

Bentonite or rather montmorillonite, has a verified high affinity for water and the cell membrane of bacterial cells is water permeable. If a bacterial cell is surrounded by bentonite with a low content of water (< 10%), it is possible that the water affinity of montmorillonite will extract water from indigenous bacteria, leaving them in a desiccated state. The phenomenon of drying cells in clay for prolonged storage is well known and commonly used in microbiology (Gherna 1994). Slow desiccation can yield higher viability, after prolonged storage, than can fast desiccation (Laroche and Gervais 2003; Potts 1994) and also increases heat resistance and viability in both spores and vegetative cells (Fine and Gervais 2005). Bacteria consequently have several mechanisms to survive prolonged periods of exposure to heat and desiccation (Meike and Stroes-Gascoyne 2000). When water saturation of the dry clay begins, spores and desiccated cells can be activated and start to metabolize. Doing so, their heat resistance may be limited due to lack of energy for metabolic activity as discussed in Section 4.7.1. The resistance of SRB to high temperatures in bentonite was recently corroborated by Haynes *et al.* (Haynes et al. 2021).

8.2.2 Pore Water Composition

The porewater composition will be constrained by transport of solutes in the groundwater, reactions between cations and the clay surface (e.g., cation exchange, surface complexation) and dissolution and precipitation of accessory minerals (e.g., gypsum, calcite). It's anticipated the pore water composition changes with the type of bentonite and the composition of the saturating groundwater. Bentonites could also vary in composition with respect to elements and minerals and the type and content of natural organic matter. The conditions for survival and activity of bacteria may, consequently vary significantly between different bentonite types as inferred by the variation in the highest wet density at which sulfide production could be detected in compacted clays (Bengtsson and Pedersen 2017).

Amongst constituents of porewater, salinity can play an important role to suppress microbial activity through decreasing the water activity due to interaction of water molecules with solute ions. Experiments using higher water salinities inhibited microbial growth at lower bentonite densities than those that used pure water (Stroes-Gascoyne et al. 2006). Further discussion on the impact of pore water composition on the microbial growth is presented in Section 8.2.

8.2.3 Porosity, Pore Space and Density

Transport of nutrients to, and metabolic products such as sulfide away from bacteria within the clay will be diffusion limited due to the low porosity of fully saturated buffer and backfill materials (Bengtsson and Pedersen 2017). The metabolic rate of bacteria in fully water saturated backfill and buffers will, consequently, be limited by the rate of diffusion of nutrients in the compacted clay matrix (Bengtsson and Pedersen 2017). The only areas not affected by diffusion barriers will be the interfaces between the rock, water bearing fractures and the excavation disturbed zone and the buffer and backfill material.

Pore space correlates with density, and the higher the density, the smaller the size of pores and voids that can be expected in the clay. A typical bacterial cell has a volume of $1 \ \mu m^3$ which consequently sets the space needed for a bacterium in compacted buffer or backfill material. In addition, there will be interfaces between the excavation disturbed zone and bentonite and between bentonite and containers where pore space may differ from the bulk of the buffer and backfill. Smaller and larger bacterial volumes exist, but the $1 \ \mu m^3$ may be used here as an example. Assuming that indigenous bacteria in dry commercial clays are desiccated (or have sporulated), they will take up water during saturation and eventually be viable when the clay is fully water saturated. During this process, the bacteria may compete with the clay over pore space and their internal turgor may counteract the swelling pressure of the clay.

8.2.4 Swelling Pressure

The swelling pressure in the highly compacted bentonite originates from separating flocs in the bentonite. This means that a mechanical pressure arises between the separating flocs, approximately equal to the swelling pressure. Even in low-density bentonites (wet density of 1500 kg m⁻³ / dry density of 1250 kg m⁻³ at 20% water content), a pore size in the nm range would theoretically not allow for bacterial existence unless the bacteria could withstand the mechanical pressure from the separating flocs (0.09 MPa at 1500 kg m⁻³). Prokaryotic cells can compensate for the mechanical pressure in compacted bentonite by their internal turgor pressure. Published data on turgor pressure in prokaryotic cells mention pressures between

0.08 Mpa and 2 Mpa (Potts 1994). An upper limit of 2 Mpa turgor pressure would mean that cell integrity is possible, though limited, at bentonite swelling pressures below 2 Mpa. However, bacterial endospores can survive much higher pressures.

8.2.5 Water Activity

Water is needed for active bacterial life and this water must be present externally because bacteria cannot keep water inside their cell membranes that are freely permeable for water. Bacterial spores contain very little water and are, therefore, desiccation resistant. Low water activity, a_w, in clays may inactivate or kill bacteria (Motamedi et al. 1996; Potts 1994). However, many bacteria survive desiccation and can be activated again when there is enough water.

There is a detailed definition of a_w in a review by Potts (1994). Briefly, the water activity of a solution is 1/100 the relative humidity of air in equilibrium with the solution (when expressed as percent). It is also equivalent to the ratio of the solution vapour pressure (P_{soln}) to that of pure water (P_{water}).

$$a_w = P_{sol}/P_{water} \tag{8-1}$$

The water activity of a solution or a solid can be determined by sealing it in a chamber and measuring the relative humidity after the system has come to an equilibrium. Several studies (Stroes-Gascoyne et al. 2010a; Dixon 2019) suggested that an a_w, <0.96 will limit bacterial activity in the compacted buffer and backfill. Many bacteria can be active at higher values, but the number of species that can be active at lower values decreases rapidly with decreasing a_w.

There is an inverse relation between water activity and suction of a bentonite clay (Dixon 2019). The total suction of a bentonite-water mixture can be calculated from the measured water activity and temperature using Kelvin's equation expressed as:

$$Total suction, \Psi = (RT/M) \ln (a_w)$$
(8-2)

where R is the universal gas constant (Jmol⁻¹K⁻¹), T is the laboratory temperature (°K), a_w is the water activity and M is the molecular mass of water. Experimental results from a recent study and from the literature demonstrated that the total suction of saturated bentonites minus the suction of the hydrating fluids used to saturate bentonites is approximately equal to the swelling pressure of saturated bentonites (Lang et al. 2019). Consequently, for bentonites saturated with a fixed TDS composition of the hydrating fluid, swelling pressure will inversely correlate with water activity. Because the proportion of montmorillonite varies between different commercial bentonites, swelling pressure and water activity will vary correspondingly over a fixed density. While water activity is difficult to measure in a closed system with compacted bentonite, swelling pressure can be measured relatively easily.

8.3 EXPERIMENTAL METHODS AND RESULTS

Pressure test cells have been used to investigate the relations between density, swelling pressure, bacterial sulfide-producing activity and culturability of SRB and other microorganisms

(such as aerobes) (e.g., Bengtsson and Pedersen 2017; Masurat et al. 2010b; Stroes-Gascoyne 2010; Motamedi et al. 1996; Pedersen et al. 2000b). Those experiments have been performed over several decades, and the methodology and conclusions have evolved over this time span. For a long period of time MX-80 was the only bentonite type studied.

For instance, Stroes-Gascoyne et al. (2010) carried out experiments (of one to three months duration) in pressure cells to determine the effects of dry density and porewater salinity on swelling pressure, water activity (a_w) and the culturable microbial community indigenous to MX-80 Wyoming bentonite. They concluded that a low a_w of ~0.96 and a swelling pressure of ~2 MPa appeared to suppress microbial aerobic culturability to below background levels (i.e., < 2.1×10^2 Colony-Forming Units/g) in as-purchased Wyoming MX-80 bentonite. They further concluded that to actually impose such conditions (an a_w of 0.96 and a swelling pressure of 2 MPa) in compacted Wyoming MX-80 bentonite in a DGR, dry density needs to be maintained at 1.6 g/cm³ or higher for porewater salinities at ≤50 g/L. High porewater salinity (100 g/L) also appeared to keep a_w at or below 0.96 and aerobic culturability below background values.

Stroes-Gascoyne et al. (2010) discussed that under their experimental conditions, microbial cells likely survived as dormant cells or inactive spores (as suggested by phospholipid fatty acid analysis, also carried out as part of this study), and that observations in natural clay-rich environments supported these findings (Fredrickson and Onstott 1996). They further concluded that interfacial locations in a DGR could form environments where (temporarily at least) the physical conditions necessary to suppress microbial activity would not always be met and that such interfaces required further study.

More recently four other bentonite clays (in addition to MX-80) were studied in Sweden at different densities and, therefore, different swelling pressures, with the purpose to capture the effects of varying clay characteristics on SRB presence and activity in bentonites. The numbers of SRB bacteria were determined with culturing, using anaerobic techniques (Bengtsson and Pedersen 2017). The SRB utilized ${}^{35}SO_4{}^{2-}$ to produce ${}^{35}S{}^{2-}$ in the clay and bacterial sulfide-producing activity was quantified as the amount of $Cu_2{}^{35}S$ that formed on copper discs in contact with the respective clays (Bengtsson and Pedersen 2017).

Bengtsson and Pedersen (2017) did not find an obvious correlation between (wet) density and amounts of $Cu_2^{35}S$ produced, nor could a specific density be identified at which the sulfideproducing activity diminished, when comparing these five clays. Because of the differences in mineral compositions between these clays, it is not surprising that the swelling pressure was different for each clay at a specific density. Swelling pressure within water-saturated bentonite materials is primarily affected by montmorillonite (smectite) content, clay density and the salinity of the permeating fluid (Dixon 2019). The clays investigated by Bengtsson and Pedersen (2017) varied in montmorillonite content from 66 to 82%. When working with one specific clay, dry density and microbial activity can be correlated (Stroes-Gascoyne et al. 2010a; Dixon 2019).

When Bengtsson and Pedersen (2017) plotted the amounts of $Cu_2^{35}S$ analyzed versus swelling pressure, there was a clear decrease in sulfide-producing activity at swelling pressures above 700 – 800 kPa., Swelling pressure in confined clays is caused by the electrically charged particles in the clay which repulse each other and try to get apart by adding water (suction). This water is very tightly bound and reduces the relative humidity in the clay, which in turn affects microbial viability and activity by holding tight on to water and perhaps even sucking it out of microbial cells. It is known that swelling pressure relates to water activity and has a direct impact on microbial activity (Dixon 2019; Stroes-Gascoyne et al. 2010; Motamedi et al. 1996). According to the data presented by Dixon (2019) and equation 8-2, a swelling pressure (suction)

of 1 MPa corresponds to a water activity of just less than 0.99. However, the TDS of the saturation fluids and the minerals that dissolve from the clay to pore water will contribute to the total suction as well. Consequently, swelling pressure and TDS in the bentonite pore water will increase with density in the clay.

Bengtsson and Pedersen (2017) concluded that, while there was a fairly well defined swelling pressure of <1MPa and also an upper wet density around 1800 kg/m³ (corresponding to 1200 kg/m³ dry density) that impeded microbial activity, some culturability of SRB was observed in their experiments to a wet density of 2000 kg/m³ (corresponding to 1560 kg/m³ dry density and a swelling pressure approaching 5 MPa). However, the overall culturability of SRB cultured from the five clay samples decreased with wet density and above a wet density of 1850 kg m⁻³ (corresponding to a dry density of about 1300 kg/m³), the bacteria that could be cultured were predominantly from samples to which bacteria had been added in the experiments. This suggested that the indigenous culturable SRB populations in the five bentonites tested largely were inactivated in the experiments with wet densities over 1850 kg m⁻³/ dry densities over 1300 kg m⁻³.

The experiments were carried out for a duration of two months and it could be argued that culturability will decrease over time. However, in the FEBEX experiment in Switzerland, bacteria could be cultured from highly compacted bentonite after 18 years since installation of the FEBEX experiment (Bengtsson et al. 2017c) which indicated that bacteria indigenous to clay can stay viable for long times in buffer and backfill. Bengtsson and Pedersen (2017) concluded that microbial activity in compacted bentonite will diminish as water activity drops below 0.96, as was concluded by Dixon (2019) but that some culturability may remain below a water activity of 0.96 as indigenous SRB can survive in commercial bentonites (Haynes et al. 2018; Lopez-Fernandez et al. 2015; Masurat et al. 2010). Thus, although low water activity prevents growth of indigenous microbial species, they are not killed; when water activity rises above 0.96, some growth is possible.

Jalique et al. (2016) describe the microbial analysis of an eight-year old highly compacted Wyoming MX-80 bentonite plug. They concluded that the results of this longer-term study validated the earlier, short-term findings of (Stroes-Gascoyne et al. 2010a) wherein highly compacted Wyoming MX-80 bentonite having an average dry density of \geq 1600 kg/m³, a swelling pressure of \geq 2.00 MPa, and an a_w of \leq 0.96 suppressed microbial culturability to at, or below, background levels, and appeared to select for Gram positive bacteria, including spore-formers. These presumably only became metabolically active when the inhibitory conditions imposed by the highly compacted bentonite were removed (i.e., during culturing). They further concluded that, provided that these inhibiting conditions are maintained, the viability of indigenous organisms would be expected to decline over the very long DGR-relevant time-scale, ultimately reaching a point where viable cells may no longer be recovered.

8.4 POREWATER CHEMISTRY AND REDOX PROCESSES IN BENTONITE

8.4.1 Chemistry and Redox Processes in Bentonite Porewater

The chemistry and redox processes in bentonite porewater have been investigated on different scales, from a laboratory scale with a few grams of clay to full scale prototype repository environments. The chemistry of the full-scale Prototype repository at Äspö Hard Rock Laboratory (Sweden) was studied for a period of 14 years, from planning of the investigations to

finalization of methods and interpretations. The project was carried out at the Äspö Hard Rock Laboratory (HRL) in crystalline rock at a depth of approximately 450 m. The prototype repository (hereafter, "Prototype") was an international project in which a full-scale model of the planned Swedish final repository for spent nuclear fuel was built and studied (Johannesson et al. 2007). The bentonite used was Na-bentonite MX-80. The Prototype differed from a real repository in that it was drained, which made the swelling pressure lower in the Prototype than in a real repository. The heat from radioactive decay was simulated by electrical heaters. The evolution of the water chemistry, gas content and composition, and microbial activity at the site were monitored with a special focus on monitoring the *in situ* microbial consumption of oxygen in the Prototype (Puigdomenech and Pedersen 1999). The results of the analyses of microbes, gases, and chemistry inside the Prototype have been presented in a series of reports over a decade (2000 – 2010) (Lydmark 2011).

The results from the Prototype investigations provided a good understanding of how chemistry, including gases, may evolve in a repository. These gases (i.e., hydrogen, helium, nitrogen, oxygen, carbon monoxide, carbon dioxide, methane and ethane) were analyzed at 16 sampling points in the Prototype. Samples from points that delivered pore water were analyzed for microbial activity, including analyses of the amount of ATP (i.e., the energy currency of active microorganisms), culturable heterotrophic aerobic bacteria (CHAB), SRB, methane-oxidizing bacteria (MOB), and iron-reducing bacteria (IRB). The pore water collected from the Prototype was subject to as many chemical analyses as the amount of water in the samples allowed. Chemical data from a previous investigation of the groundwater outside the Prototype were compared with the pore water chemistry. The results of the sampling and analysis revealed that many of the hydrochemical sampling points differed greatly from each other. The 16 sampling points were, therefore, divided into seven sampling groups, each with similar properties. The properties of one sampling group resembled those of the original groundwater composition, while others differed, for example, in microbial composition, salinity, sulfate content, and the concentrations of calcium, potassium, magnesium, sodium, and many dissolved metals, actinides, and lanthanides.

The gas composition in the sampling groups showed a uniform trend in that the proportion of nitrogen in the extracted gas was increasing while the oxygen content was decreasing with time. The chemical data indicated differences between the sampling groups. For instance, the concentrations of sodium and potassium were higher in the Prototype pore water than in the groundwater outside it, while the calcium concentration was lower than in the groundwater, indicating the occurrence of cation exchange in the montmorillonite interlayers. At sampling points containing active microbes, metals such as copper, rubidium, vanadium, and uranium were enriched up to 225 times the groundwater levels, possibly because of the excretion by microbes of compound-specific ligands. Overall, the observations strongly supported the hypothesis that the oxygen initially present in a repository will be consumed by bacteria within a short period (i.e. weeks to years), as opposed to much longer times associated with abiotic processes, such as mineral oxidation (i.e., many years). The gas data generally indicated that oxygen was disappearing and that methane-oxidizing bacteria were responsible for at least some of this decrease in oxygen. The microbes also affected the chemistry in the Prototype, both indirectly (by being active and changing the redox and pH) and possibly directly (via compound-specific ligands).

The Prototype project illustrated in many ways the challenge of investigating the pore water chemistry and physical parameters in a water-saturated bentonite buffer. It is very difficult to extract pore water from water-saturated bentonite because of the strong suction that occurs in the bentonite as long as it is not fully saturated. Pressure in excess of the ambient swelling

pressure must be applied to squeeze pore water out of the clay and this must be done in a closed compartment (Järvinen et al. 2018), which is very difficult to do in a full-scale repository prototype. Alternatively, small scale laboratory scale experiments can be performed to obtain information about pore water chemistry, including pH and Eh.

Porewater compositions for compacted bentonite often come from modelling studies (e.g., Fernández et al. 2004; Ochs et al. 2004; Wersin 2003; Wersin et al. 2016). The pore water chemistry as well as the chemistry of external water are influenced by the density of the clay, as demonstrated by Muurinen and Lehikoinen (1999). The hydrating water will have a large influence on the chemistry of free pore water in compacted bentonite-based buffer or backfill (Muurinen et al. 2004). Bradbury and Baeyens (2003) calculated pore water compositions in compacted bentonites, taking into consideration factors such as montmorillonite swelling, semi-permeable membrane effects, very low "free water" volumes, and the highly effective buffering characteristics of the exchangeable cations and the amphoteric edge sites. Subsequently, these authors experimentally tested their modelling (Bradbury and Baeyens 2009). They found that the initial pH of the pore water in highly compacted MX-80 bentonite is 8, and that the amphoteric edge sites on the montmorillonite provided an extremely powerful buffering effect that resisted strongly any change to this initial value by the water chemistry of the hydrating water. A pore water pH of 8 appears to be a good approximation for MX-80 bentonite, based on the work by Bradbury and Bayens (2003, 2009).

An interesting approach to study the interactions between the external and internal water chemistry of compacted bentonite was reported recently (Maanoja et al. 2020). Microbial activity was studied in a unique experimental setup with microorganisms growing on a porous sand layer interconnected with compacted bentonite. Results showed that organic matter, sulfate, and iron, among other compounds, dissolved from the compacted bentonites into the sand layer water. The set-up resembled the interface between compacted buffer or backfill material and a porous adjacent environment. Fredrickson et al. (1997) observed similar transport effects in a geological environment when studying a Cretaceous shale-sandstone sequence in northwest New Mexico.

A promising approach to analyzing pore water pH and Eh is to use electrodes inserted in compacted bentonite buffer. Muurinen and Carlsson (2007, 2010) developed and tested a successful *in situ* on-line method for studying the chemical conditions in compacted water-saturated bentonite. They showed that a change in the gas conditions outside the compacted clay was reflected quickly as a change in the Eh inside the bentonite, but only to a depth of 5 mm from the surface in a sample that was moved from anaerobic to aerobic conditions. After eight months of interaction, it appeared that the change in Eh was buffered by some chemical reactions and did not quickly progress deeper into the bentonite.

Taken together, the work discussed above demonstrated clearly that the pH and Eh in free pore water of compacted bentonite depend on the type of bentonite, its buffering capacity and the external conditions.

8.4.2 Bacterial Sulfide Production in Bentonite Porewater

Two factors determine the possibility of sulfide production via sulfate reducing bacteria (SRB) in buffer and backfill:

- 1. Presence of sulfur species that can be used as electron acceptors by SRB under anaerobic conditions.
- 2. A sufficiently high-water activity. This has been experimentally shown to be 0.99 and above by Pedersen and others; although the value of 0.96 or greater is more widely accepted, as water activities below 0.96 suppress nearly all microbial growth.

Sulfide producing bacteria reduce sulfur species to sulfide in their respiratory processes. Elemental sulfur does not dissolve in porewater; therefore, sulfur-reducing bacteria must be in contact with solid sulfur in the clay. Sulfate on the other hand is readily dissolved in water. While elemental sulfur can originate from sulfide oxidation in the clay, dissolved sulfate can originate either from the hydrating groundwater, or from minerals such as gypsum in the clay, or both.

Sulfate is present in both the types of reference groundwater (CR-10 and SR-270) in concentrations of 1200 to 1800 mg/L (Table 3-1). This sulfate will enter the swelling bentonite with the hydrating groundwater and introduce sulfate as well as all other dissolved species in the hydrating groundwater. In addition, there is soluble sulfate in the MX-80 bentonite itself that can add to the sulfate entering with the groundwater. Approximately 2100 mg sulfate/kg dry weight could be analyzed in MX-80 bentonite (Bengtsson and Pedersen 2017). This is close to the 3000 mg/kg that was found in porewater from MX-80 after exposure to groundwater at depth in the Äspö Hard Rock Laboratory (HRL) (Oskarshamn, Sweden) (Järvinen et al. 2018). During the Äspö experiment, the MX-80 bentonite was exposed to groundwater and this changed the porewater composition, among other things by increasing the sulfate concentration.

The ionic strength of the porewater in bentonite will influence its water activity. The ionic strength in MX-80 porewater is approximately 0.3 M (Muurinen and Lehikoinen 1999a). After exposure of MX-80 at the Äspö HRL to groundwater during the Alternative Buffer Experiment (ABM) (Svensson et al. 2011), the ionic strength had increased to 0.45 M (Järvinen et al. 2018) which corresponds to 25 g TDS/L. The hydrating water contained 14.5 g TDS/L. Therefore, infusion of hydrating groundwater water increased the TDS of the porewater in the MX-80 bentonite significantly. For very saline hydrating groundwater, ion exclusion in the clay may mitigate the rise in pore water TDS (Muurinen and Lehikoinen 1999a).

According to Dixon (2019) water with a TDS of 25 g/L would correspond to an a_w of 0.98. The MX-80 in the ABM experiment had a swelling pressure of just above 1 MPa. As discussed previously, that would correspond to a decrease in a_w of 0.01 in MX 80. The total suction caused by the swelling pressure and the TDS then corresponded to an a_w value of 0.97. During the ABM experiment, analyses of SRB were performed. According to the $a_w = 0.96$ limit for bacterial activity, it should have been possible to detect SRB in the MX-80 bentonite which was the case (Svensson et al. 2011). However, more recently, Vachon *et al.* reported microbial community profiles of initial clay DNA extracts were not dominated by SRB (Vachon et al. 2021).

In summary, swelling pressure and the amount of TDS likely can be used to predict if SRB can be active in bentonite and backfill. If the total suction created by the swelling clay and the amount of TDS after water saturation corresponds to an a_w of 0.96 or less, sulfide production in the clay is unlikely to occur.

9. MODELLING OF SULFATE AND SULFIDE FLUXES IN BUFFER AND BACKFILL

Modelling of sulfate and sulfide transport in bentonite-based buffer and backfill requires the development of numerical models and reliable values for diffusion rates that must be determined experimentally.

9.1 MODEL CONCEPT

Conceptual and numerical models of the fate of sulfide in the near-field need to be developed to quantify the different processes concerning sulfide production, transport and consumption (King et al. 2020). Posiva and SKB carried out a collaboration between 2014 and 2018 with as main goal the assessment of copper corrosion of the canisters in a KBS-3V repository design, due to the presence of sulfide. The collaboration was named the Integrated Sulfide Project (ISP) and comprised three different Work Packages: sulfide processes in the geosphere; sulfide processes in buffer and backfill; and modelling of the processes or fluxes of sulfide in the near field of a spent nuclear fuel repository. Aspects of the modeling are presented below.

Separate reactive transport models were developed to simulate the sulfide flux and evolution (sources and sinks) within different parts of a repository including the canister, buffer, rockbackfill interface and rock bolts (Idiart et al. 2019; Wersin et al. 2017). A Base Case where sulfate reduction through bacterial activity takes place only in the rock-bentonite interfaces was used in an inter-comparison and partial verification exercise(King and Kolář 2019). Furthermore, a series of Variant Cases were established to test the capabilities of the different modelling strategies implemented in the modelling tools developed (Pękala et al. 2019). The agreement between the results from these teams was reasonable, considering the significant differences between the modelling tools. Therefore, the expectation of developing tools that can provide future safety analyses with integrated models for sulfide corrosion that can replace the uncoupled or loosely coupled models used until now, may be considered at least partly achieved.

A new conceptual model was developed for reactive transport in compacted bentonite in order to assess the fate of sulfide in the near-field of a KBS-3V repository system (Idiart et al. 2019). The motivation to develop such a model was that recent experimental findings have demonstrated that interlayer pores often dominate the diffusional transport capacity in bentonite (Arcos et al. 2000; Idiart et al. 2019). In contrast, many traditional approaches to modelling bentonite chemistry treat the interlayer pores as cation exchange sorption sites that have no transport capacity. Consequently, there was a need for developing a model that takes the transport capacity of the interlayer pores into account. The model was limited to diffusion and reaction processes in water-saturated compacted bentonite. In the model, diffusion occurs exclusively within the interlayer water, while geochemical reactions - including interaction with accessory minerals - were restricted to a disconnected bulk water phase embedded in the bentonite system. Ion equilibrium (i.e. Donnan equilibrium) was maintained at all times between the interlayer and bulk pore solutions. Generally, the use of this hybrid model to simulate reactive transport in the system under study had a small effect on the results as compared to the traditional modelling approach. The general trend in the results from this model was that considering transport through interlayer pores, instead of through bulk porosity, predicted slightly reduced mackinawite precipitation and increased sulfide fluxes reaching the canister, and thus increased canister corrosion. Depending on the simulation case, container corrosion increased by a factor of 4 or decreased by 12% when using this hybrid model as compared to a traditional reactive transport model (Pekala et al., 2018). The model developed by Pekala et al. (2018) predicted that the effect of hydrogen generated by anaerobic carbon steel corrosion is small and limited to the initial several thousand years (Pekala et al. 2018). Similarly, calculations considering local buffer loss indicated that the effect would be negligible on the scale of tens of thousands of years. The model also suggested that the presence of single discrete fractures intersecting a deposition hole would likely have a small to negligible effect on the calculated sulfide flux to the canisters. The biggest impact on container corrosion was predicted for a theoretical case, where SRB activity in the backfill coincides with siderite (FeCO₃) absence in the backfill, which would prevent precipitation and immobilization of sulfide resulting from SRB activity in the backfill. The team concluded that the main challenges with this model included the characterization of in-situ microbial activity rates, the kinetics and solubility/bioavailability of solid and dissolved organic matter, the reactivity of iron-bearing minerals (not considered in the model), pH buffering processes and the transport properties of the rock-clay interface

9.2 EXPERIMENTALLY DETERMINED DIFFUSION COEFFICIENTS FOR SULFIDE AND SULFATE IN COMPACTED BENTONITE

As discussed above, sulfate is needed for bacterial production of sulfide in buffer, backfill and elsewhere. After water saturation of buffer and backfill is reached, both sulfate and sulfide move by diffusion only in the bentonite. However, data for the effective diffusion rate (D_e) of sulfide in compacted, water saturated bentonites in the literature are limited. The D_e for sulfide in 1750 kg m⁻³ wet density bentonite was estimated to be in the order of 7×10^{-12} m² s⁻¹ by King et al. (2011). Eriksen and Jacobsson (1982) determined a D_e for sulfide in the order of 9×10^{-12} m² s⁻¹ for MX-80 at 2100 kg m⁻³ wet density. The D_e for sulfide in compacted bentonite was estimated to be 1.26 × 10⁻¹¹ m⁻² s⁻¹ at 1745 kg m⁻³ wet density and 2.19 × 10⁻¹² m⁻² s⁻¹ at 2004 kg m⁻³ wet density for MX-80 (Lee et al. 2012). Pedersen (2010) calculated D_e values for H³⁵S⁻ in compacted Wyoming MX-80 bentonite from experiments in which the activity of SRB was studied. The D_e in Wyoming MX-80 at a wet density of 2000 kg m⁻³ was calculated to be 2 × 10⁻¹² m² s⁻¹ and 1.2 × 10⁻¹¹ m² s⁻¹ at 1750 kg m⁻³ wet density. The difference between the calculated values quoted above may be due to differences in experimental conditions.



200 µmole HS⁻/gdw clay

Figure 9-1: Transport of two different amounts of sulfide added to bentonite clays (2000 kg m⁻³ wet density) after 90 days of water saturation.

Bengtsson and Pedersen (2016) used a diffusion method developed for Boom clay to determine the D_e coefficient for sulfide (${}^{35}S^{-2}$) in a number of different bentonites. For Asha bentonite, compacted to saturated wet densities of 1750 kg m⁻³ and 2000 kg m⁻³, the D_e coefficients for sulfide (${}^{35}S^{-2}$) were determined to be 2.74×10⁻¹¹ m² s⁻¹ and 6.60×10⁻¹²m² s⁻¹, respectively. When the diffusion experiment was repeated with Calcigel, the added ${}^{35}S^{-2}$ did not come through the clay, likely because Calcigel immobilized all added ${}^{35}S^{-2}$. In these tests , blackening due to FeS formation clearly demonstrated how the sulfide diffused mainly in a front until exhausted, Figure 9-1.

9.3 CONTROL OF SULFIDE LEVELS BY IRON SULFIDES

9.3.1 The Thermodynamic View

The sulfide concentration in anaerobic natural waters is often controlled by iron sulfide minerals (Lemire et al. 2020). A number of different phases exist, exhibiting a range of solubilities, from the most soluble amorphous iron sulfide (FeS) to more stable crystalline pyrite (FeS₂). In this section, solubilities are considered in terms of their solubility product (Ksp), which is defined below. The relevant solubility data within a number of key thermodynamic databases were reviewed and summarised. For greater detail, the most recent Nuclear Energy Agency (NEA) Chemical Thermodynamics publication (Lemire et al. 2020) provides a comprehensive evaluation of iron sulfide phases, including their mineralogical and thermodynamic properties. The solubility product is an equilibrium constant representing the dissolution reaction of a mineral phase. It is the mathematical product of the dissolved ion activities (effective concentrations) raised to the power of their stoichiometric coefficients. For a solid phase A_xB_y, the dissolution reaction can be defined as:

$$A_x B_y = xA + yB \tag{9-1}$$

and the solubility product as:

$$K_{sp} = \{A\}^{x} \{B\}^{y}$$
(9-2)

where {A} and {B} are the activities of A and B in a saturated solution, i.e. when the solution is in equilibrium with the solid phase.

The smaller the Ksp, the lower the solubility of the solid phase. Solubility products can vary over many orders of magnitude and, therefore, are usually quoted in logarithmic form, i.e., log Ksp. The solubility products for iron sulfides are not always defined consistently, with some researchers defining the dissolution reaction as forming $H_2S_{(aq)}$:

$$FeS(s) + 2H^{+}(aq) = Fe^{2+}(aq) + H_2S(aq)$$
(9-3)

and others via the formation of HS⁻:

$$FeS(s) + H^{+}(aq) = Fe^{2+}(aq) + HS^{-}(aq)$$
(9-4)

The Nuclear Energy Agency (NEA) (Lemire et al., 2013) presents a summary of FeS solubility products defined in the form of Equation 9-3, whereas thermodynamic databases including ThermoChimie (Giffaut et al., 2014) define the reactions in the form of Equation 9-4. In this report, all log Ksp values are defined by Equation 9-4.

The term amorphous iron sulfide is used to define poorly ordered FeS precipitated directly from solution. It has no crystal structure and is assumed to have a 1:1 Fe:S ratio. The solubility product for this phase was originally calculated from experimental data by (Berner 1967), with log K_{sp} = -3.915. Davison, (Davison 1991) recalculated a value of log Ksp = -2.95 ±0.08 from the work of (Berner 1967). The solubility of this phase may be affected by the method of preparation and, therefore, the error limit may be larger than stated. More recent studies have defined this phase as a disordered, nanocrystalline form of mackinawite (Lemire et al. 2020).

Mackinawite (FeS) is a tetragonal iron sulfide. Berner (1967) determined mackinawite solubility where equilibrium was approached via under- and over-saturation with log Ksp = -4.648; this was also updated by Davison (1991). Subsequent experimental work by Benning et al. (2000) shows good agreement with the log Ksp value calculated by Davison (1991), i.e., -3.6 and -3.83, respectively (Table 9-1).

Although troilite and pyrrhotite are reported to be relatively rare at ambient temperatures in natural environments, pyrrhotites have been observed experimentally and troilite is found in strongly reducing conditions, and, therefore, it may be relevant under specific repository conditions that are extremely reducing. The pyrrhotite group is made up of many forms and is often expressed as $Fe_{1-x}S$. The two main subgroups are hexagonal pyrrhotites, which are iron-rich formations, $Fe_{10}S_{11}$, and the monoclinic pyrrhotites which have an approximate composition of Fe_7S_8 . Troilite is considered the stoichiometric end member, sometimes denoted FeS_t . Their thermodynamic properties are summarised in Table 9-1.

Greigite is a tetrahedral and octahedral mixed Fe(II/III) sulfide (Fe₃S₄) that forms from mackinawite. It is associated with freshwater systems (Rickard and Luther 2007a), but is generally considered to be metastable, existing as an intermediate phase during mineral transformations (Lemire et al. 2020). Mackinawite can transform to greigite via a solid-state mechanism due to their similar structures (Hunger and Benning 2007). The solubility of greigite is poorly known. The only direct solubility measurements were completed by Berner (1967) and subsequently recalculated by Rickard and Luther (2007) to give a value of log Ksp = -12.84. Mackinawite and greigite are considered intermediates on the pathway to pyrite formation and are also considered metastable under some environmental conditions. Greigite is considered metastable under some environmental conditions. Greigite is not listed as a solid phase within the ThermoChimie database.

Pyrite (FeS₂) is the most common sulfide mineral in natural environments and exhibits a cubic NaCI-type structure. The solubility of pyrite is extremely low and, therefore, has not been measured experimentally. Values for its solubility are based on the standard Gibbs free energy of formation, ΔG_f , from the reaction components.

For the reaction:

$$FeS_2(s) + 2H^+(aq) + 2e^- = Fe^{2+}(aq) + 2HS^-(aq)$$
(9-5)

the corresponding log Ksp is proposed to be between -15.79 (Davison 1991) and -18.50 (Hummel et al. 2002) with the electron concentration defined using the electron activity (pe). Table 9-1 summarises the solubility constants (log Ksp) for iron sulfide phases including those contained in the ThermoChimie database (Giffaut et al. 2014) and the PHREEQC database (PHREEQC Version 3.5.0, PHREEQC.dat, (Parkhurst and Appelo 2013). In general, the values used in the ThermoChimie database are based on the review by Davison (1991), and work by Bard et al. (1985) whereas the values used in the PHREEQC database are based on the older studies by Berner (1967) and Robie and Waldbaum (1968).

The log Ksp values presented for mackinawite are for the bisulfide (HS⁻) reaction (Equation 9-4). A number of sources define the solubility product using the H₂S reaction (Equation 9-3) and for these, marked with an asterisk in Table 9.1, the value has been converted using the first dissociation constant for H₂S, pK₁(H₂S) quoted in the original source. Part 1 of the NEA review of iron data (Lemire et al., 2013) considered a range of studies on mackinawite and proposed a log Ksp = 3.8 ± 0.4 (converted here to -3.19 ± 0.4). Part 2 of the review (Lemire et al. 2013) considered this and other iron sulfide phases in more detail but recommended the same mackinawite solubility value as proposed in Part 1.

Mineral	log Ksp	Database	Comment	Reference	Reaction
FeS(am)	-2.95	ThermoChimie		Davison, 1991	FeS+ H ⁺ →Fe ²⁺ +HS ⁻
	-3.00 ±0.12		I = 0.1 M, 20°C	Davison et al, 1999	
	-3.915	PHREEQC		Berner, 1967	
Mackinawite (FeS)	-3.19* ±0.4		$\label{eq:linear} \begin{array}{l} I=0\ M,\ 25^\circ C\\ \\ Conversion\ from\\ FeS+\ 2H^+\rightarrow Fe^{2+}+H_2S\\ (logK_{sp}=3.8\pm0.4)\ using\\ pK_{1H2S}=-6.99 \end{array}$	Lemire et al, 2013	

Table 9-1: Solubility product constants for selected iron sulfide minerals

Mineral	log Ksp	Database	Comment	Reference	Reaction
	-3.60	ThermoChimie		Davison, 1991	
	-3.77*		I ≈ 0.3 M, 25°C Conversion from FeS+ 2H ⁺ → Fe ²⁺ +H ₂ S (logK _{sp} = 3.21) using pK _{1H2S} = -6.98	Benning et al, 2000	
	-4.648	PHREEQC		Berner, 1967	
Troilite (FeS)	-5.31	ThermoChimie		Davison, 1991	
Pyrrhotite (Fe _{0.87} S)	-5.67	ThermoChimie		Robie and Hemingway, 1995	Fe _{0.87} S+ H ⁺ + 0.26e ⁻ → 0.87Fe ²⁺ +HS ⁻
Greigite (Fe ₃ S ₄)	-12.84		Recalculated from Berner, 1967	Rickard and Luther, 2007	Fe_3S_4 + 3H ⁺ → 0.87Fe ²⁺ +HS ⁻
Pyrite (FeS ₂)	-15.79	ThermoChimie	Based on compilation Bard et al., 1985	Davison, 1991	FeS ₂ → Fe ²⁺ - 2H ⁺ - 2e ⁻ + 2HS ⁻
	-18.479	PHREEQC		Robie and Waldbaum, 1968	
	-18.50			Hummel et al., 2002	

From the solubility products of stoichiometric iron monosulfides (FeS) it is possible to calculate the solution HS^{-} activity as a function of Fe^{2+} activity and pH (and the redox potential, defined as pe, for non-stoichiometric iron sulfides, such as pyrrhotite or pyrite). *pe* is a non-dimensional logarithmic expression of the activity of electrons in solution (a form that is equivalent to the

expression of the activity of H^+ ions with pH). It is related to the redox potential expressed as Eh (V) by,

$$Eh = 2.3 RT \frac{pe}{F}$$
(9-6)

where R is the gas constant (8.31 J/K/mol), T is the temperature in Kelvin and F is the Faraday constant (96.49 $\times 10^3$ C/mol). At 25 °C,

$$Eh = 0.059 \ pe$$
 (9-7)

For stoichiometric iron sulfides, including FeS(am), mackinawite and troilite,

$$\log\{HS^{-}\} = \log K_{sp} - \log\{Fe^{2+}\} - pH$$
(9-8)

For pyrrhotite (Fe_{0.87}S),

$$\log\{HS^{-}\} = \log K_{sp} - 0.87 \cdot \log\{Fe^{2+}\} - pH - 0.26 \cdot pe$$
(9-9)

For pyrite (FeS₂),

$$\log\{HS^{-}\} = 0.5(\log K_{sp} - \log\{Fe^{2+}\} - 2.pH - 2.pe)$$
(9-10)

This simplified approach to calculating the HS⁻ activity in solution does not require the use of a chemical speciation code such as PHREEQC. However, it is only suitable for simple systems. It requires the activity of Fe²⁺ to be known (not just the total Fe(II) concentration). In a real solution, Fe(II) could form complexes with ligands (including hydroxide), which requires a speciation model to solve. Additionally, this method fails to account for other dissolved S(II) species that may be present and mobile, such as H₂S_(aq), FeHS⁺_(aq), etc.

9.3.2 Kinetic View

The thermodynamic principles discussed in the previous section allow the most energetically favoured state of a system to be predicted. However, in most cases, the precipitation of solid phases from solution does not proceed directly to such an equilibrium state and the time-dependence of mineral phase formation must also be considered. Ostwald's 'Phase Rule' or 'Rule of Stages' states that the least stable phase is expected to form first, because although it is the least stable, the activation barrier associated with its formation is usually lower. Over time, slow rearrangement of the solid lattice or sequential dissolution and re-precipitation results in the replacement of the less soluble structures with progressively more stable phases, but this can take time, depending on the particular system (Nývlt 1995; Cao and Cao 2014). The first phase to form (the kinetic product) is not necessarily the least stable phase that could be formed from the constituent elements. Instead, it is merely the most rapid to form. During phase transformation reactions in a system, in order for a less stable phase to form as an intermediate

before a more stable alternative, it must have sufficiently rapid formation kinetics so that it can form faster than the more stable species. This is the case for all crystalline phases. Hence, in a system where more than two phases are possible, not all will necessarily form as the system equilibrates and approaches the most stable 'thermodynamic product'.

It follows from Ostwald's Rule that highly crystalline sulfide phases may form via gradual recrystallisation of less crystalline structures, if favoured thermodynamically. Such processes also could be temperature dependent. When a solution containing Fe(II) is mixed with a sulfide solution, the initial precipitate is X-ray amorphous FeS, a highly disordered gel, which rapidly forms nanoparticulate mackinawite (tetragonal FeS). Whilst further conversion to pyrite is favoured thermodynamically under moderately reducing conditions, this process can take several months or longer, depending on the presence of an oxidizing species (Benning et al., 2000). It is possible that the conversion will not occur when only H_2S is available; mackinawite has been shown to be stable for up to four months in the absence of additional oxidants (Benning et al., 2000).

9.3.3 Formation and Dissolution of Iron-Sulfide Precipitates

Mackinawite formation

It has been suggested that two competing reactions with H₂S and HS⁻ are involved in mackinawite formation in aqueous solutions (Rickard 1995). The rate laws for both reactions are governed by the exchange of water molecules between hexaqua iron(II) sulfide outer sphere complexes and the inner sphere complexes, $FeH_2S \cdot (H_2O)_5^{2+}$ and $Fe(SH) \cdot (H_2O)^{5+}$, with the subsequent nucleation of FeS happening very quickly.

The equation for the H_2S reaction is given by:

$$Fe^{2+} + H_2S \rightarrow FeS_m + 2H^+ \tag{9-11}$$

where FeS_m denotes the mackinawite form of iron monosulfide.

The rate law for this reaction is given by:

$$\frac{\partial [FeS_m]}{\partial t} = k_1 \{Fe^{2+}\}\{H_2S\}$$
(9-12)

where {Fe²⁺} and {H₂S} are activities and k_1 is the rate constant, where log $k_1 = 7 \pm 1 \text{ L mol}^{-1}\text{s}^{-1}$ (Rickard 1995).

The reaction with HS^{-} involves the formation of an intermediate complex, $Fe(SH)_2$, which then forms FeS_m (Rickard 1995).

$$Fe^{2+} + HS^- \rightarrow FeS_m + H^+$$
 (9-13)

The rate of this reaction can be described as:

$$\frac{\partial [FeS_m]}{\partial t} = k_2 \{Fe^{2+}\} \{HS^-\}^2$$
(9-14)

where {Fe²⁺} and {HS⁻} are activities and k_2 is the rate constant, where log $k_2 = 12.5 \pm 1 L^2$ mol⁻²s⁻¹, as defined by (Rickard 1995).

The competing reactions for mackinawite precipitation are dependent on pH and total sulfide concentrations in natural environments (Rickard and Luther 2007a). In sulfide rich conditions (total sulfide concentrations \geq micromolar), the rate of sulfide removal is double in neutral to alkaline conditions compared to acidic environments. The HS⁻ pathway dominates at pH > 7. This is reversed in sulfide-poor conditions where the rate is greater in neutral to acidic conditions and the H₂S pathway dominates where pH < 8.

Mackinawite dissolution

The rate of mackinawite dissolution was investigated by Pankow and Morgan (1979) and the results of their study suggested a first-order dependence on the concentration of H⁺ in acidic solutions and a constant, pH-independent rate in neutral to alkaline solutions.

$$\frac{-\partial FeS_m}{\partial T} = k_1[H^+] + k_2 \tag{9-15}$$

where [H⁺] is the hydrogen ion concentration (mol cm⁻³), $k_1 = 0.18 (\pm 0.06)$ cm min⁻¹ and $k_2 = 1.9 (\pm 0.9) \times 10^{-9}$ mol cm⁻² min⁻¹. At pH lower than ~4.3 the k_1 term is dominant, and there is a transition stage between pH 4.3 and pH 5.6 as k_2 becomes more dominant. The k_2 term is the controlling rate constant at pH >5.7 (Pankow and Morgan 1979).

Pyrite formation

Pyrite precipitation often proceeds via mackinawite. Two formation pathways are known: the polysulfide pathway and the H₂S pathway. The polysulfide reaction:

$$FeS + S(0) \rightarrow FeS_2$$
 (9-16)

where FeS corresponds to a solid iron monosulfide phase, in this case mackinawite. S(0) corresponds to polysulfide or elemental sulfur(Rickard and Luther 2007a). This pathway is favoured under high pH, higher redox potentials and higher polysulfide concentration. Rickard (1975) showed that the rate of pyrite formation was controlled by the concentration of polysulfides, increasing as the concentration of polysulfides increases. Rickard (1975) also found that the rate of pyrite formation is first order with respect to polysulfide concentration and second order with respect to FeS surface area.

$$\frac{\partial [FeS_{2p}]}{\partial t} = kA_{FeS}^2 A_{S(0)} \{S(-II)\}_T \{H^+\}$$
(9-17)

where FeS_{2p} denotes pyrite, A_{FeS} and $A_{s(0)}$ are the surface areas of FeS and S(0) respectively (in cm²), {S(-II)}_T is the total dissolved sulfide activity (H₂S, HS⁻, S²⁻) and {H⁺} is the hydrogen ion activity. It has been proposed that pyrite formation from FeS involves a dissolution-recrystallization pathway between 25 and 100 °C (Rickard 1997). At temperatures >100 °C it has been suggested that the reaction occurs via solid-state transformation through the intermediate greigite (Hunger and Benning 2007).

In the second pathway H₂S is the oxidant:

$$FeS + H_2S \rightarrow FeS_2 + H_2 \tag{9-18}$$

The generation of hydrogen is associated with progressively reducing conditions, and the dissolved H₂ concentration increases with decreasing E_h (or pe). Consequently, under strongly reducing conditions, FeS phases (mackinawite, troilite) may be thermodynamically favoured over pyrite. One problem with the H₂S pathway is that the mass balance which is achieved by the production of H₂ has never been demonstrated experimentally. Although H₂ has been detected (Wikjord et al. 1976; Rickard 1997), the quantities predicted by mass balance have never been recovered at low temperature (<100 °C). There are several possible explanations: for example, escape from the experimental set-up; reaction with other system components; and it is possible that the reaction mechanism at low temperature is dominated by the polysulfide pathway.

The rate in the H_2S pathway is dependent on the concentration of H_2S , however this concentration is also linked to the total sulfide concentration (S(-II)), which makes it indistinguishable from the rate determining concentrations of the polysulfide pathway (Rickard 2012). The lack of recovery of H_2 in this system has minimal impact on the understanding of the mechanism and kinetics of the reaction pathway, however it would be useful information, as H_2 can be used by microorganisms as a metabolite in the deep subsurface.

By combining Equation 9-17 and Equation 9-18 Rickard and Morse (2005) were able to define an overall rate of pyritization where the total rate is given by the sum of the rate laws for H_2S and S(0) reactions.

$$\frac{\partial [FeS_{2p}]}{\partial t} = k_{H_2S}[FeS][H_2S] + k_{S_n(-II)}[FeS]^2 [S(0)][S(-II)]_T[H^+]$$
(9-19)

where the rate constants k_{H_2S} and $k_{S_n(-II)}$ are experimentally measured rate constants for the H_2S and polysulfide reaction pathways, respectively. The surface area terms used in Equation 9-17 were assumed to be directly proportional to the concentration of FeS and S(0). When applying this conversion to natural systems, it is assumed that the surface area of the natural FeS is similar to the surface area of the experimental FeS. Activity was assumed to be the same as concentration (Rickard and Morse 2005). For the H_2S pathway Rickard (1997) defined k = 1.03 x 10⁻⁴ L mol⁻¹ s⁻¹ at 25 °C.

Other studies suggested that this rate of pyrite formation is too high when only hydrogen sulfide is available as an oxidant (Benning et al. 2000). The results of Benning et al. (2000) showed that no formation of pyrite was recorded after several months of incubation with H_2S , leading the authors to suggest that high rates of formation can only be achieved when alternative oxidants are available, and that in the absence of alternative oxidants the conversion would be very slow.

Benning et al (2000) suggested that in anoxic sedimentary basins, the availability of oxidised sulfur and iron species with depth will control the degree of oxidation and that these factors will govern the rate of conversion from FeS to FeS_{2p} . The second term of Equation 9-19 becomes very small as the concentration of S(0) becomes so low as to be insignificant, and at this point the rate of pyrite formation is, therefore, determined entirely by the concentrations of FeS and H₂S. The rates of both reactions are controlled by a variety of geochemical conditions including pH, temperature, and the concentrations of sulfur species.

Pyrite dissolution

Pyrite dissolution is an important process to consider in the repository environment since the mineral is a component of some bentonites and may also be found in the host rock geology. As such, depending on the environment, pyrite has the potential to act as a source of sulfide, as well as a sink. In principle, pyrite dissolution can occur via several mechanisms including oxidative and reductive dissolution, which are discussed in further detail below. In general, the latter process does not occur, and the dissolution of pyrite is dependent on the concentration of the oxidant, pH, temperature, and pressure. In addition, the reaction is governed by the surface area to volume ratio.

Oxidative dissolution

Pyrite dissolves according to a kinetic rate law, most commonly described using the rate law from Williamson and Rimstidt (1994b). The oxidation of pyrite is controlled by the concentration of oxygen and the pH of the system and in the presence of microorganisms the rate of dissolution is increased due to the increase in pH at the pyrite surface (Fowler et al. 1999). The reaction under neutral to alkaline conditions:

$$FeS_2(s) + 3.75O_2(aq) + 3.5H_2O \rightarrow Fe(OH)_3(s) + 2SO_4^{2-} + 4H^+$$
 (9-20)

The rate of this reaction (R_{py}) is defined by:

$$R_{py}(mol \ m^{-2}s^{-1}) = 10^{-8.19(\pm 0.10)} \frac{[O_2(aq)]^{0.50(\pm 0.04)}}{[H^+]^{0.11(\pm 0.01)}}$$
(9-21)

This expression is valid over the pH range 2 to 10 and for dissolved oxygen concentrations between 0.02 and 620 mg/L (Williamson and Rimstidt 1994b). Under acidic conditions it is likely that $Fe^{2+}_{(aq)}$ would be the Fe species produced as oxidation of Fe^{2+} to Fe^{3+} and precipitation of Fe(III) minerals is less likely to occur under these conditions (King 2013).

Reductive dissolution

Reductive dissolution of pyrite is of interest as it produces sulfide and a more soluble iron sulfide mineral phase (e.g. pyrrhotite or troilite). Reduction of pyrite is known to occur under high temperatures in the presence of elevated H₂ concentrations (Lambert et al. 1980, 1998). However, the reaction is not considered significant at temperatures less than 300 °C and the process exhibits a strong temperature dependence, with an activation energy of 90 kJ/mol (Lambert et al. 1998). Investigations by Truche et al. (2010) showed reductive dissolution with H₂ (8 bar) occurring at temperatures as low as 90 °C, leading to the formation of a pyrrhotite

crust on the surface of the pyrite crystals. These experiments were undertaken using ultrafine pyrite particles, and, therefore, under repository conditions the kinetics of this reaction are expected to be much slower due to the lower reactivity of the *in-situ* pyrite and the lower temperatures expected. Although experiments have been attempted at lower temperatures (35 and 55 °C) using bacterial communities, no reduction of pyrite was observed (Hol et al. 2010). The reductive dissolution reaction is described by Lambert et al. (1998) as:

$$FeS_2 + (1-x)H_2 \to FeS_{1+x} + (1-x)H_2S$$
 (9-22)

Summary

In summary, there have been a number of studies of the reaction pathways of iron sulfide phases. The crystallisation of mackinawite from amorphous FeS occurs over several months at room temperature (Csákberényi-Malasics et al. 2012). The mechanism of the conversion and recrystallisation of mackinawite to other phases is subject to some debate, although a number of authors have defined rate equations and constants for these processes. These include the dissolution of phases, although it should be noted that all of these kinetically defined processes will occur only if there is a thermodynamic driving force for the reaction. Whilst it may be possible to utilise the rate equations to predict the time-dependence of these processes within and around a repository, caution must be applied, since the rates will be highly condition-dependent and may not be applicable outside of the conditions under which the experiments were undertaken.

When considering the solubility of sulfide produced from SRB activity, a key factor is the relative rates of sulfide generation and those of its precipitation from solution and subsequent mineral transformations. In a dynamic system in which SRB provide a continuous source of sulfide from readily available sulfate, the identity of the solubility limiting phase will depend upon the relative rates of sulfide production and the rates of conversion of amorphous FeS to crystalline forms. If the rate of sulfide production by SRB is similar to, or faster than, the conversion of FeS or mackinawite to less soluble phases, this could lead to control of sulfide production by more soluble phases (amorphous FeS or mackinawite). If the rate of sulfide production is lower, then control by pyrite might be more likely, which would in turn result in a lower sulfide concentration.

10. APPLICATION OF SOLUBILITY CALCULATIONS TO REFERENCE GROUNDWATERS

This section evaluates reference groundwater compositions for the Canadian disposal system and presents the results of chemical speciation modelling to predict the solubility of sulfide phases under relevant conditions.

10.1 GROUNDWATER DATA

To allow the calculation of sulfide concentrations at a specific repository site, the groundwater composition would need to be determined. Various reference groundwaters have been defined for both crystalline and sedimentary rock formations, based on a combination of measured and modelled groundwater data in Canadian Shield and Michigan Basin environments, respectively (Gobien et al. 2016, 2018). Groundwater compositions of this nature were proposed by Duro et al. (2010), who performed chemical speciation modelling to define charge-balanced solutions in equilibrium with a range of solid phases assumed to be present in the geosphere. These compositions are presented in Table 10-1 ('CR-10 Equilibrated') and Table 10-2 ('SR-270 Equilibrated'); as noted previously, it is expected that these references will be updated in the future with more site-specific data. However, as can be seen in Table 10-2, species such as iron are heavily impacted by the equilibration process with bentonite for highly saline conditions. This is because the system is dominated by FeCl⁺; thus, it is unlikely that variations in the minor constituents of the groundwater will affect the equilibrated concentrations, as it is overwhelmed by the affects of chloride.

The crystalline rock reference groundwater CR-10 (Table 10-1) has a moderate ionic strength of approximately 0.25 M; however the sedimentary rock reference groundwater SR-270 (Table 10-2) is extremely saline, with an ionic strength of approximately 5.8 M. This has implications for thermodynamic modelling, which are discussed further below.

Duro et al. (2010) also defined equivalent solutions representing the groundwaters after passing through a bentonite buffer and interacting with the internal carbon steel components of a used fuel container. These solutions (also given in Table 10-1 and Table 10-2) are significantly more alkaline and chemically reducing than the standard groundwaters. These 'bentonite-iron equilibration' solutions were defined in order to calculate the solubility of radionuclides released from a failed container. As such, they are less relevant to the prediction of sulfide levels prior to container failure. However, they may serve as bounding cases for the redox conditions expected within the repository environment.

It is notable that in all the reference groundwaters, sulfur is defined as sulfate only, with no sulfide included. Dissolved sulfide has not been measured in deep groundwaters in potential locations for a Canadian repository (King et al. 2017), and it is assumed that the only source of sulfide in the repository will be via the microbial reduction of dissolved sulfate. Analysis of fracture minerals in the Canadian Shield indicates the presence of calcite, quartz, chlorite and clays, but there is little evidence of the presence of sulfide minerals such as pyrite that are more commonly found in fractured geologies in Sweden and Finland (Blyth et al. 2009). Despite the uncertainty regarding the prevalence of sulfide minerals in potential Canadian host rock geologies, it is possible that low solubility sulfide minerals are present (Gascoyne and Kamineni 1994) and the correspondingly low dissolved sulfide concentrations may not be measurable, partly due to the extremely low solubilities of minerals such as pyrite and partly due

to the potential for oxidation of sulfide (both dissolved and precipitated) during sample extraction and processing (Pearson et al, 2003).

In defining the reference groundwaters, Duro et al. (2010) assumed that sulfate reduction to sulfide does not occur and that any sulfide present in solution can be easily oxidized to sulfate, if thermodynamically favoured.

Composition	CR-10 Equilibrated	CR-10 Bentonite-Iron Equilibration
рН	7.1	8.7
Environment	Reducing	Reducing
Eh (mV)	-194	-575
Element	Solutes (mg/L)	
Na	1,899	6,255
K	15	80
Са	2,217	870
Mg	60	182
HCO ₃	50	4
SO ₄	1,243	4,314
CI	6,099	6,059
Br	-	-
Sr	25	25
Li	-	-
F	2	2
	-	-
В	-	-
Si	5	10
Fe	8	7
NO ₃	1	1
PO ₄	1	1
Total	11,625	17,810
Dissolved		
SOIIOS	0.0504	0.0444
(M) (calculated in this work)	0.2501	0.3444

Table 10-1: Reference crystalline rock groundwater CR-10 (and after interaction with
bentonite buffer and steel container), (Gobien et al. 2016).

Composition	SR-270 Equilibrated	SR-270 Bentonite-Iron Equilibration
рН	6.3	8.7
Environment	Reducing	Reducing
Eh (mV)	-200	-535
Density	1.192	1.192
Element	Solutes (mg/L)	
Na	50,025	48,673
К	12,486	3,482
Са	32,494	37,285
Mg	8,173	9,940
HCO ₃	135	3
SO ₄	1,784	1,813
CI	168,058	168,744
Br	1,698	1,703
Sr	1,198	1,200
Li	5	5
F	1	1
Ι	3	3
В	80	80
Si	4	10
Fe	30	579
NO ₃	10	10
PO ₄	-	-
Total	276,184	273,531
Dissolved Solids		
Ionic Strength (mol/kg _w)	5.78	5.88

Table 10-2: Reference sedimentary rock groundwater SR-270 (and after interaction with bentonite buffer and steel container), (Gobien et al. 2018)

10.2 THERMODYNAMIC MODELLING

To investigate the potential for iron phases to control sulfide solubility is this document, modelling calculations have been performed by the National Nuclear Laboratory (NNL) in UK. These calculations predict the solubility of iron sulfides in thermodynamic equilibrium with the reference groundwaters detailed above. A limitation of this type of modelling is that it cannot predict any kinetic effects. Instead, the models predict the final, equilibrium state of the systems.

Pourbaix diagrams of simplified Fe-S systems have been generated using Geochemist's Workbench (GWB) Version 14.0.1 (Act2 module) (Bethke 2010). These diagrams show the regions of predominance for S in the presence of Fe across a range of pH and Eh. Speciation and solubility calculations have been performed using PHREEQC Interactive (Parkhurst and Appelo 2013) Version 3.5.0.14000. For both GWB and PHREEQC calculations, the ThermoChimie database (Giffaut et al. 2014) Version 10 was used

(ThermoChimie_GWB_electron.v10a and ThermoChimie_PhreeqC_SIT_electron_v10a.dat, respectively). The database contains solubility data for the iron sulfide phases given in Table 10-3. The modelling calculated the total sulfide solubility when each of these mineral phases

individually is considered to be in equilibrium with the reference groundwater compositions in Table 10-1 and Table 10-2. This is to provide a range of potential solubilities, depending on the solubility controlling phase. The identity of the solubility-controlling phase is uncertain, due to the thermodynamic and kinetic considerations discussed above.

Phase name	Reaction	Log K _{sp}
FeS(am)	$FeS_{(am)} + H^+ = Fe^{2+} + HS^-$	-2.95
Mackinawite	$FeS_m + H^+ = Fe^{2+} + HS^-$	-3.6
Troilite	$FeS_t + H^+ = Fe^{2+} + HS^-$	-5.31
Pyrrhotite	Fe _{0.87} S + H ⁺ + 0.26e ⁻ = 0.87Fe ²⁺ + HS ⁻	-5.67
Pyrite	$FeS_2 + 2H^+ + 2e^- = Fe^{2+} + 2HS^-$	-15.79

As solutions become more saline, their non-ideality must be accounted for via the use of an activity coefficient that relates the concentration of a species to its activity. A number of approaches exist to estimate the activity coefficient. The ThermoChimie database utilises the extended Debye-Hückel Specific Interaction Theory (SIT), also known as the Brønsted-Guggenheim-Scatchard model, to correct for ionic strength effects. It is claimed that this can provide adequate corrections of data up to the range of 6 – 10 M, depending on the system (Giffaut et al. 2014). However, above an ionic strength of approximately 4 M, the Pitzer model (another empirical extension of Debye-Hückel) is superior to SIT (Grenthe and Puigdomènech, 1997), but this requires a larger number of empirical parameters, which are not available for many of the important solution species considered here. As such, the SIT approach has been used in the modelling here, although it should be recognised that the predictions of the more saline SR-270 groundwaters (5.8 M) should be treated with more caution, because these are close to the limits of SIT applicability.

Figure 10-1 and Figure 10-2 show the predicted S predominance regions at 25 °C and 85 °C, respectively in a simplified Fe-S system (Fe and S chemical activities = 10⁻⁵ M, no other species present). These diagrams show what are expected to be the most thermodynamically stable sulfide phases, i.e., they do not account for any kinetic effects that may be important (in reality, the more soluble amorphous phases would be expected to form initially, see above). Also plotted are the pH and Eh conditions of the four reference groundwaters for CR-10 and SR-270 given in Table 10-15 and Table 10-2. The CR-10 and SR-270 groundwaters are circum-neutral to moderately acidic and moderately reducing. At 25 °C the CR-10 solution is on the boundary between sulfate and pyrite predominance, whereas the SR-270 solution is within the pyrite stability region. The 'bentonite-iron' equilibrated solutions of CR-10 and SR-270 are more alkaline and extremely reducing, which places them in the troilite stability region, close to the boundary for the stability of water at 25 °C. At 85 °C, these highly reducing solutions are predicted to be within or close to the troilite stability region. At this higher temperature, the nonbentonite equilibrated CR-10 and SR-270 solutions are within the sulfate stability region, and sulfide would be expected to oxidise to sulfate under these conditions. However, these observations should be treated with caution - the size and position of stability regions within Pourbaix diagrams are highly sensitive to the conditions of the simulation (such as the activities of Fe, S and other solution species, and the temperature, etc.). Instead, these diagrams should be viewed as an indication that pyrite may not always be the most thermodynamically stable sulfide phase in these systems. Under ambient groundwater redox conditions, pyrite is likely to

be the most stable phase, but under more reducing conditions, fully reduced sulfide minerals $(Fe^{2+}S^{2-})$ such as troilite will be favoured over pyrite, in which the formal S oxidation state is (-1), $Fe^{2+}S_2^{2-}$. Section 9.3.3 (Pyrite formation) discusses the pathways from FeS to FeS₂ and Equation 9-17 indicates the thermodynamic favourability of FeS phases over pyrite under strongly reducing conditions. The effect of pH is more complex however, because several processes are dependent on it, i.e., the redox chemistry of sulfur, and the solubility of each sulfide phase. A computer speciation model is required to solve these reactions.



Figure 10-1: Pourbaix diagram for S in a simplified Fe-S system, 25°C. Fe, S activity = 10^{-5} M. Symbols show conditions of reference groundwaters


Figure 10-2: Pourbaix diagram for S in a simplified Fe-S system, 85 °C. Fe, S activity = 10⁻⁵ M. Symbols show conditions of reference groundwaters

Chemical speciation calculations were performed using PHREEQC to predict sulfide solubility when controlled by different iron sulfide phases under a range of conditions. All calculations were performed at 25 °C.

In the model input, the full solution compositions were specified, as defined by the reference groundwaters given in Table 10-1 and Table 10-2 Concentrations were entered as mg/L and the solution density also specified. Sulfate was entered specifically as S(VI), rather than allowing the model to partition the element between the potential oxidation states based on the redox potential, which remained fixed. Sulfide solubility was calculated as follows:

In the models, sulfide was introduced by specifying that the solution (either CR-10 equilibrated, CR-10 bentonite-iron equilibrated, SR-270 equilibrated, or SR-270 bentonite-iron equilibrated) was in equilibrium with a single iron sulfide mineral phase (either FeS(am), mackinawite, troilite, pyrrhotite, or pyrite). The model code introduces sulfide to the solution to achieve an equilibrium state (iron sulfide phase saturation index = 0) that corresponds to the Fe solution concentration given in the reference groundwater. For example, the CR-10 groundwater contains 8 mg/L Fe. The model calculates a sulfide concentration that would correspond to 8 mg/L Fe when both species are in equilibrium with the iron sulfide phase. Sulfide solubility is determined by the solubility product of the phase and the specific solution conditions. No sulfide redox reactions (conversion of S(-II) to S(VI) or vice versa) were allowed. Due to the redox potential, Fe is predicted to be present entirely as Fe²⁺ in all calculations. The model concept is shown in Figure 10-3 (left).

 Variation calculations were also performed, which were identical to those described above, except that instead of using a fixed Fe solution concentration equal to that specified in the reference groundwater, the Fe concentration was controlled by equilibrium with the siderite (FeCO₃) mineral phase, as shown in Figure 10-3(right). This was done to explore the role of Fe(II) availability in determining sulfide solubility.

Modelling performed by Nagra (Cloet et al., 2017) and SKB (Gimeno et al., 2009) to estimate copper canister corrosion in a repository environment has assumed mackinawite as the solubility limiting phase for sulfide and the sources of Fe^{2+} to be siderite (FeCO₃) in the geosphere and goethite (FeOOH) within bentonite.

Since the reference groundwaters have been defined with assumed equilibrium with relevant mineral phases, the modelling approaches adopted here assume that the Fe content of the groundwaters is supported by, i.e. is in equilibrium with, a mineral phase(s). For example, if the 8 mg/L Fe in the CR-10 equilibrated solution were not in equilibrium with an Fe-bearing mineral phase, the solution would become depleted in Fe following the introduction of sulfide (and precipitation of iron sulfide), after which, upon continued sulfide supply, sulfide concentrations would increase and no longer be solubility-limited. This would not be realistic, since Fe-bearing minerals are common in these geologies and will also be present within the bentonite buffer. Instead, the calculations assume that the Fe content of the groundwaters (e.g. 8 mg/L) is an equilibrium concentration that would be maintained (buffered) even as it precipitates with sulfide.



Figure 10-3: Thermodynamic model concept for calculating sulfide solubility based on reference groundwater compositions. Left: Fe concentration fixed according to groundwater composition. Right: Fe concentration buffered by siderite.

Figure 10-4 to Figure 10-7 present the calculated total sulfide concentration in moles/kg (which includes all dissolved sulfide species, such as $HS^{-}_{(aq)}$, $H_2S_{(aq)}$, $Fe(HS)^{+}_{(aq)}$, $S_2^{-2}_{(aq)}$, etc) with one of the following minerals present as the solubility-controlling phase: FeS(am), mackinawite, troilite, pyrrhotite, or pyrite. Note the log scale on the y-axis.

Figure 10-4 shows maximum sulfide solubility for the CR-10 equilibrated groundwater. For both sources of iron (fixed at 8 mg/L and buffered by siderite), solubility is of the order: FeS(am) >

mackinawite > troilite > pyrrhotite > pyrite, which follows the order of decreasing Ksp given in Table 10-3. In other words, pyrite is predicted to be the most thermodynamically stable phase in this system with a total maximum sulfide concentration, $[S(-II)]_{tot}$, of 1.07 x 10⁻⁹ M and FeS(am) the least stable with $[S(-II)]_{tot} = 8.95 \times 10^{-6}$ M for the fixed Fe scenario. This is consistent with the Pourbaix diagram (Figure 10-1), that indicates that the redox potential of -194 mV lies closer to the pyrite stability region than the troilite region. Dissolved sulfide would be expected to first form FeS(am), followed by conversion to the more stable phases with time. The solubilities are slightly lower for the siderite scenario (Figure 10-4).



Figure 10-4: Calculated S(-II) solubilities for several iron sulfide phases in CR-10 reference groundwater system (25 °C). Fe either fixed or buffered by siderite

Figure 10-5 shows maximum sulfide solubility for the CR-10 bentonite-iron equilibrated groundwater. Again, the two iron scenarios produce similar predicted sulfide concentrations. For this system, however, pyrite is no longer the most thermodynamically stable phase (due to the redox conditions discussed above). In this case, with iron fixed at 7 mg/L, the lowest solubility phase is predicted to be troilite (FeS), with [S(-II)]_{tot} = 1.04×10^{-9} M. Sulfide would be expected to first form FeS(am) ([S(-II)]_{tot} = 2.37×10^{-7} M), before converting to a more stable phase with time. Further conversion to pyrrhotite or pyrite would not occur, as these mixed S(-1/-2) phases are not favoured under these redox conditions.



Figure 10-5: Calculated S(-II) solubilities for several iron sulfide phases in CR-10 (bentonite equilibrated) reference groundwater system (25 °C). Fe either fixed or buffered by siderite

Figure 10-6 shows sulfide solubility for the SR-270 equilibrated groundwater. In the fixed Fe system, which has a significantly greater Fe concentration (30 mg/L) than the CR-10 groundwater (8 mg/L) shown in Figure 10-4, it might be expected that sulfide concentration would be lower. However, it is the availability of the $Fe^{2+}_{(aq)}$ species that is important, and in this highly saline solution, the aqueous Fe is dominated by $FeCl_{3}^{-}_{(aq)}$, meaning that less Fe^{2+} is available for precipitation with sulfide, despite the larger total Fe concentration. Additionally, the lower pH of this groundwater (pH 6.3) increases the solubility further, with $[S(-II)]_{tot} = 9.40 \times 10^{-3}$ M. In the simulation with Fe buffered by siderite, sulfide solubility is significantly lower for all sulfide phases, due to the greater availability of $Fe^{2+}_{(aq)}$, a result of the greater solubility of siderite at this lower pH. Due to the redox potential of this solution (-200 mV), pyrite is predicted to be the most stable phase ($[S(-II)]_{tot} = 1.59 \times 10^{-7}$ M).

Figure 10-7 shows the calculated sulfide solubilities for the SR-270 bentonite-iron equilibrated solution. Due to the extremely low redox potential (-535 mV), troilite is predicted to the most stable phase, with $[S(-II)]_{tot} = 2.75 \times 10^{-9}$ M. However, FeS(am) would form first, with $[S(-II)]_{tot} = 6.30 \times 10^{-7}$ M. This lower solubility compared to the SR-270 equilibrated groundwater is due to the greater availability of Fe²⁺ and the higher pH (8.7).



Figure 10-6: Calculated S(-II) solubilities for several iron sulfide phases in SR-270 reference groundwater system (25 °C). Fe either fixed or buffered by siderite



Figure 10-7: Calculated S(-II) solubilities for several iron sulfide phases in SR-270 (bentonite equilibrated) reference groundwater system (25 °C). Fe either fixed or buffered by siderite

10.2.1 Influence of Other Metal Ions on Sulfide Solubility

In addition to Fe^{2+} , sulfide can form stable, low solubility mineral phases with other dissolved metal ions. As a soft base, sulfide has great affinity for soft and borderline metal ions, such as Fe^{2+} , Pb^{2+} and Ni^{2+} .

The groundwater composition data above (Table 10-1 and Table 10-2) include major solution components but exclude minor components that also may be important in controlling sulfide chemistry in the geosphere. McMurry (2004) defined groundwater compositions for crystalline rock in the Canadian Shield at 50 and 750 m depth and included minor components. Table 10-4 shows the average of 18 groundwater analyses, with an average depth of about 750 m. Minor solute concentrations are derived from a subset of five groundwater analyses for which trace element data were available from this depth interval. It is notable that appreciable concentrations of both Pb ($30 \mu g/L$) and Ni ($20 \mu g/L$) were included.

The principal ore of Pb is galena (PbS), which has very low solubility (ThermoChimie log Ksp = - 14.84) and groundwaters in contact with galena deposits typically have Pb concentrations less than 10 μ g/L(Bryan 2016). Millerite (NiS) is also sparingly soluble (ThermoChimie log Ksp = - 10.13) and microcosm experiments containing elevated Ni concentrations have observed its rapid precipitation (as NiS) with sulfide arising from microbial sulfate reduction (Kuippers et al, 2018).

In the context of controlling sulfide levels within and around a deep geological repository, there must be a sufficient source of a suitable metal ion, such as Fe²⁺, Pb²⁺, or Ni²⁺, beyond that which is dissolved in solution, i.e., a mineral phase or phases that can continue to supply the solution with the metal ion as it precipitates with sulfide. The concentrations of Pb and Ni in the CS-750 groundwater are slightly higher than might be expected if they were solubility-controlled by galena or millerite, but it cannot be ruled out based on these data alone. Duro et al. (2010) propose that Pb may be solubility limited by carbonates or phosphates in the CR-10 groundwater, but not solubility controlled at all in SR-270 due to low levels of carbonate and phosphate. The authors also recognise the possibility of Pb and sulfide precipitating as galena in these systems. If the trace levels of Pb and Ni present in CS-750 (Table 10-4) were a result of equilibrium with sufficiently reactive Pb- and/or Ni-bearing mineral phases, then it may be expected that these elements could also influence sulfide solubility. Solubility calculations were performed for the CS-750 groundwater in the same manner as for the other groundwater systems. This time, however, sulfide solubility control by galena and millerite was also simulated using the solubility data from ThermoChimie.

Figure 10-8 shows the calculated total sulfide solubility for the CS-750 groundwater when solubility limited by each of the different phases. Again, the calculations have used either a fixed quantity of Fe(II) (2 mg/L), as specified in the groundwater, or a system buffered by siderite. All calculations assumed a fixed quantity of Pb and Ni (30 and 20 ppb, respectively). In the fixed Fe(II) scenario, the model cannot converge to a numerical solution for sulfide solubility controlled by FeS(am), due to its very high solubility under these conditions. A much greater range in solubility is exhibited for the different iron sulfide minerals (more than 12 orders of magnitude) compared to the CR-10 and SR-270 systems. When assuming that galena controls sulfide solubility, a total sulfide concentration of 7 x 10^{-15} M is calculated, compared to around 2 x 10^{-12} M for pyrite under these conditions. The predicted solubility of millerite is greater than that of galena or pyrite, but still lower than for the other iron sulfide phases.

In this groundwater system, sulfide control by galena would limit its solubility significantly compared to the iron sulfide phases considered above, provided there was a sufficient source of Pb²⁺. However, control of sulfide levels by Pb²⁺ is more speculative than that of Fe²⁺, since Fe(II) minerals are known to be prevalent in these environments.

Composition	CS-750		
Element	Major Solutes (mg/L)		
Na	3,080		
K	22		
Са	4,110		
Mg	60		
HCO₃	30		
SO ₄	560		
CI	11,925		
Br	55		
Sr	35		
Li	< 1		
F	2		
	< 1		
В	< 1		
Si	5		
Fe	2		
NO ₃	< 1		
PO ₄	< 1		
	Minor Solutes (µg/L)		
Vin	200		
AI	50		
За	100		
Ρ	70		
Pb	30		
Ni	20		
Cu	10		
Zn	100		
As	< 25		
Cd	< 35		
V	< 2.5		
Cr	< 50		
Со	< 50		
U	2.5		
TDS (g/L)	22.1		
pH	8.0		
Eh (mv)	-80		

 Table 10-4: Reference crystalline rock groundwater CS-750, (McMurry 2004)



Figure 10-8: Calculated S(-II) solubilities for several iron and lead sulfide phases in CS-750 reference groundwater system (25 °C). Fe either fixed or buffered by siderite.

10.3 DISCUSSION AND CONCLUSIONS

One of the key controls on sulfide solubility in the chemically reducing subsurface environment is equilibrium with iron sulfide phases. The iron sulfide minerals observed in low temperature environments show a large range of solubilities, controlled by the highly soluble amorphous FeS through to less soluble phases, such as pyrite (FeS₂). Most thermodynamic data are based on only a few experimental studies, and, therefore, there is uncertainty in the value of some solubilities, for example, for greigite, for which only one measurement is reported. For other iron sulfide phases, such as mackinawite, there have been several studies that have measured (e.g., Berner 1967; Benning et al.,2000) or calculated the solubility product (Davison 1991), with values for log Ksp ranging from -3.19 (Lemire et al., 2013) to -4.648 (Berner, 1967). Pyrite solubility has not been measured experimentally due to its low solubility; however, several studies have calculated a value based on the Gibbs free energy of formation. The calculated log Ksp values range from -15.79 (Davison, 1991) to -18.50 (Hummel et al., 2002). The solubility controlling phase is highly dependent on the pH and Eh of the system and under strongly reducing conditions, iron monosulfides (FeS phases) are favoured over pyrite.

The rates of formation for the primary phases are very fast, aqueous iron and sulfide ions react immediately to form disordered clusters, which transform to an amorphous FeS precipitate. In months this undergoes further transformation to form the ordered FeS, mackinawite (Csákberényi-Malasics et al., 2012). The reaction to form mackinawite can follow two pathways with H₂S and HS⁻ in competition and with a dependence on pH. This behaviour is mirrored in pyrite formation, which also has two proposed pathways, one involving polysulfides/elemental sulfur and an alternative with H₂S as the oxidant. The polysulfide pathway is preferred at higher pH and the rate of this reaction increases with increasing polysulfide concentration, whilst the

H₂S pathway is defined less clearly. Rate equations and constants for these reactions are proposed in the literature, but these may not be applicable outside of the conditions under which the experiments were undertaken. In a dynamic system in which SRB provide a continuous source of sulfide, the identity of the solubility limiting phase will depend upon the relative rates of sulfide production and the rates of conversion of amorphous FeS to crystalline forms. If the rate of sulfide production by SRB is similar to, or faster than, the conversion of FeS or mackinawite to less soluble phases, sulfide solubility will be controlled by the most soluble phase present, i.e., amorphous FeS or mackinawite.

Reference groundwaters from crystalline (CR-10) and sedimentary (SR-270) geologies have been evaluated via chemical speciation modelling to predict the solubility of sulfide when it is controlled by amorphous FeS, mackinawite, troilite, pyrrhotite and pyrite. This modelling utilised thermodynamic data only and does not consider the kinetics of these processes. For both CR-10 and SR-270 groundwaters, pyrite is predicted to be the most stable iron sulfide phase, controlling sulfide concentrations from approximately 10⁻⁹ to 10⁻⁷ M. The initial precipitation of FeS(am) is predicted to control sulfide concentrations to approximately 10⁻⁵ M in the CR-10 groundwater and almost 10⁻² M in the SR-270 groundwater. This high predicted sulfide solubility in the saline system is due to the domination of solution Fe speciation by chloride, and hence lower availability of Fe²⁺ for reaction with sulfide. Additionally, the lower pH of the sedimentary groundwater acts to increase the solubility of FeS phases.

The availability of Fe²⁺ in these systems is crucial in controlling sulfide solubility. When the assumption is made that Fe²⁺ can be supplied by siderite (FeCO₃), the models predict a much lower sulfide solubility of between $2x10^{-8}$ and $3x10^{-5}$ M (depending on the controlling phase) for the SR-270 system, compared to calculations with a fixed Fe(II) concentration as defined in the groundwater. For the CR-10 system, the siderite buffered values are much closer to those for the fixed composition, since the Fe(II) levels in the groundwater are already close to those buffered by siderite. Under strongly reducing conditions, pyrite is not the most thermodynamically stable iron sulfide phase, with FeS phases preferred. For CR-10, this gives a sulfide solubility between 10^{-9} for troilite and $2x10^{-7}$ M for FeS(am), and for SR-270, between $4x10^{-10}$ and $6x10^{-7}$ M, depending on the assumed availability of Fe²⁺.

The use of mackinawite solubility is consistent with reactive transport modelling performed by other waste management organizations to estimate copper corrosion, including Nagra (Cloet et al., 2017) and SKB (Gimeno et al., 2009).

The solution properties that determine mackinawite solubility are:

- <u>The availability of Fe²⁺(aq)</u>. This may be provided by reactive Fe(II) minerals such as siderite (FeCO₃) in the geosphere, other Fe phases in the bentonite, or Fe(III) minerals that are subject to bio-reduction by iron-reducing bacteria (IRB). It is important to note that, in addition to the total dissolved Fe, solution speciation is important, and extremely saline solutions can affect Fe(II) speciation, thereby increasing sulfide solubility;
- <u>The pH.</u> All iron sulfides exhibit increasing solubility with decreasing pH. A complication is that many Fe minerals also have a similar pH dependence for solubility, resulting in a greater supply of Fe²⁺, which can act to partly offset the increase in iron sulfide solubility.

The mackinawite solubilities calculated for the Canadian reference groundwaters range from around $2x10^{-6}$ M total sulfide concentration in the crystalline CR-10 to around $2x10^{-3}$ M total sulfide in the sedimentary SR-270 groundwater assuming a fixed Fe concentration as defined in the groundwater recipes. If Fe²⁺ is buffered by a sufficient source of siderite, the predicted

sulfide solubility is approximately the same (10^{-6} M) in the crystalline groundwater, but considerably lower $(6x10^{-6} \text{ M})$ in the sedimentary groundwater.

11. GENERAL EVALUATION OF SULFIDE FROM ALL SOURCES

11.1 NATURAL SOURCES

11.1.1 Sulfate/Sulfide in Host Rock

The crystalline site:

The major sulfur-bearing species in the crystalline host rocks are sulfide minerals, dominated by pyrite. The solubility of pyrite is very low, and thus will not contribute notable amounts of dissolved sulfide to groundwater. Pyrite oxidation by oxidants produced by water radiolysis (IROP) is not efficient, and the amount of sulfate produced by this process will likely be negligible. The main impact of host-rock sulfide on groundwater composition is through oxidative weathering by free O₂ when the system is exposed to air. However, the amount of sulfate that can be transported from host rock into groundwater and subsequently reduced into sulfide in the groundwater is difficult to quantify, due to a lack of site-specific data.

The sedimentary site:

The sedimentary host rocks contain both sulfide minerals (dominated by pyrite) and sulfate minerals (dominated by gypsum and anhydrite). Dissolution of pyrite and background pyrite oxidation by IROP should not affect the sulfide content in the groundwater. Oxidative weathering of pyrite, if the system is exposed to air, and dissolution of sulfate minerals might contribute significant amounts of sulfate and thus sulfide (after reduction) into the groundwater. One unique geochemical feature of a limestone based sedimentary rock site is that the carbonate-buffered water system contains high amounts of Ca²⁺, which can regulate the sulfate level by the precipitation of CaSO₄ once it is oversaturated.

11.2 ENGINEERED SOURCES

11.2.1 Sulfate/Sulfide in Buffer

Case with negligible microbial activity

In this case sulfide concentrations are controlled by pyrite equilibrium or those of the surrounding groundwater.

Case with microbial sulfate reduction

Sulfide concentrations in this case will be constrained by FeS. The availability of Fe²⁺ in these systems is crucial in controlling sulfide solubility. As discussed in previous chapters, the most likely FeS phase to form is mackinawite. Temporarily, higher sulfide concentrations might develop in the case of intense SRB activity and slow iron dissolution kinetics.

11.3 ESTIMATE CORROSION DAMAGE FROM SULFIDE

The potential for microbial activity in the low permeability crystalline and sedimentary rock structures, such as those under consideration in the Canadian DGR concepts is low. However, cracks and fissures may exist in the host rock as part of a discrete fracture network, and the integrity of the rock is likely to be damaged in the so-called excavation damaged zone (EDZ),

the region of macro- and micro-fractures and general rearrangement of rock structures. As a result, it's possible that there will be some SRB activity at the bentonite-rock boundaries or within the rock near the bentonite within the EDZ. Additional SRB activity in remote cracks and fissures of the host rock may also supply dissolved sulfide that may diffuse into the repository toward the UFC surfaces. However, as noted in previous section, the availability of Fe²⁺ in these systems is crucial in controlling sulfide solubility, which could prevent sulfide from reaching the container. Moreover, for sulfide to reach the UFC surfaces it must diffuse through the HCB buffer material, and the diffusion coefficient of aqueous sulfide in saturated HCB is very small, on the order of 10^{-11} m² s⁻¹(King 1996).

The damage to UFCs caused by microbial induced corrosion was quantified in a recent review paper (Hall et al. 2021). Assuming fixed sulfide concentrations of 0.1 ppm at bentonite-rock interface for "expected value" and 1 ppm for "maximum value", the reasonably expected corrosion allowance by sulfide was calculated to 80 µm and the extreme upper bond was 800 µm. As noted, sulfide concentrations comprise a background sulfide level (i.e. through geological processes such as slow dissolution of sulfide containing minerals), and an enhanced sulfide level (i.e. through remote microbiological processes). The sulfide values should be updated once site-specific data is available.

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APPENDIX A:

CONTENTS

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A.1 Underground Laboratories for Research (URL)

Table 1: Underground laboratories for research (URL) and development of radioactive waste disposal where microbiological research has been performed along with a note regarding the presence of sulfide-producing prokaryotes (bacteria and archaea)

URL	Host rock, location, depth	Managing organization/remarks	Selection of significant peer reviewed papers on microbiology in groundwater	Sulfide- producing prokaryotes observed
Stripa Mine	Granite Near the Guldsmedshyttan region of Sweden 360-410 m	Swedish Nuclear Fuel and Waste management Co Galleries in former iron mine. Operated 1976-1992.	(Ekendahl et al. 1994; Pedersen and Ekendahl 1992)	Not found but sulfide was present
AECL Undergroun d Research Laboratory	Granite Lac du Bonnet, Manitoba, Canada 240-420 m.	Atomic Energy Canada Limited Operated 1984-2006. URL officially closed in 2010.	(Brown et al. 1998; Brown and Sherriff 1999; Stroes- Gascoyne and Gascoyne 1998; Stroes-Gascoyne and West 1997; Vilks et al. 1998; Jain et al. 1997; Stroes-Gascoyne et al. 1994)	Largely in buffer, but also found in groundwater
Äspö Hard Rock Laboratory	Granite Oskarshamn, Sweden. 450 m.	Swedish Nuclear Fuel and Waste management Co Operating since 1995. Activities at Äspö have received a significant amount of experience and knowledge gained from the Stripa Mine.	(Anderson et al. 2006; Ekendahl et al. 2003a; Kalyuzhnaya et al. 1999; Kotelnikova et al. 1998; Motamedi and Pedersen 1998; Nielsen et al. 2006; Pedersen 2012, 1997a, 2000; Smart et al. 2014; Stroes-Gascoyne and West 1997; Wu et al. 2017)	Yes, generally in large numbers

ONKALO	Granit Eurajoki, Finland 500 m	Posiva Oy Received a building permit for the facility in August 2003 and excavation began in 2004	Bell et al. 2020; Bomberg et al. 2016; Haveman et al. 1999; Miettinen et al. 2018; Nyyssönen et al. 2012; Pedersen 2008; Pedersen et al. 2014; Sohlberg et al. 2015)	Yes, large numbers in mixing groundwater
Grimsel Test Site (GTS)	Granite In the Grimsel region of Switzerland 450 m	Nagra Gallery from a service tunnel of a hydroelectric project. Operating since 1984.	(Engel et al. 2019; Konno et al. 2013)	Yes
Mizunami Undergroun d Research Laboratory (MIU)	Granite. Gifu Prefecture, central Japan. Research galleries at 300 m to 1 000 m (planned).	Japan Atomic Energy Agency Under construction since 2002. Excavation of two shafts started in 2003 and construction of research galleries completed at 300 m level in 2008 and started at 500 m level in 2011. R&D during excavation ongoing since 2004 and R&D at research gallery at 300 m level ongoing since 2010.	(Fukuda et al. 2010; Ino et al. 2018b, 2016; Suzuki et al. 2014a)	Yes
Bure	Shale (indurated clays), Callovo-Oxfordian Argillites. Meuse/Haute Marne France. 450-500 m.	ANDRA Potential repository site, in operation since October 2004. The URL is not allowed to receive any waste and will not be integrated in the repository.	Very dry rock with very low probability of microbial life	Not studied
Tournemire Facility	Sediments (hard clay). Auvergne, France. 250 m.	IRSN Former railway tunnel and adjacent galleries. Operating since 1990.	(L. Urios et al. 2014; Urios et al. 2012)	Yes
Mont Terri	Opalinus clay (hard clay). In the Mont Terri region of north western Switzerland. 250-320 m.	Swisstopo Gallery from a highway tunnel. Initiated in 1995	(Bagnoud et al. 2016b, a, c; Leupin et al. 2017; Stroes- Gascoyne et al. 2011a)	Yes, at least in disturbed conditions
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Horonobe Undergroun d Research Laboratory	Neogene sedimentary rock. Hokkaidō Prefecture, northern Japan. Research galleries at 140 m and 250 m (in operation), 350 m (to be constructed) and 500 m (planned).	JAEA Under construction since 2005. Excavation of two shafts started in 2005 and construction of research galleries at 140 m level in 2009 and at 250 m level in 2011. Excavation of third shaft started in 2011. R&D during excavation ongoing since 2005 and R&D at research galleries ongoing since 2010.	(Hernsdorf et al. 2017; Ise et al. 2017; Saitoh et al. 2019)	Yes
Tono Mine	Neogene sedimentary rock. Gifu prefecture, central Japan 130 m	JAEA Galleries in former uranium mine. Operated 1986- 2004.	(Amano et al. 2017a; Mills et al. 2010; Murakami et al. 2002, 1999)	Yes
High- Activity Disposal Experiment Site Undergroun d Research Facility (HADES- URF)	Boom clay (plastic clay). Mol/Dessel, Belgium. 230 m.	EIG EURIDICE. Shaft sinking began 1980, operating since 1984 and the extension of the lab with the test drift (1987), the construction of the second access shaft (1997-1999) and the realization of the connection gallery (2001- 2002).	(Mijnendonckx et al. 2019; Wouters et al. 2013)	Yes

A.2 SULFIDE IN DEEP GROUNDWATERS ANNOTATED BIBLIOGRAPHY

0011005					CONCE	INTRATIO	N (ppm)	NOTEO
SOURCE	LOCATION	SPECIES	LITHOLOGY	DEPTH (MDSI)	Min.	Max.	Avg.	NOTES
	·	·						
AECL/ NWMO	Shore of	HS ⁻	Altered sandstone	345.0-348.6	<0.002	0.009	-	- These concentrations are the
(Cramer and Smellie 1994)	and Cigar		Lower sandstone	242.3-245.9	<0.002	<0.002	-	representative values as determined
	Lakes		Upper sandstone	154.5-158.1	0.040	0.088	-	contamination, range of variation,
			Lower sandstone	440.0-444.0		0.058	-	consideration of analytical variability,
			Clay	403.0-408.0	<0.002	0.07	-	etc.
			Lower sandstone	439.0-443.0	<0.002	0.021	-	chromatography
			Ore-clay contact	415.0-422.0	<0.002	<0.002	-	· · · · · · · · · · · · · · · · · · ·
			Altered basement	445.5-452.0	<0.07	<0.07	-	
			Altered sandstone	415.0-418.6	<0.002	<0.002	-	
			Outflow	413.0-416.6	<0.002	<0.002	-	
			Ore	432.0-439.5	<0.002	<0.002	-	
POSIVA (Pitkänen et al. 1996a)	Olkiluoto site at Eurajoki	HS ⁻	Granite, magmatic mica gneiss	~ 240-320	<0.01	3.0	-	 Analysis results from 1987-1992 on the most representative samples used in the first interpretation (Appendix 1 of report) 1 Small flushing water contamination Packer leakage and contamination by cemented upper part of borehole
POSIVA	Romuvaara	S ²⁻	Tonalite gneiss	145.0-175.0	-	-	<0.01	- Data classified as representative
(Pitkänen et al. si 1996b)	site			175.0-205.0	-	-	<0.05	 These concentrations are the representative values as determined through criteria like exclusion of contamination, range of variation, consideration of analytical variability, etc. Sulphide content determined by ion chromatography Analysis results from 1987-1992 on the most representative samples used in the first interpretation (Appendix 1 of report) 1 Small flushing water contamination Packer leakage and contamination by cemented upper part of borehole Data classified as representative through field and laboratory analyses From Archaean age bedrocks
		Le	Leucotoncalite gneiss	230.0-260.0	-	-	0.070	
				260.0-305.0	-	-	0.024	

¹ Summarises results from: Lampen and Snellman 1993; Pitkänen et al. 1992a, b, c; Pitkänen and Snellman 1990; Blomqvist et al. 1992; Laaksoharju et al. 1994; Wickstrom and Helenius 1990; Snellman et al. 1995

COURCE		OCATION SPECIES			CONCE	ENTRATIO	N (ppm)	NOTES
SOURCE	LUCATION	SPECIES	LITHOLOGY	DEPTH (MDSI)	Min.	Max.	Avg.	NOTES
				305.0-345.0	-	-	<0.01	
				345.0-375.0	-	-	0.340	
			Tonalite gneiss	375.0-415.0	-	-	<0.05	
				415.0-500.0	-	-	<0.05	
			Leucotoncalite gneiss	45.0-85.0	-	-	<0.01	
			Metadiabase	140.0-170.0	-	-	<0.05	
			Leucotoncalite gneiss	170.0-200.0	-	-	<0.01	
			Tonalite gneiss	325.0-360.0	-	-	<0.05	
			Tonalite gneiss, amphibolite	360.0-390.0	-	-	0.150	
			Tonalite gneiss	415.0-500.0	-	-	0.600	
			Tonalite gneiss	70.0-100.0	-	-	<0.01	
			Amphibolite, tonalite gneiss, granodiorite	160.0-210.0	0.330	0.350	0.340	
			Tonalite gneiss	255.0-295.0	-	-	<0.05	
			Tonalite gneiss	295.0-350.0	-	-	0.026	
			Tonalite gneiss, granodiorite	365.0-390.0	-	-	0.160	
			Tonalite gneiss	475.0-500.0	-	-	1.000	
			Tonalite gneiss	135.0-165.0	-	-	<0.01	-
			Tonalite gneiss, metadiabase	165.0-195.0	-	-	2.800	
			Metadiabase	220.0-250.0	-	-	1.400	
			Tonalite gneiss, metadiabase	305.0-330.0	0.550	0.850	0.700	
			Metadiabase	460.0-500.0	-	-	<0.03	
POSIVA	Olkluoto site	S ²⁻	Migmatic mica gneiss	612-618	-	-	0.28	- OL-KR1
(Hirvonen et al. 2004)	at Eurajoki		Migmatic mica gneiss	81-85	-	-	<0.01	- OL-KR4
			Granite	120-127	-	-	0.04	- OL-KR8
			Migmatic mica gneiss	347-350	-	-	4.2	- OL-KR8 - Unacceptable RSD (RSD>5%) of 6%

SOURCE		SDECIES			CONCE	INTRATIC	ON (ppm)	NOTES
SOURCE	LOCATION	SPECIES	LITHOLOGY	DEPTH (IIIDSI)	Min.	Max.	Avg.	NOTES
			Migmatic mica gneiss	556-561	-	-	0.05	- OL-KR8
			Migmatic mica gneiss	498-503	-	-	0.01	- OL-KR10
POSIVA (Posiva 2012)	Olkiluoto site at Eurajoki	HS [.]	Migmatitic gneiss, tonalitic- granodioritic-granitic gneiss, mica gneiss, quartz gneiss, mafic gneiss and pegmatitic granite	306.54	-	12.4	0.42-0.71	- Anomalously high concentrations (12.4 ppm) observed in initial sample is suspected to be caused by disturbances during investigation (e.g. open drillhole flow, pumping effect, etc.), which allowed for incubation of SRB in the open borehole
POSIVA (Wersin et al. 2014b)	Olkiluoto site	HS ⁻	High-grade metamorphic supracrustal rocks (veined gneiss, tonalitic- granodioritic-granite gneiss)	360.5-364.5	<0.01	0.6	-	 Monitoring shows rapid decrease of high HS- concentrations (artificially induced water mixing enhancing SRB activity) (min. 2.6 from last sample) 94% below 1 ppm, 78% below 0.1 ppm
POSIVA (Edlund et al. 2016)	Olkiluoto site	S ²⁻	Veined gneiss (62.9%), diatexitic gneiss (18.3%), pegmatitic granite (10.8%), and mica gneiss (8.0%)	350.7-351.7	<0.02	0.1	-	 Sulphide content analysed using spectrophotometry (uncertainty of ~24%) ONK-PVA6 (sulphate-rich ≈1 mM SO₄)
			Veined gneiss (51.7%), pegmatitic granite (22.9%), diatexitic gneiss (16.6%), and quartz gneiss (8.8%)	462.9-463.9	<0.02	<0.02	-	 Sulphide content analysed using spectrophotometry ONK-KR15 (sulphate-poor, but rich in methane, ≈6 mM CH₄)
POSIVA (Lamminmaki et al. 2017)	Olkiluoto site	HS⁻	Diatexitic gneiss, veined gneiss	399.7	<0.02	0.02	-	 Borehole ONK-KR15 T1 (chemically valid samples with no significant sampling or analytical issues)
			Diatexitic gneiss	421.5	0.15	1.8	0.89	- Borehole ONK-KR16 - T1
				421.4	<0.02	<0.02	-	- Borehole ONK-PH21

SOURCE					CONCENTRATION (ppm)		N (ppm)	NOTES
SOURCE	LOCATION	SPECIES	LITHOLOGY	DEPTH (MDSI)	Min.	Max.	Avg.	NOTES
								- T1, E1 (includes samples with severe quality problems)
				420.3	0.02	2.2	1.18	- Borehole ONK-PH22 - T1
				428.2	<0.02	<0.02	-	- Borehole ONK-PH23 - T1
			Pegmatitic granite, diatexitic gneiss, veined gneiss, migmatite	423.1	<0.02	0.95	-	 Borehole ONK-PH28 T1, T2 (samples with poor analytical programme / anomalous charge balance)
			Diatexitic gneiss	151.2	-	0.03	-	- Borehole ONK-PVA4 - T1
			Diatexitic gneiss, veined gneiss	242.4	0.72	0.83	0.78	- Borehole ONK-PVA5 - T1
			Veined gneiss, mica gneiss, pegmatitic granite	327.7	0.19	0.27	0.24	- Borehole ONK-PVA6 - T1
				279.3	2.1	3.3	2.94	- Borehole ONK-PVA8 - T1
				425.6	0.13	0.68	0.39	- Borehole ONK-PVA9 - T1
				379.4	<0.02	0.03	-	- Borehole ONK-PVA10 - T1
				436.8	<0.02	<0.02	-	- Borehole ONK-PVA11 - T1
SKB	Ävrö	S-2	Granitic	420	-	-	0.59	- Borehole KAV01
(Pedersen 1989)				522	-	-	1.20	
				558	-	-	0.81	_
				635	-	-	<0.01	
	Äspö	S ⁻²	Granitic	202	-	-	0.48	- Borehole KAS02
				314	-	-	0.143	

SOURCE		SDECIES			CONCENTRATION (ppm)		N (ppm)	NOTES
SOURCE	LOCATION	SPECIES	LITHOLOGY	DEPTH (IIIDSI)	Min.	Max.	Avg.	NOTES
				463	-	-	0.13	
				860	-	-	0.715	
				129	-	-	0.586	- Borehole KAS03
	Laxemar	S-2	Granitic	272	-	-	0.473	- Borehole KLX01
				466	-	-	0.460	
				701	-	-	2.55	
SKB	Finnsjön site	HS ⁻	Red and grey granodiorite,	94	-	-	0.22	- Borehole KF109
(Pedersen 1997b)			borehole	360	-	-	0.03	
	Kliperås site	HS ⁻	Granite matrix (73.86%), greenstone (15.52%), poryphyry (9.75%), aplite (0.87%)	404	-	-	0.10	- Borehole KKL01
			Granite matrix (81.22%), porphyry (10.00%), greenstone (6.68%), mafic dyke (1.85%), aplite (0.25%)	581	-	-	0.01	- Borehole KKL09
	Äspö site	HS ⁻	Ävrö granodiorite	129	-	-	0.70	- Borehole KAS03
			Fine-grained granite, Ävrö granodiorite	860	-	-	1.10	
SKB	Forsmark site	S ²⁻	Granitic	110-121	-	-	<0.01	- Borehole KFM01
(Pedersen 2005)				177-184	-	-	<0.01	
,				509-516	-	-	0.01	- Borehole KFM02
				448-453	-	-	<0.01	- Borehole KFM03
				639-646	-	-	<0.01	
				940-947	-	-	<0.01	
				980-1002	-	-	0.03	
	Simpevarp	S ²⁻	Granitic	157-167	-	-	<0.01	- Borehole KSH01A
s	SITE			245-262	-	-	<0.01	
				548-565	-	-	0.05	

SOURCE		SDECIES			CONCENTRATION (ppm)		N (ppm)	NOTES
SOURCE	LOCATION	SPECIES	LITHOLOGY	DEFTH (IIIDSI)	Min.	Max.	Avg.	NOTES
	Äspö,	S ²⁻	Granitic	448.2	-	-	0.01	- Boreholes KJ0050F01, KJ0052F01,
	Droject			450.6	-	-	0.226	KJ0052F03
	F J			447.6	-	-	0.004	- very sensitive to sampling method
SKB (Tullborg et al. 2010)	Laxemar area	\$ ²⁻	Granitic	475	0.013	0.08	-	 Borehole KLX06 Highest in first section (water exposed to fracture walls, downhole equipment)
	Forsmark, SR-Site	S ²⁻	Granitic	111.74-977.66	<0.006	0.068	<0.02	 Complete Chemical Characterisation (CCC) - Higher values due to long delay between drilling & investigation Boreholes KFM01, KFM02, KFM03, KFM06, KFM07, KFM08, KFM09, KFM10, KFM11, KFM12
	Forsmark, SR-Site	S ²⁻	Granitic	27.46-969.13	<0.006	3.850	0.264	 Monitoring sampling - more unstable and higher than CCC (significant >650m) Boreholes HFM01, HFM02, HFM04, HFM13, HFM15, HFM16, HFM21, HFM27, HFM32, KFM01, KFM02, KFM03, KFM06, KFM07, KFM08, KFM11, KFM12
SKB	Äspö site	S ²⁻	Granitic	97.45-241.40	0.09	0.95	0.47	- CCC and monitoring analysis
(Rosdahl et al. 2011)				613.34-984.13	0.6	2.1	-	- Borehole KAS03
- /		HS ⁻		97.45-241.40	9.08	9.40	-	- Borehole KAS03
				613.34-984.13	0.587	6.75	-	
	Äspö site	S ²⁻	Granitic		0.05	5.6	0.87	- Borehole KAS09
		HS [.]		95.99-125.09	92.3	102	-	 Borehole KAS09 The extremely high values are attributed to the water from the standpipe mixing with section water during pumping and sampling from the section, since the pump and filter

COURCE					CONCE	INTRATIO	N (ppm)	NOTES
SOURCE	LUCATION	SPECIES	LITHOLOGY	DEPTH (MDSI)	Min.	Max.	Avg.	NOTES
								could not be lowered completely in the standpipe
	Laxemar	S ²⁻	Granitic	475 07 404 70	0.5	1.0	-	- Borehole KLX06
		HS ⁻		475.27-481.78	0.08	9.18	1.95	- Borehole KLX06
SKB (Hallbeck et al. 2017)	Äspö, MiniCan project	S ²⁻	Granitic	420	<0.019	0.031	<0.022	 All groundwater samples (vs. container samples) were <0.019 ppm Containers packed with bentonite
NAGRA, SKB,	Osamu	S ²⁻	Mainly subvolcanic &	96.5-125.7	0.0038	0.0056	0.0045	- Borehole F1
(Nordstrom et	Utsumi mine, Brazil		minor voicanic phonolites	45-60	0.0015	0.019	0.0061	- Borehole F2
al. 1990)				50-77.6	<0.0001	0.0028	<0.001	- Borehole F3
			275-300	<0.001	<0.001	<0.001	- Borehole F5	
Morro do	Morro do	S ²⁻	Magnetic breccia	30-70	<0.0001	<0.001	<0.0005	- Borehole MF 10
	Ferro site, Brazil		(contained by 2 magnetite dykes)	30-40	<0.0001	<0.001	<0.0007	- Borehole MF 11
				20-70	<0.001	<0.002	<0.0015	- Borehole MF 12
				45-71	<0.001	<0.001	<0.001	- Borehole MF 13
NAGRA (Pearson, Jr. et al. 1989) ²	Böttstein	Total Sulfide (H₂S, HS ⁻ , S2 ⁻)	Upper muschelkalk	123.2-202.5	-	-	n.d.	 Drilling and sampling make it likely that the values are higher than expected (for all results from this study) Block 1 (low drilling fluid contamination – well represents groundwater)
			Buntsandstein/weathered	305.6-327.6	-	-	0.01	- Block 2 (intermediate contamination
				305.2-319.8	-	-	0.042	 reasonable representation; corrected) Interpret results with caution
			Crystalline	393.9-405.1	-	-	0.009	- Block 1
			Crystalline	618.5-624.1	-	-	n.d.	- Block 1
			Crystalline	608.0-628.8	-	-	n.d.	- Block 1

² Raw data from Wittwer (1986) and Pearson, Jr. (1985) evaluated to provide a set of water analyses corrected for sampling artifacts.

SOURCE LOCATIO		SPECIES	ECIES LITHOLOGY DEPTH (mbsl)	CONCE	INTRATIC	N (ppm)	NOTES	
SOURCE	LUCATION	SPECIES	LITHOLOGY	DEPTH (MDSI)	Min.	Max.	Avg.	NOTES
			Crystalline	1321.0-1331.4	-	-	n.d.	- Block 2
	Weiach		Massenkalk	242.9-267.0	-	-	0.13	- Block 2, but deemed representative
			Upper muschelkalk	822.0-869.1	-	-	4.0	- Block 1
			Buntsandstein	981.0-989.6	-	-	0.04	- Block 1
			Perm	1109.2-1123.8	-	-	0.04	- Block 2
			Perm	1401.1-1415.7	-	-	0.015	- Block 2
			Crystalline	2211.6-2224.6	-	-	0.014	- Block 2
			Crystalline	2260.5-2273.5	-	-	0.017	- Block 2
	Riniken	H ₂ S	Dolomite	501.0-530.5	-	-	0.99	- Block 1
			Upper muschelkalk	617.3-696.0	-	-	0.35	- Block 1
			Buntsandstein	793.0-820.2	-	-	0.01	- Block 1
			Perm	958.4-972.5	-	-	0.008	- Block 2
			Perm	977.0-1010.0	-	-	22	 Block 2 Some 170m³ of brine mud were lost in zone 977.0-1010.0m while being drilled (contamination of ~5%)
			Perm	1354.0-1369.0	0.00	1.40	0.82	- Block 2
	Schafisheim	H₂S	Lower Süsswassermolasse	553.0-563.0	-	-	n.d.	- Major dissolved H ₂ S are H ₂ S _(aq) and HS ⁻ _(aq)
			Upper muschelkalk	1227.8-1293.0	-	-	743	- Extremely high values not explained
			Upper muschelkalk	1240.7-1261.1	-	-	950	adequately, but likely caused by
			Buntsandstein/weathered crystalline	1476.0-1500.4	-	-	0.32	rock matrix (Bodzioch and Kowal
			Crystalline	1564.5-1577.7	-	-	0.083	- High H ₂ S caused rapid corrosion of
			Crystalline	1883.5-1892.3	-	-	0.072	pumps and sampling apparatus, making sample collection difficult
	Kaisten		Buntsandstein	97.0-129.9	-	-	0.01	- Block 1
			Perm	276.0-292.5	-	-	n.d.	- Block 1
			Crystalline	299.3-321.5	-	-	n.d.	- Block 1

SOURCE		enecies			CONCE	ENTRATIC	ON (ppm)	NOTES
SOURCE	LUCATION	SPECIES	LITHOLOGY	DEPTH (MDSI)	Min.	Max.	Avg.	NOTES
			Crystalline	475.5-489.8	-	-	n.d.	- Block 1
			Crystalline	816.0-822.9	-	-	n.d.	- Block 1
			Crystalline	1021.0-1040.9	-	-	n.d.	- Block 1
			Crystalline	1140.8-1165.8	-	-	0.4	- Block 1
			Crystalline	1238.0-1305.8	-	-	0.23	- Block 1
	Leuggern		Upper muschelkalk	53.5-96.4	-	-	n.d.	- Block 1
			Buntsandstein	208.2-227.5	-	-	n.d.	- Block 2
			Crystalline	235.1-267.5	-	-	n.d.	- Block 1
			Crystalline	440.4-448.1	-	-	n.d.	- Block 1
			Crystalline	507.4-568.6	-	-	n.d.	- Block 1
			Crystalline	702.0-709.5	-	-	n.d.	- Block 1
			Crystalline	834.5-859.5	-	-	0.04	- Block 2 (contamination between 2.5-5%)
			Crystalline	916.2-929.7	-	-	n.d.	- Block 2
			Crystalline	1179.3-1227.2	-	-	0.32	- Block 2
			Crystalline	1427.4-1439.4	-	-	0.6	 Block 2 Other borehole water contaminants Inconsistent results (use with caution)
			Crystalline	1637.4-1649.3	-	-	n.d.	- Block 1
NAGRA (Frick et al. 1992)	Aare Massif of the Central Swiss Alps, Grimsel Test Site	S ²⁻	Crystalline rock: Pre- Hercynian gneisses and Hercynian granites. Aplitic and more mafic dykes intersect rock mass	~450	-	-	<0.3	- Range in sulphide concentration from all known analyses taken within or near Grimsel prior to this source
		HS [.]	Gneissose granodiorite.		-	-	0.0331	- AU 96m site (migration site)
		H ₂ S	plagioclase (albite), K- feldspar and biotite	96	-	-	0.0341	1
NAGRA	Böttstein	H ₂ S	Crystalline	305.6-405.1	-	-	<0.005	
(Pearson, Jr.	Leuggern			1637.0-1689.0	-	-	<0.005	
1993)	Zurzach			402.6-469.0	-	-	< 0.005	

SOURCE		SDECIES			CONCE	INTRATIC	N (ppm)	NOTES
SOURCE	LOCATION	SPECIES	LITHOLOGY	DEPTH (IIIDSI)	Min.	Max.	Avg.	NOTES
	Kaisten			1140.8-1305.8	-	-	<0.005	 Collection of results of several sources ³ Results are either below detection, or attributable to contamination 'detection limit' not defined, so values should be used with caution
	Böttstein- Leuggern- Zurzach- Kaisten			See above	0	0.32	<0.005	 Base reference water composition for the Böttstein-Leuggern-Zurzach- Kaisten region (see above)
	Saline Leuggern			916.0-930.0	-	-	<0.005	- Contains 5-10% drilling fluid, but the result is corrected
JNC/JAEA (Iwatsuki et al. 2005)	Mizunami Underground Research Laboratory	S ²⁻	Akeyo formation (Siltstone-sandstone alternations)	20.8-31.3	<0.01	<0.01	-	 Contamination corrected by mass balance calculation (for all results in study) Borehole MSB-2
			Akeyo formation	20.7-30.2	<0.01	<0.01		- Borehole MSB-4
			Akeyo formation	67.8	-	-	0.03	- Borehole DH-15
			Akeyo, Hongo formation (interbedded sandstone, siltstone and mudstone)	54.0-73.3	0.02	0.04	-	- Borehole MSB-2
			Akeyo, Hongo formation	48.5-70.0	<0.01	0.10	-	- Borehole MSB-4
			Hongo, Toki lignite-bearing formation (lignite-bearing fluivial sediment)	91.0	-	-	1.28	- Borehole DH-15
			Toki lignite-bearing formation	99.3-143.0	<0.01	0.082	<0.059	- Borehole MSB-2
			Toki lignite-bearing formation	79.8-88.3	<0.01	0.11	-	- Borehole MSB-4
			Toki lignite-bearing formation	118.2-184.3	1.88	4.45	-	- Borehole DH-15
			Toki granite (biotite granite, felsic granite, etc.)	173.5	-	-	0.048	- Borehole MSB-2

³ Summarises results from: Brütsch et al. 1991; Degueldre 1994; NAGRA 1989; Pearson, Jr. et al. 1989; Schmassmann et al. 1992

SOURCE		SPECIES			CONCE	NTRATIO	N (ppm)	NOTES
SOURCE	LOCATION	SFECIES	LITHOLOGI	DEFTH (IIIDSI)	Min.	Max.	Avg.	NOTES
			Toki granite	96.9-97.3	0.07	0.5	-	- Borehole MSB-4
			Toki granite	208.5-455.5	n.m.	n.m.	n.m.	- Borehole DH-2
			Toki granite	236.8-995.3	0.04	7.04	1.54	- Borehole DH-15 - 7.04 is an outlier (other values all <1)
			Toki granite	114.7-687.5	0.02	4.49	1.16	 Borehole MIZ-1 4.49 is an outlier (other values all <0.1)
	Mizunami	H ₂ S	Akeyo formation	37.8	-	-	<0.0004	- Borehole DH-15
	Research Laboratory	und	Hongo, Toki lignite-bearing formation	91.0	-	-	<0.0004	- Hydraulic pumping was used (so degassing occurred)
	Laboratory		Toki lignite-bearing formation	118.2-184.3	-	-	<0.0004	Only appropriate for qualitative discussion (assuming ~ each gas
			Toki granite	236.8-995.3	<0.0004	0.003	<0.0011	degassed equally)
JNC/JAEA (Amano et al. 2012)	Horonobe Underground Research Laboratory	HS	Siliceous mudstone	328.62	-	-	<0.1	 Absorptiometry used to measure sulphide content (for all results below) Borehole HDB-2
			Siliceous mudstone	218.45-236.53	-	-	0.00006	- Borehole HDB-4
			Siliceous mudstone	223.93-233.78	-	-	0.007	
			Siliceous mudstone	281.05-290.76	-	-	0.017	
			Siliceous mudstone	474.79-484.61	-	-	0.025	
			Siliceous mudstone	368.6-377.4	-	-	<0.1	- Borehole HDB-5
			Siliceous mudstone	280.95-312.00	<0.1	<0.1	<0.1	- Borehole HDB-6
			Siliceous mudstone	363.95-409.00	<0.1	<0.1	<0.1	
			Diatomaceous mudstone	100.69-200.00	<0.1	<0.1	<0.1	
			Siliceous mudstone	299.67-620.00	<0.1	<0.1	<0.1	
			Siliceous mudstone	288.66-302.9	-	-	0.005	
				362.39-385.7	-	-	0.022	
				386.60-396.41	<0.1	0.013	-	
			Sandy mudstone	100.00-324.00	<0.1	<0.1	<0.1	- Borehole HDB-7

SOURCE	LOCATION	SPECIES	LITHOLOGY		CONCENTRATION (ppm)			NOTES
SOORCE					Min.	Max.	Avg.	NOTES
			Diatomaceous mudstone	400.00-520.00	<0.1	<0.1	<0.1	
			Diatomaceous mudstone	57.5-89.05	<0.1	<0.1	<0.1	- Borehole HDB-8
			Siliceous mudstone	168.01-184.06	<0.1	<0.1	<0.1	
			Diatomaceous, siliceous mudstone	98.86-469.94	<0.1	<0.1	<0.1	
			Siliceous mudstone	26.5-82.6	<0.1	<0.1	<0.1	- Borehole HDB-9
			Siliceous mudstone	216.9-257.5	<0.1	<0.1	<0.1	
			Diatomaceous mudstone	41.33-59.88	<0.1	<0.1	<0.1	- Borehole HDB-10
			Siliceous mudstone	445.84-469.89	<0.1	<0.1	<0.1	
			Diatomaceous, siliceous mudstone	100.03-550.00	<0.1	<0.1	<0.1	
			Siliceous mudstone	495.89-550.00	0.025	0.028	-	
			Diatomaceous mudstone	171.00-237.05	<0.1	<0.1	<0.1	- Borehole HDB-11
			Siliceous mudstone	606.00-644.15	<0.1	<0.1	<0.1	
			Diatomaceous mudstone	224.96-236.3	-	-	0.018	
			Diatomaceous mudstone	295.61-404.45	-	-	0.032	
			Siliceous mudstone	621.13-631.99	-	-	0.062	
			Diatomaceous, siliceous mudstone	233.86-247.91	<0.1	<0.1	<0.1	- Borehole PB-V01
			Siliceous mudstone	263.3-277.41	<0.1	<0.1	<0.1	
			Siliceous mudstone	355.8-370.85	<0.1	<0.1	<0.1	
Horonobe Underground Research Laboratory	Horonobe Underground Research Laboratory	HS ⁻	Diatomaceous, siliceous mudstone	266.5-286.55	-	-	<0.001	- Borehole SAB-1
			Siliceous mudstone	270.0-289.0	-	-	0.0013	
			Siliceous mudstone	319.3-328.0	-	-	<0.001	
			Siliceous mudstone	310.0-339.0	0.0033	0.004	-	
			Siliceous mudstone	465.0-512.0	0.0033	0.008	-	
			Diatomaceous mudstone	138.676	<0.1	0.026	-	- Borehole 07-V140-M01
		Diatomaceous mudstone	139.739	<0.1	0.004	-	- Borehole 07-V140-M03	

COURCE	LOCATION	SPECIES	LITHOLOGY	DEPTH (mbsl)	CONCENTRATION (ppm)			NOTES
SOURCE					Min.	Max.	Avg.	NOTES
			Diatomaceous mudstone	157.55-218.7	0	0.025	0.0074	- Borehole 08-E140-C01
			Diatomaceous mudstone	139.132	0.004	0.005	-	- Borehole 08-E140-M01
			Diatomaceous mudstone	139.182	0.004	0.009	0.00675	- Borehole 08-E140-M02
			Diatomaceous mudstone	249.146	0.007	0.041	-	- Borehole 09-V250-M01
			Diatomaceous, siliceous mudstone	249.146	0.001	0.004	0.00267	- Borehole 09-V250-M02
			Diatomaceous, siliceous mudstone	250.15-270.15	0.061	0.082	-	- Borehole 09-V250-M03
JNC/JAEA (Amano et al. 2017b)	Tono uranium deposit	ranium S ²⁻	Tertiary sedimentary rocks, Seto and Mizunami group	158.8-199.4	-	-	0.079	 Borehole KNA6-SW Std. dev.: 0.002 Results from measuring groundwater continuously from 1995 (for ~10 years)
			Late cretaceous toki granite		-	-	0.010	- Borehole KNA6-GW - Std. dev.: 0.001
JNC/JAEA (Miyakawa et al. 2017)	Horonobe Underground Research Laboratory	e HS ⁻ pund n ry	Diatomaceous mudstone	136.9-138.7	0.0047	0.0077	0.0057	 Summarizes data obtained for 3 years (2014-2016) Analysed sulphide content using methylene blue absorption spectrophotometry (for all results) Borehole 07-V140-M01
				142.3-150.1	0	0.0057	0.0036	- Borehole 07-V140-M03
				157.6-218.7	0	0.0093	0.0035	- Borehole 08-E140-C01
			Diatomaceous mudstone/Hard shale	248.9-248.9	0	0.0027	0.0009	- Borehole 09-V250-M02
				247.0-248.8	0.0010	0.0040	0.0028	- Borehole 10-E250-M01
				252.7-280.4	0.0017	0.0037	0.0027	- Borehole 11-V250-TR02
			Hard shale	252.8-309.9	-	-	0.0030	- Borehole 11-W250-TR01
				252.8-368.8	-	-	0.0047	- Borehole 11-W250-TR03
				347.4-349.3	0.0037	0.0073	0.0059	- Borehole 12-P350-M02
				347.3-345.9	0.0040	0.0040	0.0040	- Borehole 13-350LGE-M01
					-	-	0	- Borehole 13-350LGE-M02

SOURCE	LOCATION	SPECIES	LITHOLOGY	DEPTH (mbsl)	CONCENTRATION (ppm)			NOTES
SOURCE					Min.	Max.	Avg.	NOTES
				348.5-349.0	0.0040	0.0047	0.0044	- Borehole 13-350-C01
				348.3-348.6	0.0010	0.0063	0.0037	- Borehole 13-350-C05
				347.6-348.7	0	0.0073	0.0021	- Borehole 13-350-C06
				338.1-339.6	-	-	0.021	- Borehole 13-350-C07
				348.9-348.9	0.0027	0.0067	0.0042	- Borehole 13-350-C08
				359.2-366.7	-	-	0.044	- Borehole 13-350-C09
				348.6-364.5	0	0.079	0.019	- Borehole 14-350-C04
				347.6-349.4	-	-	0.0040	- Borehole 14-350-GAS01
			Diatomaceous mudstone	140.0-163.0	0	0.0043	0.0022	- Borehole E140G
JOURNAL ART	ICLES	•				-		
(Pauwels et al. 2002)	La Zarza site, Iberian Pyrite Belt (IPB), Spain	H ₂ S	Late Devonian to Early Carboniferous rocks Phyllites and quartzites, volcano-sedimentary sequence, culm, massive sulphides	61.5-368	0.54	1.34	0.76	 Mining contamination (for all results in study) Borehole ZA2
				200.0-430.0	<0.03	<0.03	<0.03	- Borehole ZA3 - All not detected
				40.0	<0.03	<0.03	<0.03	- Borehole ZA20 - All not detected
				65.0	<0.03	<0.03	<0.03	- Borehole ZA26 - All not detected
	Masa Valverde site		Culm, Stockwork, massive sulphides undifferentiated volcano-sedimentary complex	111.0-140.0	<0.03	<0.03	<0.03	 Boreholes A4, A8, A13, A18, A19, A25 All not detected Approximation of concentration is 0.0003-0.007 ppm
(Schulze- Makuch et al. 2003)	Southern Jornada del Muerto Basin, New Mexico	H ₂ S (analyzed as total sulfide)	Sedimentary, igneous, metamorphic rocks Metal sulfide deposits present	12.8	-	-	1.1	- Borehole A-1
				87.0	-	-	<1.0	- Borehole O-1
				26.5	-	-	<1.0	- Borehole B-1
				20.0	-	-	<1.0	- Borehole B-2
				146.0	-	-	<1.0	- Borehole JP-2
				146.0	-	-	<1.0	- Borehole JP-3

	LOCATION	SPECIES	LITHOLOGY	DEPTH (mbsl)	CONCENTRATION (ppm)			NOTES
SOURCE					Min.	Max.	Avg.	NOTES
				107.0	-	-	<1.0	- Borehole JP-4
				102.0	-	-	<1.0	- Borehole M-2
				101.0	-	-	<1.0	- Borehole M-3
				76.0	-	-	<1.0	- Borehole LC-1
(Einsiedl et al. 2008)	Franconian Alb, southern Germany	H₂S	Limestone and marls of the Kimmeridge or Tertiary sediments	200	<0.01	<0.01	<0.01	- All below detection limit
(Suzuki et al. 2014b)	Mizunami Underground	HS [.]	Cretaceous Toki granite	200	0.12	0.85	0.58	- Borehole 07MI07, Intervals 1,2,3,4,5 (interval 5 closest to borehole orifice)
	Laboratorv			300	0.11	0.85	0.44	- Borehole 09MI20, Intervals 1,2,3,4,5
				400	0.11	0.43	0.29	- Borehole 10MI26, Intervals 1,3,4,5
(Alakangas et	Äspö Hard Rock Laboratory (HRL)	HS	Granitoids, crystalline rock	143.0-144.9	0.046	0.060	0.053	- Borehole KA1061A
al. 2014)				267.5-292.7	<0.019	0.075	<0.044	- Borehole KA1755A
				450.51-450.52	0.019	0.041	0.026	- Borehole KJ0052F01
(Guo et al. 2016)	Northwest Hetao basin	t S ²⁻ sin	Jurassic to Cretaceous metamorphic sedimentary (sandstone, mudstone, shale), Mesoproterozoic metamorphic (quartz, slate, quartzite, phyllite, marble, schist, two-mica schist) & intrusive rocks (granite, diorite)	40.0-110.0	<0.0001	0.059	0.0057	- All samples - Number of samples (n) = 299 - Median = 0.003 ppm
				40.0-110.0	<0.0001	0.021	0.0041	 Deep groundwater in alluvial fans n = 117 Median = 0.002 ppm
				50.0-110.0	<0.0001	0.056	0.0056	 Deep groundwater in transition area n = 35 Median = 0.002 ppm
				40.0-110.0	<0.0001	0.059	0.0071	- Deep groundwater in flat plain - n = 147 - Median = 0.005 ppm
(Neely et al. 2018)	Mývatn, north- east Iceland, NVZ	H ₂ S	Basalt, olivine basalt, tholeiite, alkali basalt, basanite, pillow basalt, flood basalt		<0.01	22.4	<0.01	- Boreholes M01-M20
	Þeistareykir, westernmost, NVZ				<0.01	0.03	<0.01	- Boreholes Þ01-Þ11

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