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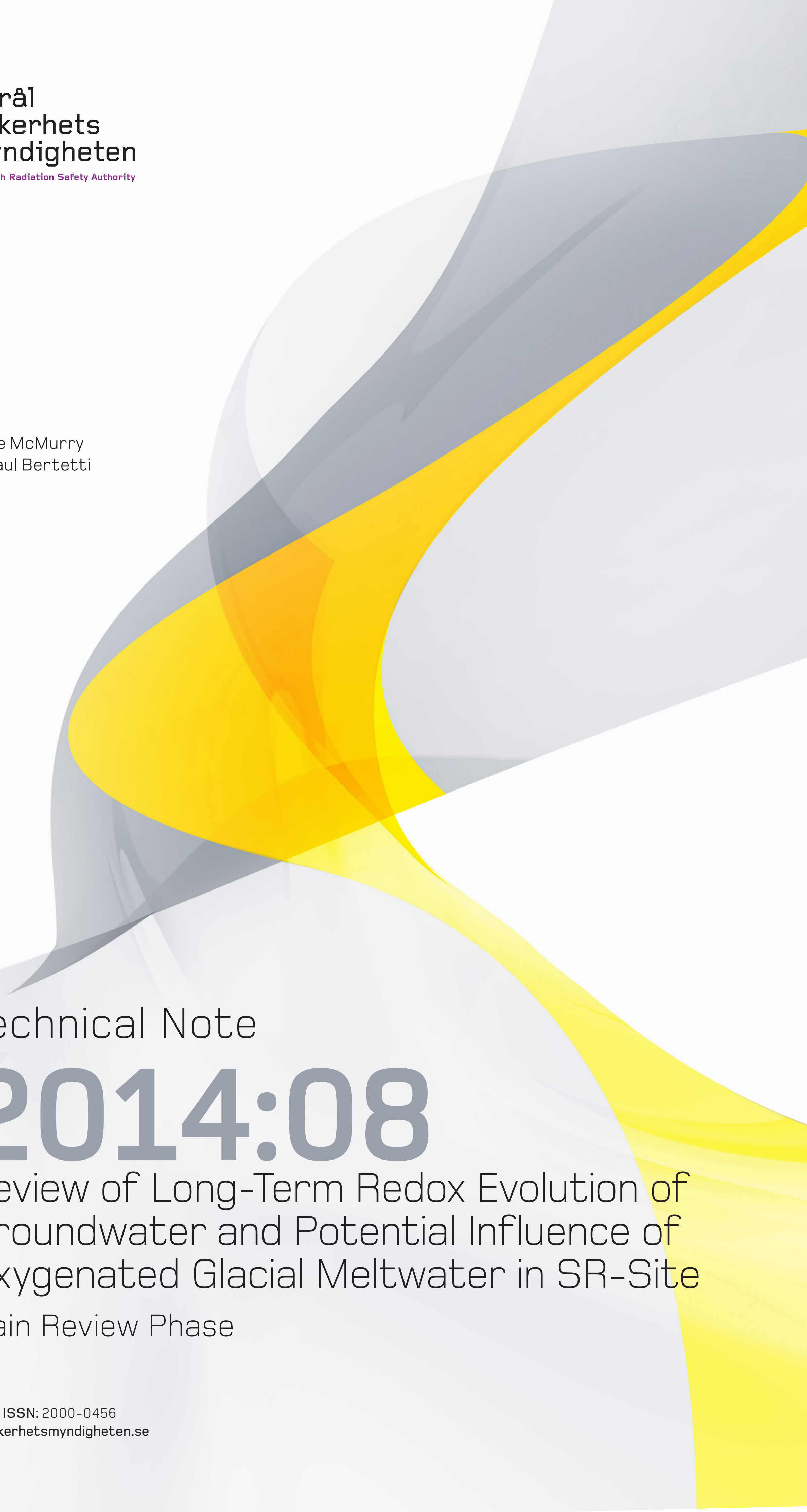

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Technical Note

2014:08

Review of Long-Term Redox Evolution of Groundwater and Potential Influence of Oxygenated Glacial Meltwater in SR-Site

Main Review Phase

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SSM perspektiv

Bakgrund

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

Projektets syfte

Syftet med detta uppdrag är att avgöra om SKB:s hantering av långsiktig utveckling av redox-betingelser i grundvatten är försvarbar och om det finns faktorer eller förutsättningar som inte beaktats i SKB:s analys som kan medföra förändringar av det förväntade Eh-intervallet. Den mest väsentliga potentiella störningen av grundvattnets Eh-buffring förväntas vara inflöde av syresatta glaciala smältvatten nära deponeringspositioner för kopparkapslar i slutförvaret.

Författarnas sammanfattning

Strålsäkerhetsmyndigheten (SSM) granskar en ansökan från Svensk Kärnbränslehantering AB (SKB) inlämnad under 2011 för att bygga, äga och driva ett djupt geologiskt slutförvar för använt kärnbränsle i Forsmark i Östhammars kommun, Sverige. SKB har presenterat uppgifter om den långsiktiga säkerheten, i en huvudrapport SR-Site (SKB, 2011, TR-11-01) och i flera tekniska stödjande dokument som citeras av huvudrapporten. Vid framtagandet av säkerhetsanalysen SR-Site, identifierade SKB närvaron av reducerande förhållanden i grundvattnet som en viktig säkerhetsfunktion som bidrar till optimal funktion av slutförvarssystemet. SKB konstaterade att ett grundläggande krav för den barriärfunktion som tillhandahålls av kopparkapseln är att undvika korrosion av kapseln med syre. SKB identifierade också reducerande grundvattenförhållanden som en säkerhetsfunktion relaterad till fördröjning av radionuklider med avseende på att upprätthålla (i) en låg upplösningshastighet för använt kärnbränsle i kontakt med grundvatten, (ii) låga elementära lösligheter av vissa radionuklider, och (iii) höga sorptionskoefficienter (Kd-värden) för vissa radionuklider. Syftet med denna tekniska granskning är att avgöra om SKB: s representation av framtida redox-förhållanden i ett djupt geologiskt slutförvar i Forsmark är försvarbart och om det finns faktorer som inte finns redovisade SKB: s analys som väsentligt kan ändra intervallet för representerade förhållanden. Granskningen utvärderade grunden för SKB:s modeller för långsiktig redox utvecklingen av grundvatten i Forsmark, med betoning på den potentiella intrång av syresatt glacialt smältvatten till förvarsdjup. Viktiga faktorer var huruvida SKB har tillgång till tillräcklig data för den avsedda tillämpningen, giltigheten av SKB:s modeller för redox-utveckling, och lämpligheten av SKB:s konceptuella förståelse och behandling av osäkerheter.

SKB har använt redox-mätningar av grundvatten, geokemiska och isotopanalyser, samt fördelningsprofiler för sprickfyllnadsmineral från borrhålsstudier för att utveckla modeller för hur redox-förhållanden förväntas variera till följd av vatten-berg interaktioner och blandning av grundvattentyper under förväntade tempererade och glaciala perioder i referensutvecklingen i säkerhetsanalysen. SKB konstaterade att förutom i de översta tiotals meter berg gav redox-mätning i grundvatten Eh-värden inom intervallet ca - 140 tom. - 280 mV. SKB har identifierat sammansättningar för typvatten för utveckling av hydrogeologiska och hydrokemiska modeller för utveckling av grundvatten i Forsmark vid tempererade och glaciala klimatförhållanden. Modelleringen gav information om den förväntade utvecklingen av redox-förhållanden vid Forsmark på grund av (i) blandning av vattentyper med olika initiala Eh-värden och (ii) kemisk jämvikt med antingen en järnoxihydroxid eller en amorf järnsulfid. Grundvattensystemet förutspåddes att upprätthålla negativa Eh (reducerande) betingelser under alla modellerade tidsperioder, men redox-förhållanden i berget i de övre hundratalen meter spås bli något mindre reducerande på grund av ökad inträngning av förändrat meteoriskt vatten och glaciärt vatten. I granskningen jämfördes SKB:s konceptualisering och modellresultat med information om redox-känslig sprickmineralisering och grundvattenkemi från undersökningar av kristallin berggrund på annan plats i den Fennoskandiska skölden och i Nordamerika. Vid denna granskning drogs slutsatsen att SKB:s integration av platskarakteriseringsdata och modelleringsmetoder är tillräckliga för att förutsäga hur grundvattnets redox-förhållanden vid Forsmark sannolikt kommer att utvecklas under lång tid framöver.

SKB har identifierat att under perioder av nedisning kan stora förändringar i den hydrauliska gradienten förekomma när en brant is-front passerar över en förvarsplats. Med tanke på den stora säkerhetsbetydelsen av att upprätthålla reducerande förhållanden på djupet så att kapseln inte påverkas av korrosion genom upplöst (molekylärt) syre så har SKB genomfört en separat detaljerad analys för att undersöka risken för inträngning av stora volymer av syresatt glacialt smältvatten längs djupa flödesvägar i berget. I SKB:s analys identifierades att under sådana djupa flödesförhållanden och i avsaknad av mikrobiell aktivitet eller ytnära abiotiska reaktioner med finfördelat subglacial sten som konsumerar syre skulle den huvudsakliga reducerande kapaciteten av geosfären bero på reaktioner mellan syresatt vatten och järnhaltiga mineraler i berget. SKB har utvecklat en upplösnings- och reaktionsmodell i två steg för att ta hänsyn till reaktionen av O2 med biotit, vilken är den mest förekommande källan för Fe2+-joner i Forsmarks bergarter. SKB har kombinerat den beräknade O2 förbrukning med platsspecifika parametrar från SKB:s hydrogeologiska flödesmodeller för att identifiera huruvida O2 skulle kunna tränga ner till en kapselposition i slutförvaret efter en 1000-årig period med infiltration av glaciala smältvatten. Resultaten visar att under de mest pessimistiska förhållanden som fanns med i modellen skulle endast ett fåtal av totalt 6000 kapselpositioner kunna nås av en liten koncentration av syre i mängder som inte skulle kunna leda till kapselbrott. SKB noterar att många pessimistiska antaganden krävs för att uppnå dessa modellresultat och SKB uteslöt följaktligen korrosion av kapslar med syresatt grundvatten från referensutvecklingen samt från det speciella kapselkorrosionsfallet i SR-Site. Under denna granskning drogs slutsatsen att SKB:s analys av syreinträngning med glaciala smältvatten är tillräckligt omfattande för att bedöma SKB:s slutsats att reducerande förhållanden i djupa grundvatten kommer att bibehållas som en säkerhetsfunktion för förvaret.

Inom säkerhetsanalysen SR-Site konstaterade SKB att oxiderande grundvattenförhållanden kan påverka upplösningshastigheten av använt bränsle i en havererad kapsel. SKB konstaterade också att inträngning av syresatt glacialt smältvatten till förvarsdjup har uteslutits för kapselkorrosionsscenariot i SR-Site på grund av att även om de pessimistiskt modellerade förhållanden skulle inträffa skulle de vara otillräckliga för att äventyra kapselns integritet. SKB identifierade vidare att i händelse av att syre tränger in i en havererad kapsel skulle korrosion av de metalliska inre delarna av kapseln upprätthålla reducerande förhållanden inuti kapseln. Denna granskning undersökt de argument som SKB presenterar kring potentialen för oxiderande förhållanden att påverka använt bränsles löslighet. Som en del av denna granskning konstateras att SKB på ett lämpligt sätt har underbyggt slutsatsen att löst syre inte kommer att tränga in till deponeringspositioner i bergvolymen i Forsmark, och av denna anledning har SKB också tillräckligt stöd för antagandet att oxiderande grundvattenförhållanden inte påtagligt påverkar bränsleupplösningshastigheter eller radionuklidernas löslighet i närområdet under förväntade förvarsförhållanden.

Inom modellering av radionuklidtransport i geosfären i SR-Site beaktar SKB den långsiktiga utvecklingen av redox-förhållanden vid val sorptionsparametrar (Kd-värden) för redox-känsliga radionuklider. SKB har identifierat förväntade variationer av redox-förhållanden under tempererade och glaciala framtida stadier baserat på modeller av grundvattenkemisk utveckling i Forsmark under olika klimatförhållanden, och konstaterar att med undantag av uran kommer modellerade förändringar i redox i geosfären inte förändra dominerande kemiska förekomstformer för varje redox-känslig radionuklid av intresse. För uran har SKB adresserat osäkerhet om den tidsmässiga och rumsliga variationen av redox-förhållanden på platsen genom att propagera både reducerande och oxiderande förekomstformer i radionuklidtransportmodelleringen för både tempererade och glaciala perioder. Inom denna granskning konstaterades att tillvägagångssättet är lämpligt eftersom man därigenom undviker antagandet att val av lägre Kd-värde för sorption är alltid konservativ inom dos beräkningar.

Sammanfattningsvis har SKB på ett lämpligt sätt identifierat de komponenter som i analysen av förvarets långsiktiga säkerhet är mest känsliga för förändringar av grundvattnets redox-förhållanden över tiden. SKB har också på ett lämpligt sätt identifierat att den mest säkerhetsbetydande potentiella störning av redox-förhållanden i grundvatten sannolikt är inflöde av syresatt vatten nära kapseldeponeringspositioner. SKB har också identifierat och på ett lämpligt sätt hanterat den potentiella effekten av förändringar i redox-förhållanden på oxiderande upplösning av använt bränsle, på löslighetsstyrd rörlighet av redox-känsliga radionuklider, och på sorptionsegenskaperna hos redox-känsliga radionuklider. Inom denna granskning har det inte framkommit några väsentliga faktorer utöver de som SKB har tagit upp som skulle kunna ändra förväntade redox-förhållanden på ett sätt som skulle påverka förvarets säkerhetsfunktioner.

SKB har understött viktiga slutsatser om den långsiktiga utvecklingen av redox-förhållanden med en detaljerad karaktärisering av platsens grundvattenkemi och mineralogi, med modeller för vatten-berg interaktioner och blandningsmodeller som illustrerar förväntade förändringar under specificerade framtida förhållanden, och genom att identifiera ett antal ytterligare styrande faktorer för redox utveckling som observeras i dagens förhållanden och sannolikt kommer att finnas kvar i framtiden men som är pessimistiskt uteslutna från SKB modellberäkningar. SKB har korrekt tolkat och använt platskarakteriseringsdata för att utveckla rimliga konceptuella, analytiska och numeriska modeller för att representera den långsiktiga utvecklingen av redox-förhållanden i Forsmark, inklusive undersökningar av den potentiella inträngningen av syresatta glaciala smältvatten till förvarsdjupet. Denna granskning uppmanar SKB att överväga en fortsatt petrologisk karakterisering av fördelning, sammansättning, och förändring av redox-känsliga mineralfaser både i sprickor och inuti bergmatrisen på samtliga djup vid Forsmarksplatsen, inklusive baslinjemätningar från mycket nära ytan eftersom berget i sig är bland de tydligaste indikatorerna på eventuella tidigare förändringar i redox som skulle kan ge en förbättrad förståelse för utvecklingen av redox-förhållanden i framtiden.

Projektinformation

Kontaktperson på SSM: Bo Strömberg
Diarienummer ramavtal: SSM2011-3639
Diarienummer avrop: SSM2013-2218
Aktivitetsnummer: 3030012-4065

SSM perspective

Background

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

Objectives of the project

The objective of this assignment is to determine if SKB's handling of long-term redox evolution in groundwater is defensible and whether there are factors or conditions that are unaccounted for in SKB's analysis that may alter the Eh range. The most essential perturbation of the groundwater Eh buffering could be expected to be inflow of oxygenated water near canister deposition positions in the repository.

Summary by the authors

The Swedish Radiation Safety Authority (SSM) is reviewing an application submitted by the Swedish Nuclear Fuel and Waste Management Company (SKB) in 2011 to construct, possess, and operate a deep geologic repository for spent nuclear fuel at the Forsmark site in the municipality of Östhammar, Sweden. SKB has presented details of its long-term safety assessment, SR-Site, in a main report (SKB, 2011, TR-11-01) and in multiple supporting technical documents that are cited by the main report. In developing the safety case for SR-Site, SKB identified the presence of reducing conditions in groundwater as an important safety function that contributes to the optimum performance of the disposal system. SKB stated that a fundamental requirement for the barrier effect provided by the copper canister is to avoid corrosion of the canister by oxygen. SKB also identified reducing groundwater conditions as a safety function related to the retardation of radionuclides with respect to maintaining (i) a low dissolution rate for spent nuclear fuel in contact with water, (ii) low elemental solubilities of certain radionuclides, and (iii) high sorption coefficients (Kd values) for certain radionuclides. The objective of this technical review is to determine if SKB's representation of future redox conditions in a deep geologic repository at the Forsmark site is defensible and whether there are factors unaccounted for in SKB's analysis that may significantly alter the range of represented conditions. The review examined the basis for SKB models for long-term redox evolution of groundwater at the Forsmark site, with an emphasis on the potential ingress of oxygenated glacial meltwater to repository depth. Key considerations were the adequacy of SKB data for the intended application, the validity of the SKB models for redox evolution, and the adequacy of SKB's conceptual understanding and treatment of uncertainties.

SKB used site groundwater redox measurements, geochemical and isotope analyses, and fracture mineral distribution profiles from borehole studies to develop models of how redox conditions would be expected to vary in response to water-rock interactions and groundwater mixing during the expected temperate and glacial periods in the reference evolution safety case. SKB observed that except in the uppermost tens of meters of rock, groundwater redox measurements gave Eh values in the range of about −140 to −280 V. SKB identified end-member groundwater compositions at the Forsmark site and used them to develop hydrogeological and hydrochemical evolution models for temperate and glacial climate conditions. The modelling provided information about the expected evolution of redox conditions at the Forsmark site due to (i) mixing of water types that had different initial Eh values and (ii) equilibration of the mixture with either an iron oxyhydroxide or amorphous iron sulphide phase. The groundwater system was predicted to maintain negative Eh (reducing) conditions over all modelled times, although redox conditions in the upper several hundred meters of rock were predicted to become less reducing due to increased ingress by altered meteoric and glacial waters. The review compared the SKB conceptualization and model results with information about redox-sensitive fracture mineralization and groundwater chemistry from investigations of crystalline bedrock elsewhere in the Fennoscandian Shield and North America. The review concluded that the SKB integration of site characterization data and modelling approaches is adequate to predict how groundwater redox conditions at the Forsmark site are likely to evolve over long times in the future.

SKB identified that during periods of glaciation, large changes in hydraulic gradient may occur where a steep ice front margin passes over a repository location. Given the safety importance attributed to maintaining reducing conditions at depth so that canister performance is not compromised by corrosion by dissolved (molecular) oxygen, SKB conducted a separate detailed analysis to investigate the potential ingress of large volumes of oxygenated glacial meltwater along deep recharge flow paths. The SKB analysis identified that under such deep recharge conditions and in the absence of microbial activity or near-surface abiotic reduction reactions with finely crushed subglacial rock debris, the main reducing capacity of the geosphere would depend on reactions between the oxygenated water and ferrous minerals in the rock. SKB developed a two-part dissolution and reaction model to account for the reaction of O2 with biotite, the most abundant source of Fe2+ ions in the Forsmark rocks. SKB combined the calculated O2 consumption rate with site-specific parameters from SKB hydrogeological flow models to identify whether O2 would penetrate to a repository canister location during 1,000 years of deep recharge by glacial meltwaters. The results indicated that under the most pessimistic conditions modelled, only a few of the 6,000 canister positions could be accessed by a small concentration of oxygen in amounts that would not result in canister failure. SKB noted the numerous pessimistic assumptions required to achieve these model results, and SKB accordingly excluded the corrosion of canisters by oxygenated groundwater from the reference evolution case as well as from the special canister corrosion case in SR-Site. The technical review concluded that the SKB analysis of oxygen ingress by glacial meltwaters is sufficiently comprehensive to address the SKB conclusion that deep groundwater reducing conditions will be maintained as a safety function at the repository location.

For the SR-Site safety assessment, SKB described that oxidizing groundwater conditions could affect the dissolution rate of spent fuel in a failed canister. SKB noted that the ingress of oxygenated glacial meltwater to repository depth had been ruled out for the canister corrosion scenario in SR-Site, on the basis that even if the pessimistically modelled conditions were to occur, they would be insufficient to compromise the canister integrity. SKB further identified that in the event of oxygen ingress for a compromised canister, the corrosion of the metal internal parts of the canister would maintain reducing conditions inside the canister. The technical review examined the arguments that SKB presented about the potential for oxidizing conditions to affect spent fuel solubility. The review concluded that SKB adequately supported the conclusion that dissolved oxygen will not penetrate to canister deposition positions in the target rock volume at the Forsmark site, and so SKB has also adequately supported the assumption that oxidizing groundwater conditions will not significantly affect spent fuel dissolution rates or other radionuclides solubilities in the near field under expected repository conditions.

For models of radionuclide transport in the geosphere for SR-Site, SKB considered the long-term evolution of redox conditions when selecting sorption parameters (Kd values) for redox-sensitive radionuclides. SKB identified the expected variations in redox conditions during temperate and glacial future stages from the SKB models of how the groundwater chemistry at the Forsmark site was expected to evolve under future temperate and glacial climate conditions, and determined that, with the exception of uranium, the modeled changes in redox in the geosphere would not change the dominant chemical species for each redox-sensitive radionuclide of interest. For uranium, SKB addressed uncertainty about the temporal and spatial variability of redox conditions at the site by propagating reduced as well as oxidized species in radionuclide transport modelling for temperate as well as glacial periods. The review considered this approach to be appropriate because it avoided the assumption that the selection of lower sorption values is always conservative with respect to dose calculation.

In summary, SKB has appropriately identified the components of repository safety that are most sensitive to changes over time in groundwater redox conditions. SKB appropriately identified that the most safety-significant potential perturbation of the groundwater redox conditions is likely to be inflow of oxygenated water near canister deposition positions. SKB also identified and adequately addressed the potential effect of changes in redox conditions on the oxidative dissolution of spent fuel, the solubility-controlled mobility of redox-sensitive radionuclides, and the sorption properties of redox-sensitive radionuclides. The review has not identified any significant factors that were not addressed by SKB that would alter the range of anticipated redox conditions in a way that would affect repository safety functions.

SKB supported key conclusions about the long-term evolution of redox conditions by a detailed characterization of site groundwater chemistry and mineralogy, by water-rock and mixing models that illustrate the expected changes under specified future conditions, and by identifying numerous additional controls on redox evolution that are observed under present-day conditions and are likely to persist in the future but were pessimistically excluded from SKB modelling calculations. SKB has appropriately interpreted and applied site characterization data to develop reasonable conceptual, analytical, and numerical models to represent the long-term evolution of redox conditions at the Forsmark site, including investigations of the potential ingress of oxygenated glacial meltwaters to a repository location at depth. The review recommends that SKB consider a continued petrological characterization of the distribution, composition, and alteration of redox-sensitive mineral phases in fractures and rock matrix at all depths at the Forsmark site, including baseline data from bedrock at or very near the surface, because the rocks themselves are among the clearest indicators of any past changes in redox that would inform an understanding of the evolution of redox conditions in the future.

Project information

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Technical Note 48

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Review of Long-Term Redox Evolution of Groundwater and Potential Influence of Oxygenated Glacial Meltwater in SR-Site

Main Review Phase

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Content

1. Introduction

The Swedish Radiation Safety Authority (SSM) is tasked, under the Act on Nuclear Activities, to review applications submitted by the Swedish Nuclear Fuel and Waste Management Company (SKB) for a repository for spent nuclear fuel and for an encapsulation facility. SSM is reviewing an application submitted by SKB in 2011 to construct, possess, and operate a deep geologic repository for spent nuclear fuel at the Forsmark site in the municipality of Östhammar, Sweden. SKB has presented details of its long-term safety assessment, SR-Site, in a main report (SKB, 2011) and in multiple supporting technical documents that are cited by the main report. In developing the safety case for SR-Site, SKB identified the presence of reducing conditions in groundwater as an important geosphere safety function that contributes to the optimum performance of the disposal system (SKB, 2011, Figures 8-2 and 8-3). The objective of this technical review is to determine if SKB's representation of long-term redox conditions in a deep geologic repository at the Forsmark site is defensible and whether there are factors unaccounted for in SKB's analysis that may significantly alter the range of represented conditions.

The review examines the basis for SKB models for long-term evolution of groundwater at the Forsmark site and for the potential ingress of oxygenated glacial meltwater to repository depth, then examines how the information was used to assess the long-term safety of a repository at the Forsmark site. The review also assesses whether there are risk-significant factors that SKB has not accounted for that may alter the expected range of redox conditions over time at the Forsmark site. Key considerations are the adequacy of data for the intended application, the validity of the SKB models, and adequacy of SKB's conceptual understanding and treatment of uncertainties.

1.1. Application to Safety Functions

SKB stated that a key safety function of the copper canister is to provide a corrosion barrier. A fundamental requirement of the barrier is to avoid corrosion of the canister by oxygen. SKB identified that the particular redox-sensitive data of interest were dissolved oxygen, sulphide, and sulphate (SKB, 2010, TR-10-52, Section 5.3.1). Oxygen and sulphide contribute to different copper corrosion mechanisms, but both potentially could affect the canister integrity as a containment barrier. SKB identified that sulphate is of interest for container corrosion processes because it can be reduced to sulphide by microbial activity. Oxygen and sulphide are redox-sensitive markers in water because (i) the presence of detectable amounts of dissolved (molecular) oxygen is a definitive indicator that the water has an oxidizing redox capacity, and (ii) the presence of detectable amounts of sulphide is an indicator of anoxic (reducing) conditions.

Apart from the influence of oxygen, there may be other changes over time in groundwater redox conditions due to changes in the geosphere in the concentration of redox-buffering constituents such as organic matter, ferrous iron, aqueous manganese species, and the corrosion agent bisulphide (HS^-). For each of these factors, SKB noted that it is important to establish the current redox conditions at the site and to consider whether, or how, the redox conditions are likely to evolve in the future.

Given the importance attributed to long-term containment of spent fuel by the SKB repository design, the most significant effect of a change in groundwater redox conditions for the SKB safety case would likely be an inflow of oxygenated water near canister deposition positions, potentially leading to copper corrosion and compromise of the canisters. SKB also noted that if there were a loss of containment from the canisters for any reason, the presence of reducing conditions in the repository would support the disposal system performance because the spent fuel itself will have a limited solubility under reducing conditions. In addition, reducing conditions could limit the solubility or enhance the sorption behavior of certain redox-sensitive radionuclides (SKB, 2011, Section 8.3.4). Accordingly, SKB also identified reducing (Eh limited) geosphere conditions as a safety function for the retardation of radionuclides in the near field environment and in the geosphere.

1.2. Redox Potential in Natural Waters

Redox (reduction–oxidation) reactions involve chemical elements that can exist in more than one valence state, depending on their acquisition or loss of electrons. Oxidized species of the element are those that have given up electrons, and reduced species are those that have acquired electrons. Unlike the activity of H^+ ions (protons) in solution, which determine a solution’s pH, free electrons do not exist in measureable quantities in a solution. For every reaction that releases an electron, another reaction must occur simultaneously to acquire the electron. In the written expression of a chemical reaction, the transfer of electrons typically is not shown explicitly but instead is indicated by the difference in valence states of ions, as shown in the following example for oxidation of Fe(II) (ferrous iron) to Fe(III) (ferric iron):

$$4Fe^{+2} + O_2 + 4H^+ = 4Fe^{+3} + 2H_2O$$

Redox potential measurements (Eh) describe the relative total activities of oxidized and reduced species of elements in solution. Positive Eh values indicate that the overall tendency of the solution is for oxidation reactions, and negative values indicate an overall tendency for reducing reactions. Another convention for expressing redox potential is pe, a unitless term that is defined, by analogy with pH and hydrogen ions, as the negative log of the activity of electrons in solution. Although the “activity” of electrons does not correspond to a measurable concentration of free electrons in solution, the term provides a convenient formalism for expressing redox reactions thermodynamically (Drever, 1988).

Redox potential is straightforward to express in electrochemical cells where the test solution contains a single redox couple, such as Fe_2O_3 and Fe^{+2}. Redox potential in groundwater is more problematic to interpret for several reasons. First, groundwater generally contains multiple chemical elements that are redox-sensitive (e.g., iron, sulphur, manganese), so the Eh measurement is based on the relative activities of oxidized and reduced species of all these elements, not just a single chemical element. Second, not all the redox reactions are likely to be at thermodynamic equilibrium, and their individual contributions to the total Eh measurement are difficult to quantify. Third, even with careful sampling procedures, redox measurements can be compromised significantly by small amounts of dissolved oxygen transferred into the groundwater from the drilling water in boreholes or from exposure of the groundwater sample to air.

Water at the earth's surface that falls as rain or snow has an oxidizing redox potential because it is in equilibrium with air and so contains dissolved O_2. As meteoric water enters the subsurface along recharge pathways, the redox potential of the water changes from oxidizing to reducing typically over a distance of a few tens of meters as the oxygen is consumed by reactions with organic matter in soils and overburden and by other interactions catalyzed by subsurface microbial activity. The presence of reduced iron, sulphur, and manganese ions in groundwater along the recharge flow path; the continued effects of microbial activity; and the precipitation of reactive solid phases such as $Fe(OH)_3$, Fe_2O_3, and MnO_2 tend to buffer the redox potential of the groundwater and promote further scavenging of oxygen. These factors, plus the circulation rate of the groundwater, are the most important variables controlling redox conditions in natural systems. With few exceptions, such as arid sedimentary basins that have sparse organic matter, fractured aquifers with rapid recharge rates, or certain active hydrothermal systems (Winograd and Robertson, 1982; Levley and Chapelle, 1995), deep groundwater in crystalline rocks worldwide is characterized by reducing conditions (Gascoyne, 1999).

1.3. Glaciation Effects

Glaciation processes are likely to produce two significant changes in subsurface water chemistry: (i) dilution of groundwater salinity, from displacement of or mixing of meltwater with more saline groundwaters, and (ii) changes in redox potential, particularly if the glacial meltwaters have a greater oxidizing capacity than meteoric water. The chemical attributes associated with these changes may result in precipitation of solid phases from solution or the dissolution of solids contacted by the altered water composition. Density differences associated with lower salinity can also affect flow and mixing relationships on a large scale hydrogeologically.

Meteoric water is oxidizing because it is equilibrated with atmospheric oxygen. Glacial meltwater may develop a higher oxidizing capacity than meteoric water if the meltwaters incorporate additional dissolved oxygen from air bubbles that were entrapped in the glacier during formation of the ice sheet. Although observations of microbial activity from present-day glaciers are inconclusive, it is likely that there is diminished biogenic activity under an ice sheet. In such a case, the limits on the depth to which large volumes of oxygenated water could penetrate the underlying rocks would be controlled by site-specific conditions in the geosphere such as the meltwater residence time beneath a large ice sheet, the microbial activity in the deeper rocks, the hydrogeological flow regime, mineralogy, and existing groundwater chemistry (Tranter, 2013; McMurry, 2000).

The most extreme hydrogeological changes associated with the advance or retreat of a kilometers-thick ice sheet are likely to occur at the leading edge of the ice sheet, where large contrasts in hydraulic pressures may result in the upconing of deep saline waters as well as the recharge of meltwater along deep, transmissive flow paths (e.g., SKB, 2010, TR-10-48, Figure 5-1). The possibility that the recharge path could carry dissolved oxygen to repository depth would depend on the balance between the initial oxygen concentration, the flow rate, and chemical reaction rates that would otherwise consume the oxygen along the transport path.

1.4. Forsmark Site Features

SKB developed a present-day hydrogeochemical conceptual model (Laaksoharju et al., 2008a; Salas et al., 2010) for the Forsmark site in the context of the spatial distribution of analyzed groundwater compositions and their relation to (i) rock domains, which SKB defined as large volumes of rock of similar lithology, (ii) deformation zones, a general SKB term referring to essentially planar features (e.g., fracture zones), along which there is a concentration of brittle or ductile deformation, and (iii) fracture domains, which SKB defined as large volumes of rock outside of fracture zones, in which the units have similar fracture frequency characteristics (SKB, 2008). Within the repository target volume itself (i.e., the northwestern part of the candidate area for the Forsmark site investigation and its extension to depth (Follin, 2008)), the lithology is relatively homogeneous and is dominated by metagranites.

SKB identified that the deformation zones at the Forsmark site include (i) steeply dipping fracture zones that transect the site more or less vertically, and (ii) gently dipping (subhorizontal) fracture zones (e.g., SKB, 2011, Figure 4-13). SKB identified that the target volume for the repository comprised parts of two fracture domains, termed FFM01 and FFM06, of which FFM01 is the larger volume of rock. Near the surface, FFM01 and FFM06 are overlain by fracture domain FFM02, which is characterized by subhorizontal fractures. SKB stated that these subhorizontal fractures in the uppermost 150 m of bedrock appear to have been the structures most affected by loading and unloading stresses associated with erosion and glaciation. The shallow fractures create a well-connected, highly transmissive network of subhorizontal flow structures for present-day meteoric recharge. Another large fracture domain, FFM03, extends from the surface to a depth of more than 500 m in the southeastern part of the candidate area. It is more transmissive than FFM01 and FFM06, which have a low frequency of open or partly open fractures (e.g., SKB, 2011, Figure 4-23). Two deeper subhorizontal fracture zones, ZFMA2 and ZFMF1, separate the fracture domains in the northwestern part of the candidate area from the southeastern part. SKB identified that the target repository location is on the footwall side of these fracture zones, at a nominal depth of 500 m, and fracture domain FFM03 is on the hanging wall side. The hanging wall side is characterized by a high frequency of open and partly open vertical fractures and gently dipping fractures compared to the footwall side, and it is more transmissive.

Based on site hydrogeochemical data, SKB described several distinctive groundwater types in the present-day system at Forsmark, several of which are mixtures with one or more other water types (Laaksoharju et al., 2008b). SKB developed a paleohydrological model to describe the observed water compositions in terms of evolution from past groundwater characteristics, including site-scale changes in groundwater chemistry that resulted from the last glaciation (Laaksoharju et al., 2008a). In the paleohydrology model, the observed present-day groundwater compositions were described as having evolved from five reference end-member waters with distinct geochemical and isotopic characteristics. SKB applied a widely used statistical analysis technique, principal component analysis, to the large geochemical and isotope data set and interpreted the results to define the reference end-member groundwater compositions at the Forsmark site as the following water types (Laaksoharju et al., 2008a, Table 1-1):

(i) dilute meteoric recharge, analogous to the present-day “altered meteoric” composition
(ii) dilute water with a glacial (cold climate) isotopic signature
(iii) “old meteoric” recharge water,
(iv) Littorina Sea (brackish) water, which has distinctive chemical characteristics
(v) deep, highly saline groundwater

The “old meteoric” recharge water has a warm-climate isotopic signature similar to that of present-day meteoric recharge water, but it occurs deeper in the rock and has experienced prolonged water-rock interactions (from before the last glaciation and perhaps much longer). SKB has no deep sample of highly saline groundwater (e.g., brine) at Forsmark from depths below 1000 m, but based on predictions from the principal component analysis and on observations from deep and ancient crystalline rocks globally (Fritz and Frape, 1987), SKB assumes this end-member is present. SKB represents it for modelling purposes with a slightly modified composition of the highly saline water (e.g., brine) that SKB sampled at a depth of 1,500 m from a single deep borehole at Laxemar (Laaksoharju et al., 2008a; SKB, 2009, Section 9).

SKB used the five reference end-member water compositions, and conceptual insights from the paleohydrogeology model, to develop and test various SKB hydrogeological flow models for the Forsmark site. In particular, the hydrochemical data were applied in three sets of flow models relevant to SR-Site. Data initially were applied as part of the site descriptive modelling (Selroos and Follin, 2010; Follin, 2008). For SR-Site, SKB also developed a regional-scale hydrogeological model for conditions expected during a temperate climate, over the equivalent of the period from 8,000 BC to 12,000 AD (Joyce et al., 2010), and a regional-scale model for the longer time periods during periglacial and glacial climate conditions (Vidstrand et al., 2010). Subsequently, SKB used the results from the regional-scale hydrogeological modelling (Joyce, et al., 2010; Vidstrand et al., 2010) as input data for geochemical mixing and equilibration models that SKB used to examine the site-wide evolution of groundwater chemistry, including redox conditions, over long time periods in the future (Salas et al., 2010; Gimeno, et al., 2008).

2. Site-Wide Reference Evolution of Redox Conditions

This section reviews how SKB used site characterization data and hydrochemical modelling to characterize present-day and future redox conditions at the Forsmark site. SKB used the results of these investigations to describe how redox conditions, expressed in terms of Eh or pe, would be expected to vary in response to groundwater mixing and water-rock interactions during temperate and glacial periods for the reference evolution safety case (SKB, 2011, Section 10). SKB's assessment of the potential migration of dissolved oxygen in glacial meltwater along deep recharge flow paths was developed as a separate analysis, which is reviewed in Section 3.

2.1. Distribution of Redox-Sensitive Fracture Minerals

SKB used geologic observations of the existing fracture mineralization from site borehole studies to establish an understanding of present and past redox conditions at the Forsmark site (Sidborn et al., 2010; Sandström et al., 2008; Sandström, et al., 2009). SKB analyses of the distribution of redox-sensitive minerals in fracture coatings and in the rock matrix in borehole cores found virtually no evidence of low-temperature mineral oxidation reactions below the upper few tens of meters of bedrock, indicating little or no exposure of the rock to oxygenated water at depth (SKB, 2008, Section 9; SKB, 2010, TR-10-52, Section 6.1). In addition to inline fracture mineral mapping in seven boreholes at the Forsmark site with SKB's Borehole Imaging Processing System (SKB, 2008, Section 2.3), SKB carried out detailed petrographic and geochemical studies of fracture surfaces and altered rock adjacent to fractures from more than 200 selected fractures in 22 drill cores and from one bedrock surface exposed by trenching at a drill site (Sandström et al., 2008; SKB, 2008, Section 2.2.1). The analyses included identification of redox-sensitive mineral phases, petrographic study of fracture minerals in thin sections, isotopic analysis of individual minerals, and chemical determinations of degrees of alteration with respect to past and present groundwater redox conditions (Laaksoharju et al., 2008a).

SKB identified four generations of fracture mineralization in the Forsmark rocks, each of which encompassed geologically long periods of time. SKB determined that the two oldest assemblages of fracture minerals originated at elevated temperatures when the Forsmark rocks were deeper in the crust during widespread tectonothermal events more than a billion years ago. Many of these ancient fracture minerals are in closed (sealed) fractures and are associated with reddened hydrothermal alteration zones in the adjacent rock conspicuously marked by the iron oxide mineral hematite (Sandström and Tullborg, 2006). By the beginning of the Paleozoic Era, these deep-seated crystalline rocks had been eroded to a peneplain at the earth's surface that has persisted as a large-scale geomorphic feature, the Fennoscandian Shield, ever since. This means that the bedrock currently exposed to erosion at Forsmark has been at or near the surface, or covered by layers of sedimentary rocks, for at least 500 million years (SKB, 2008, Section 5.2.5).

SKB identified that a third generation of fracture minerals crystallized during the Paleozoic Era, hundreds of millions of years ago. The Generation 3 fracture mineral assemblage, which formed under lower temperatures than the Generation 1 and 2 fracture minerals, is noteworthy because it includes pyrite, a ferrous iron sulphide that crystallizes under reducing conditions, and asphaltite, which is a general term for accumulations of black, tarry, highly viscous to solid hydrocarbons in pore spaces in the rock. SKB reported that the asphaltite is conspicuous in the upper 150 m of the bedrock at Forsmark, and it is sparsely distributed in a few transmissive fracture zones to depths of about 400 m (Sandström et al., 2008, Section 4.3). SKB stated the most plausible source of the asphaltite is organic matter which migrated into the fractures from thick layers of oil shale that was deposited regionally during the early Paleozoic and has been removed by erosion since then. SKB postulated that microbial or thermochemical reduction of sulphate species in the groundwater in the presence of the organic materials led to the precipitation of the pyrite in the Generation 3 fracture minerals.

SKB estimated that the most recent set of fracture minerals, Generation 4, formed over a timeframe of tens of millions of years during the Cenozoic Era up to the present. The Generation 4 fracture mineral assemblages typically occur in hydraulically conductive (open) fractures, where they form mixed chlorite and clay minerals and thin, low-temperature coatings of calcite. SKB identified that some calcites in the upper 200 m of rock from this mineral set have oxygen isotope ratios similar to the present-day groundwater compositions at the same depth, and these may be relatively recent precipitates; other calcites have cold-climate isotope ratios and are thought to have precipitated from an earlier groundwater that had more of a glacial meltwater component.

SKB did not acquire mineral data for the uppermost few meters of overburden and bedrock at the Forsmark site, where oxidizing conditions are most likely to be found, because samples were not available from borehole lengths above 5.20 m for any of the mapped boreholes (Sandström et al., 2008). The only low-temperature redox-sensitive iron oxide mineral identified in fractures as evidence of oxidizing groundwater conditions was goethite (FeOOH). Most of the observed goethite was sparsely distributed as brownish to rust-red, fine-grained precipitates that occurred predominantly in gently dipping fractures in the upper 50 m of deformation zone FFM02. Minor occurrences of goethite were also noted in a few steeply dipping fracture zones, to depths of about 200 m (e.g., Sandström et al, 2008, Figure 6-6). SKB also cited a detailed analytical study of iron oxide fracture-filling phases from Äspö and Oskarshamn, in which low-temperature naturally occurring iron oxides were similarly limited to depths of less than about 100 m (Dideriksen et al., 2007). One deep fracture sample from Forsmark, from a depth of 642 m in borehole KFM02A, contained a very fine-grained low-temperature amorphous iron oxide phase, but its origin was attributed to contamination by drilling water (Dideriksen et al., 2007).

SKB noted that the pyrite which precipitated under reducing conditions at the Forsmark site as a Generation 3 fracture mineral has persisted without alteration, even in shallow fractures where the presence of goethite as a late-stage fracture mineral indicates that oxidizing groundwater conditions have existed at this location since the pyrite originated. SKB stated that the juxtaposition of pyrite and goethite at these locations may be due to localized heterogeneities in redox conditions along the flow paths or may be due to localized microbial environments which resulted in goethite precipitation in some locations and which aided pyrite preservation in others.

Sandström et al. (2008) examined the distribution and texture of calcite in fractures as a secondary indicator of changes in redox conditions. Calcite ($CaCO_3$) is a pH-sensitive mineral but not strictly a redox-sensitive mineral. However, other studies in similar crystalline bedrock in Sweden have noted an apparent relation between the location of a redox front and dissolution of calcite, and researchers have attributed these observations to the commonly greater acidity of oxygenated water (Tullborg, 1989). Observations of calcite distribution at Forsmark were inconclusive. Moreover, the field investigation lacked data from the uppermost 5 m of bedrock, where oxidizing conditions were most likely to be present (Sandström et al., 2008).

2.2. Groundwater Variations in Redox Capacity

The SKB safety function R1(a) stated that the geosphere, in providing chemically favourable conditions for repository safety, should “provide reducing conditions (Eh limited)” (SKB, 2011, Section 8.2). SKB models of the geochemical evolution of the Forsmark site during temperate, periglacial, and glaciated conditions included general estimates of the expected changes in Eh over time. Redox-related site characterization data at the Forsmark site included a modest number of Eh measurements in groundwater, as well as measured concentrations of redox-sensitive chemical elements and ionic species in groundwater (e.g., iron, manganese, uranium, sulphate, bisulphide).

SKB reported that except in the upper few meters to tens of meters of bedrock, redox measurements in groundwater at the Forsmark site gave negative Eh values ranging from -143 to -281 V, though there was no consistent correlation between depth of the sample and measured Eh (Gimeno et al., 2008). The investigators stated that some of the observed variability between Eh and depth may have resulted from perturbation of the redox system during sampling but that the variability also could be due to intrinsic differences in hydrogeology (i.e., some samples from similar depths were collected from sub-vertical flow zones and others were from sub-horizontal flow zones, for which flow rates and mixing relationships are different). The investigators also noted that, based on paleohydrology models, some older waters appear to have been preserved in isolated lenses with different redox potentials than groundwater elsewhere in the system at comparable depths.

SKB reported that populations of sulphate-reducing bacteria, iron-reducing bacteria, and manganese-reducing bacteria were present in groundwater in variable concentrations at all measured depths, although microbial activity was barely detectable in some of the deepest groundwaters, sampled at borehole lengths of about 900 m (SKB, 2008, Section 9.5.4). SKB stated that measured Eh values in groundwater generally correlated with the numbers of sulphate-reducing bacteria detected at the same horizon, indicating that sulphate-reducing bacteria help to moderate the redox state of the groundwater, but effects of microbial activity are not specifically included in the SKB groundwater evolution models.

SKB identified that the role of microbes was a factor affecting the SKB safety function R1(d), to limit the concentrations of HS^-, H_2, CH_4, K^+ and Fe (SKB, 2011, Sections 8.3 and 8.4). Microbes can metabolize or produce redox-sensitive chemical components (e.g., reactions between SO_4^{2-} and H_2 to reduce the sulphate and produce HS^-, a potential canister corrodant). With the exception of potassium ions (K^+) and Fe species, the groundwater components listed in safety function R1(d) typically are present only in trace amounts in groundwater. SKB addressed the significance of these species on an individual basis instead of as part of a groundwater evolution model (Salas et al., 2010). In general, SKB stated that the trace components provided to the groundwater system by surface processes would tend to be less abundant during periods of glaciation than under present-day conditions. For other components, including those such as methane and hydrogen gas that can have deep-seated sources, SKB concluded that with no additional information available about how or why these sources would be expected to change markedly in the future, the maximum observed present-day concentrations were reasonably conservative estimates to use for future conditions.

To model how the Forsmark site groundwater chemistry is expected to evolve under temperate climate conditions over approximately the next 10,000 years, Salas et al. (2010) obtained the mixing proportions of the five end-member reference waters at Forsmark (Laaksoharju et al., 2008) from the output of a site hydrogeological flow model (Joyce et al., 2010) at times of 2000, 3000, 5000, and 9000 AD. The flow model calculated mixing proportions at each time for thousands of individual locations (cells) in the model volume, from which Salas et al. (2010) selected cell-by-cell information for several key cross sections through the model that were relevant to the repository location. To obtain more detailed compositions of the reference waters to use in the geochemical evolution modelling, Salas et al. (2010) noted that several of the reference end-member water compositions lacked certain geochemical parameters such as pH, Eh, and concentrations of Al, Fe, P, and sulphide species. Salas et al. (2010) accordingly used the modelling software PHREEQC (Parkhurst and Appelo, 1999) to simulate equilibrium of each of the end-member water compositions with selected solubility-controlling mineral phases to estimate the missing information for the starting end-member compositions. Salas et al. (2010) then reacted the end-member water compositions, in the mixing proportions specified at each cell by the flow model, with a set of simple mineral phases generally representative of the host rock geology and used the model results to construct a set of detailed three-dimensional cross sections through the candidate site volume as a series of "snapshots in time" to depict the geochemical evolution of the site at future times during a temperate climate period (Salas et al. 2010).

The modelling results included information about the evolution of redox conditions in the system, where redox (Eh) values were influenced by (i) mixing waters that had different initial Eh values and (ii) equilibrating the mixture with either an Fe(III) oxyhydroxide or amorphous Fe(II) sulphide phase. SKB explained that the PHREEQC modelling assumed that oxygenated waters would not be present in the modelled system because, under the chemical equilibrium conditions of the model, any dissolved oxygen would be instantly consumed by the ferrous minerals included in the model (Salas et al., 2010). All of the starting (reference) end-member waters except the near-surface Altered Meteoric water had reducing (negative pe) values, and the entire system was predicted to maintain reducing conditions in the future although the persistent ingress of the altered meteoric water to depth over time made redox conditions in the upper several hundred meters of rock become less reducing (i.e., less negative) than under present conditions (Salas, et al., 2010).

Salas et al. (2010) used a similar mixing and chemical equilibration approach to model the geochemical evolution of groundwater chemistry at longer times, during parts of a glacial cycle spanning conditions of approximately 100,000 years. In the glaciation hydrogeological modelling (Vidstrand et al., 2010), the mixing proportions in the model were derived from two end-member water salinities that were differentiated by their chloride concentrations – a deep saline reference groundwater and a dilute water of meteoric origin – instead of from the five more detailed groundwater compositions used in the temperate flow modelling. With the advance and retreat of the glacier, a third end-member, representing glacial meltwater, was included in the flow modelling to achieve additional dilution later in the model sequence (SKB, 2011, Section 10.4.7). Vidstrand et al. (2010) developed separate sets of flow model results to examine different stages or conditions of glacial cycles, including a submerged saline period, infiltration of glacial meltwaters, upconing of deep saline waters associated with the advance of an ice sheet, and the effects of a frozen soil underneath an ice sheet.

After obtaining cell-by-cell mixing proportions of the two (or three) end-members from the glaciation flow models, Salas et al. (2010) again used the geochemical modelling software PHREEQC to simulate mixing and equilibration of the end-member waters with a set of specified minerals. The PHREEQC modelling included effects of deep recharge of glacial meltwater during the advance of an ice sheet. However, the modelling assumed that dissolved oxygen was not present in the system, and redox capacity across the system was modelled by equilibrating the mixtures with either an Fe(III) oxyhydroxide or amorphous Fe(II) sulphide phase (Salas et al., 2010). During the advance of an ice sheet above the repository, the modelled redox evolution of the system at repository depth initially became more reducing than at present, due to upconing of more saline water from depth. After the ground above the repository was covered by an ice sheet, and during the retreat of the ice sheet, the modelled water at repository depth became less reducing as recharging meltwater displaced and mixed with the more saline water.

2.3. Technical Review of Long-Term Evolution of Redox Conditions

SKB has appropriately supported assumptions about past and present reducing conditions in fracture groundwaters with a detailed characterization of fracture mineral assemblages at the Forsmark site. In particular, SKB recognized that iron oxide phases are important indicators of past redox conditions because, although they tend to precipitate readily from Fe-oversaturated solutions in oxidizing groundwaters, their dissolution under reducing groundwater conditions is strongly hindered kinetically (Drever, 1988). Another example of this persistence is the preservation of ancient secondary hematite, a crystalline iron oxide, in the fracture mineral assemblage at Forsmark, despite its being exposed to reducing groundwater conditions for at least hundreds of millions of years. The distribution of low-temperature fracture mineral assemblages at Forsmark, including the observed localization of goethite within tens of meters from the surface but not in deeper rocks except perhaps along highly transmissive fracture zone, compares closely with similar analyses of redox-sensitive fracture mineralization in crystalline bedrock worldwide (e.g., Blyth et al., 2009; Bath et al., 2000; Gascoyne, 1999; Gascoyne et al., 2004; McMurry and Ejeckam, 2002; Tullborg 1989). SKB studies of natural uranium distribution in fractures, and uranium-series decay isotope analyses in particular, suggested that uranium (another redox-sensitive element) has been mobile in the upper 150 m of the bedrock over the past million years or so (Sandstrom et al., 2008). SKB also found evidence of the mobility of U(VI) in some deeper rocks, but noted that these examples probably did not represent oxidizing conditions because mildly reducing groundwaters with sufficient bicarbonate concentrations also are capable of keeping U(VI) mobile at depth (Laaksoharju et al., 2008). Other redox anomalies, such as evidence for cerium oxidation in some fracture linings at depth, were ambiguous because the cerium was associated with ancient hydrothermal alteration (Sandstrom et al., 2008).

Previous reviews of SR-Site (e.g., McMurry and Bertetti, 2012; Bath, 2012) found that SKB implemented a comprehensive and integrated hydrochemical characterization during the Forsmark site investigation that included sampling for a wide range of relevant chemical parameters such as major ions, trace metals, stable and radiogenic isotopes, dissolved gases, organic and inorganic carbon, microbes, and colloids (Laaksoharju et al., 2008; SKB, 2008, TR-08-05, Section 6.1). SKB recognized the practical difficulty of collecting reliable redox (Eh) measurements from boreholes and developed a refined method based on continuous logging of three different electrodes over long time periods in borehole sections isolated by packers (Auqué et al., 2008). The Eh measurements were supplemented and checked by monitoring other parameters in the same borehole sections such as pH, dissolved O_2, and conductivity. Although at least some drilling water was detected in most borehole samples, the multiple SKB constraints provided reasonable confidence in the redox measurements for the samples in which the percentage of drilling water was less than 10 percent. Moreover, the measured Eh values were within expected ranges for groundwaters at comparable depths worldwide, and variations in Eh with depth across the site correlated reasonably with identified differences in transmissivity of the rock in the northwestern, footwall portion of the site (FFM02 and FFM01, including the target repository volume) as compared with the southeastern, more transmissive hanging wall portion of the site (FFM03 and FFM01). Where redox measurements were not performed or were not considered reliable, SKB used other indicators such as measured sulphide concentrations to establish a general understanding of the reducing conditions in the sampled waters. Based on the broad scope and duration of the SKB groundwater sampling program, and SKB's detailed screening of data and use of other indicators to support assumptions, this review considers that despite the modest data set, the SKB borehole redox measurements are reasonably complete and acceptable for this stage of site characterization.

SKB did not include microbial effects in geochemical models of long-term redox evolution but acknowledged the pervasiveness of microbes in the geosphere and the established role of microbial activity in rapidly consuming dissolved O_2 in the shallow subsurface environment under temperate conditions. SKB also cited the REX Experiment, an *in situ* study at the Äspö Hard Rock Laboratory, which has supported SKB assumptions about the effectiveness of microbial activity in consuming dissolved oxygen in the deeper subsurface (Puigdomenech et al., 2001). Rather than specify or predict the role of microbial impacts in establishing or maintaining a reducing capacity in groundwater for the SR-Site safety assessment, SKB chemical models of redox evolution in general and oxygen consumption in particular have assumed that the groundwater redox capacity is controlled only by abiotic reactions. For the SKB safety function R1(a), this assumption is conservative with respect to the likely extent of ingress by oxidizing waters in the Forsmark rocks.

SKB developed a conceptual model for the Forsmark site for the past and future evolution of groundwater chemistry, including redox characteristics, that appropriately drew upon multiple sources of data obtained during the site investigation as well as from broader knowledge of Fennoscandian Shield geology. The SKB site description of Forsmark at the completion of the surface-based site investigation phase documented how SKB had collected, compiled, and qualified geological, hydrogeological, and geochemical data for use in the SR-Site assessment (SKB, 2008). SKB conducted the acquisition and interpretation of site data at Forsmark in stages, during which times the efforts of analytical and modelling groups were integrated to address and target the ongoing resolution of uncertainties to carry out during the next stage of work. Comparable stages of site investigation and model integration also were carried out during the same timeframe at Laxemar-Simpevarp, the other area SKB investigated as a potential repository site (SKB, 2009). This review notes that the lack of site-specific data for deep (presumably highly saline) groundwater at the Forsmark site, and the substitution of a modified deep water composition from Laxemar as a reference end-member water for modelling purposes, has introduced some uncertainty to the SKB hydrochemical modelling. However, based on what SKB has identified as the future long-term evolution of redox conditions at the site, and given what is known of the reducing characteristics of deep groundwater chemistry in similar geologic settings worldwide, the reviewers concur with the SKB assumption that the deep saline groundwater at Forsmark will have sufficient redox capacity to maintain reducing conditions at repository depth regardless of its detailed composition.

SKB's integration of site characterization data and modelling approaches for the evolution of groundwater redox conditions and other geochemical properties was best constrained for temperate climate conditions. The input for the temperate-climate PHREEQC modelling was closely tied to the SKB groundwater flow model that SKB developed using the five representative end-member groundwater compositions (which, in turn, were developed from geochemical site characterization data). The conceptual uncertainties in the PHREEQC modelling for future glacial cycle conditions were larger, and the geochemical calibration of the glacial cycle hydrogeological models is less robust, because the glacial cycle modelling relied on only two generalized groundwater types (a saline water and a dilute water) and relied only on salinity values to constrain the flow model calibration and mixing calculations. With respect to the broader time frame and large changes in hydrogeological properties that the glaciation modelling addresses, however, this review considers that the SKB approach for modelling future glacial conditions is acceptable.

SKB conceptual models incorporated the Forsmark hydrochemical data and used them for detailed interpretations, appropriately providing support for the development of the reference end-member water compositions (Salas et al., 2010; Laaksoharju et al., 2008; SKB, 2008). The end-member water compositions are important because they form the basis for the detailed modelling SKB used to examine future hydrochemical evolution of the site (Salas et al., 2010). The geochemical modelling included appropriately screened site data and reasonable assumptions to address uncertainties about the mixing-related precipitation and dissolution of specific mineral phases, and about hydrogeological characteristics of the Forsmark flow system characteristics. To address uncertainties about the redox-controlling mineral phase at depth in the PHREEQC redox evolution modelling, SKB completed two independent sets of redox evolution calculations based on equilibration with Fe(III) oxyhydroxides and on equilibration with amorphous Fe(II) sulphides. Both sets of results predicted that Eh values throughout the modelled volume would remain negative (reducing) over the temperate and glacial time periods (Salas et al., 2010, TR-10-58). Based on the current knowledge of the Forsmark site, this review considers that SKB's redox evolution modelling results are acceptable as an evaluation of the expected site-wide, long-term evolution of redox conditions.

3. Groundwater Variations in Dissolved Oxygen

SKB related the geosphere safety function R1(a), “the geosphere should provide reducing conditions,” to the canister safety function Can1, “provide corrosion barrier (copper thickness greater than 0)” (SKB, 2011, Figure 8-2), because corrosion in the presence of dissolved oxygen (O_2) is one of the two main mechanisms SKB identified that could corrode the copper canisters in the repository. SKB stated that the two most plausible settings in which dissolved oxygen could be made available for corrosion of a container surface in a repository are (i) the migration of atmospheric oxygen to the canister surface from air trapped in the resaturating backfill and buffer materials at the end of the operations phase, and (ii) the advection of oxygenated glacial meltwater to repository depth during a future glaciation event (TR-10-66, Sec. 3.2). In the repository resaturation period, SKB estimated that microbial activity and reactions with minerals such as pyrite, carbonates, and Fe(II)-bearing silicates in the backfill and buffer materials would rapidly consume most of the free oxygen before it could diffuse to a container, resulting in less than 0.5 mm of canister corrosion (SKB, 2011, Sec.10.2.5). This review of long-term groundwater redox evolution focuses on SKB’s evaluation of the second setting, involving changes at the container surface that may occur by the transport of dissolved oxygen in meltwater during a glacial cycle. For SR-Site, SKB described results of several redox evolution analyses that assessed whether oxygenated meltwater could penetrate to repository depth under glaciation conditions (SKB, 2011, Section 10.4.7). SKB considered the potential effect for the reference evolution case and also for alternate safety cases that focused specifically on canister corrosion processes beyond those included in the reference evolution.

3.1. Oxygen Ingress Calculations for the Reference Evolution Case

SKB noted that during periods of glaciation, large changes in hydraulic gradient may occur when the glacial ice front margin passes over a repository, in which case the higher gradient may drive large volumes of potentially oxygenated glacial meltwater downwards along steep flow paths in the rock (SKB, 2011, Section 10.4.7). SKB identified that although the theoretical maximum possible concentration of dissolved oxygen in glacial melt water is greater than that for meteoric water, such elevated dissolved oxygen concentrations have not been measured in meltwaters from existing glaciers (e.g., Gascoyne 1999). SKB stated the lower observed concentrations are realistically what would be expected, due to several potential influences in and beneath the glacier such as microbial activity on the glacier surface (Hallbeck, 2009) and abiotic reduction by reactions with debris and finely crushed rock minerals in and under the ice that provide larger reactive surface areas than intact minerals do (Wadham et al., 2010). SKB stated that in the absence of these conditions or without additional microbial reduction in the geosphere itself, the main reducing capacity of the system would depend on abiotic reactions of oxygenated water with Fe(II)-bearing minerals in the rock. SKB accordingly developed a water-mineral interaction model and integrated it with a hydrogeological model of expected advective conditions at the Forsmark site to estimate the depth to which oxygenated water might penetrate in the subsurface for various assumptions about glacial conditions (Sidborn, et al., 2010). The conceptual model identified that the depth to which dissolved oxygen would penetrate in the subsurface before it was depleted from the meltwater depended on the flow rate, the rate at which reactions with ferrous minerals scavenged the oxygen from the meltwater, and the time period covered by the modelling. The hydrogeology of the flow system would change markedly depending on the location of the edge of the ice sheet, so Sidborn et al. (2010) performed oxygen ingress calculations for several separate stages of the modelled advance of an ice sheet over the repository. For each set of calculations, it was assumed that the ice sheet at that location remained stationary for a specified time of hundreds to thousands of years.

The water-rock interaction model conservatively assumed that dissolved oxygen in water flowing in a fracture would react only with biotite, a mafic silicate that is the most abundant Fe(II)-bearing mineral in the Forsmark host rocks (Sidborn et al., 2010). Oxidation of the ferrous iron was assumed to occur in two steps: (i) dissolution of Fe(II) from the biotite crystal lattice and (ii) subsequent oxidation of the aqueous Fe^{2+} ions. The migration of the dissolved oxygen through the rock was represented by two models. First, as oxygenated water entered the fracture flow path, the oxidation of biotite at the fracture surface was determined by the balance between the rate of O_2 recharge along the fracture flow path and the rate of O_2 consumption by Fe(II) ions that were released according to the dissolution rate of biotite. Second, as the supply of Fe(II) ions from biotite at the fracture surface was depleted, the oxidation of biotite in the rock matrix was determined by the rate of diffusion of O_2 into the rock, where the O_2 would encounter Fe^{2+} ions that had been released from the biotite.

SKB identified that the overall migration of oxygen over time along the fracture flow path was determined primarily by the second model, as a combination of the flow rate and the O_2 matrix diffusion rate. SKB related the consumption rate of dissolved oxygen by biotite in the matrix to the oxygen diffusion resistance in pores of the rock matrix, which SKB stated could be expressed by a key hydrogeological parameter called the flow-wetted surface to flow rate ratio, or *F*-factor (Sidborn and Neretnieks, 2008). By supplying *F*-factors from an SKB discrete fracture network flow model for glacial conditions at Forsmark (Joyce, et al., 2010), Sidborn et al. (2010) estimated that for the most pessimistic glacial situation—an unlikely case where (i) the initial glacial meltwater contained the maximum theoretical amount of dissolved O_2 (approximately 1.5 mM) and (ii) the ice front margin remained stationary at the worst possible hydraulic position above the repository for 1,000 years—a small but measureable concentration of dissolved oxygen (exceeding 0.3 μM) might reach as many as 14 canister deposition locations (Table 1). SKB also stated that the specific canister locations identified as those exposed to the highest oxygen concentrations were not the same locations as those predicted by the hydrogeological modelling to have advective conditions that would compromise buffer performance by erosion. SKB further noted that the oxygen ingress model calculations conservatively did not account for the additional barrier provided in the near field by migration of dissolved oxygen through intact buffer to reach container surfaces. For a more likely initial oxygen concentration of 0.3 mM in glacial melt water, Sidborn et al. (2010) calculated that, depending on the flow-path distance corresponding to the F-factor in the cases modelled, the concentration of oxygen reaching the canister positions dropped by an order of magnitude or more.

In the SR-Site main report, SKB summarized the oxygen ingress model developed by Sidborn et al. (2010) and identified that, based on the results of the model calculations as applied to site-specific hydrogeological conditions, “a few” deposition locations could be reached by oxygen concentrations exceeding 0.1 μM under the assumed conditions (SKB, 2011, Section 10.4.7). Citing the numerous pessimistic assumptions that were incorporated by the oxygen ingress modelling, as well as the scarcity of field evidence to indicate that oxygenated glacial meltwater has penetrated deeply in the subsurface at the Forsmark site or anywhere in the world (except perhaps in a few steeply dipping, highly transmissive fracture pathways), SKB concluded that oxygen at “non-negligible concentrations” would not reach canisters in a repository at Forsmark in the SR-Site reference evolution case. SKB therefore stated that anoxic conditions will persist in the repository throughout a glacial event and that the safety function indicator criterion R1(a) will be satisfied during all the time periods considered for the SR-Site reference case.

3.2. Oxygen Ingress Calculations for Canister Corrosion Cases

Because SKB ruled out the possibility that oxygenated groundwater would reach canister deposition holes, the safety assessment calculations for the reference evolution safety case in SR-Site did not address any effects attributable to the corrosion of canisters by oxygenated groundwater (SKB, 2011, Section 10.4.7). SKB also investigated the potential effects of oxygen ingress by glacial meltwater for an alternate safety case, the canister corrosion case, which examined the effects of various other repository evolution scenarios on canister integrity (SKB, 2011, Section 12.6.2). In a supporting report, the Corrosion Calculations Report (SKB, 2010, TR-10-66, Section 5.2.3), SKB further summarized the assumptions and results of the alternative case corrosion scenario calculations and provided additional information about the specific canister corrosion processes, the repository environment, and how the corrosion rates were estimated.

For the corrosion case studies, SKB slightly adapted the oxygen ingress modelling approach documented by Sidborn et al. (2010) by using flow-related transport resistance values (F-factors) from a variant representation of the groundwater flow model. SKB stated that the variant model, termed the extended spatial variability case, was based on up-scaling the explicit discrete fracture network (DFN) model used by Joyce et al. (2010) to account for fractures in the full hydrogeological domain during the glacial scenario. SKB stated that the special case included representative recharge flow paths close to the ground surface, in addition to the DFN features that were used to model the part of the flow domain that hosts the repository. Using a pessimistic initial dissolved maximum oxygen concentration of 1.5 mM and F-factors from the extended spatial variability case for flow modelling, SKB identified that if the modelled conditions persisted for 1,000 years, then 31 of 6,000 canister deposition positions would experience oxygen concentrations above 0.1 μM (Table 1). Of these 31 positions, SKB stated that 6 would be exposed to oxygen concentrations above 1.0 mM. In the second-worst case modelled, where the leading edge of the ice sheet was at a different location above the repository, SKB estimated that the most-affected deposition canister positions would have O_2 concentrations less than 0.15 mM after 1,000 years (SKB, 2011, Section 12.6.2).

SKB stated that although the corrosion case analyses predicted a few canisters in the repository would be exposed to oxidizing waters in some of the modeled examples, for all the analyses the maximum effect on canister corrosion would be insufficient to compromise containment integrity. To support this statement, SKB calculated canister corrosion rates based on the maximum estimated oxygen concentrations at these canister positions. For the corrosion rate calculations, SKB assumed that (i) advective conditions prevailed at the canister positions (i.e., partially eroded buffer), and (ii) all the exposed canister positions were subject to the same high-end flow rate that SKB had used in a separate sensitivity analysis which investigated canister corrosion rates in the presence of sulphides (SKB, 2010, TR-10-66, Section 4.3). Applying the theoretical maximum initial oxygen concentration and the highest flow rate, SKB estimated a maximum canister corrosion rate of slightly less than 6 microns/yr, which would result in a canister corrosion depth of about 6 mm if these oxygen ingress conditions persisted as modelled for 1,000 years. Citing the many pessimistic assumptions that went into estimating the oxygen ingress corrosion rates, SKB concluded in the SR-Site Main Report that any effects of oxygen penetration to repository depth could be excluded from the canister corrosion scenario (SKB, 2011, Section 12.6.2).

Table 1. SKB Example Estimates of Dissolved Oxygen Ingress and Canister Effects

Initial O_2 Concentration in Meltwater	**F-factor (yr/m)**	**Concentration of O_2 at Canister Positions after 1,000 years**	**No. of Affected Canister Positions**	**Estimated Canister Corrosion Rate**	**Source (SKB Report No.)**
1.5 mM (theoretical maximum)	~5,400	greater than or equal to 0.3 mM	14	Not estimated	TR-10-57 (Sidborn et al., 2010)
1.5 mM	~9,400	greater than or equal to 0.003 mM	25	Not estimated	TR-10-57 (Sidborn et al., 2010)
0.3 mM	~3,000	greater than or equal to 0.03 mM	7	Not estimated	TR-10-57 (Sidborn et al., 2010)
0.3 mM	~4,000	greater than or equal to 0.003 mM	11	Not estimated	TR-10-57 (Sidborn et al., 2010)
0.3 mM	Not stated	greater than 0.1 μM	"a few"	Not estimated	TR-11-01, Section 10.4.7 (Reference Evolution)
1.5 mM	ECPM variant model	greater than or equal to 1.0 μM	6	$< 6 \times 10^{-6}$ m/yr	TR-11-01, Section 12.6.2 (Alternative Case, Corrosion Scenario) Advective Conditions
1.5 mM	Near-field oxygen source	1.5 mM	Not estimated	3×10^{-7} m/yr	TR-11-01, Sec. 12.6.2 (Alternative Case, Corrosion Scenario) Diffusive Conditions

3.3. Technical Review of Redox Evolution by Oxygenated Glacial Meltwater

SKB's evaluation of the potential for oxygenated glacial meltwater to reach canister deposition positions was documented primarily by the Sidborn et al. (2010) technical report, which summarized the processes expected to have the greatest influence on oxygen ingress and which clearly described the development and application of a modelling approach to evaluate this scenario quantitatively and included relevant observations of low-temperature redox effects at other locations in the Fennoscandian Shield. SKB noted that the characterization of the subsurface redox transition at Forsmark from near-surface oxidizing to deeper reducing groundwater compositions is limited by the lack of observations from the uppermost few meters of rock, where the transition zone is most likely to be discernible. Sidborn et al. (2010) instead summarized information about redox-sensitive minerals in the shallow subsurface from detailed SKB investigations at Laxemar (Drake et al. 2009). In particular, near-surface examples (at depths between 15 cm and 2 m) of the replacement of pyrite by goethite and of the precipitation of an iron oxyhydroxide phase on chlorite adjacent to an open fracture in the Laxemar rocks indicated that the mineral oxidation reactions described by Sidborn et al. (2010) are valid at shallow depths where groundwaters have an oxidizing capacity in present-day geological environments similar to those at the Forsmark site.

Sidborn et al. (2010) presented a conceptual model for the depletion of oxygen in a fracture and in the adjacent rock matrix by specific reaction pathways that realistically described the range of expected processes under these conditions. For a detailed model, Sidborn et al. (2010) appropriately focused on the slowest reaction pathway so as not to overestimate the effectiveness of the rate at which oxygen would be removed during transport along a fracture. The detailed model used site-specific data from the Forsmark site for conductivities and for estimating effective diffusivity in the rock matrix. Sidborn et al. (2010) identified that biotite and chlorite are the main Fe(II)-bearing minerals in the Forsmark rocks. Biotite is the dominant mafic mineral in the rock matrix and accounts for almost all of the Fe content of the rocks. The model pessimistically excluded all other oxygen scavenging processes, including all microbial activity and degradation of organic material, reaction of the water with minor but reactive ferrous oxide and sulphide phases, and reaction with the main fracture-coating mineral (chlorite).
Sidborn et al. (2010) chose biotite as the only reacting solid in the oxygen ingress model and appropriately used Forsmark petrographic data to estimate the average available reactive surface area of biotite for the model.

The reaction path model addressed oxidation of biotite at two locations, at the fracture surface and in the adjacent rock matrix. Separate analytical model solutions were developed to describe the rates of oxygen migration through the fracture and into the rock matrix. For both, the model conservatively used a two-step dissolution and reaction process for the removal of Fe(II) ions from the biotite crystal lattice and subsequent oxidation of the ions in solution. The model reasonably accounted for changes with time and distance along the flow path, by representing effects of diffusion farther and farther into the rock matrix. The numerical term for the rate of ferrous iron release from biotite was taken from experimental studies conducted under geochemical conditions that are comparable to those simulated by the SKB modelling (Malmström and Banwart, 1997). Sidborn et al. (2010) validated the analytical solutions for the flow path and matrix concentration profiles by performing numerical simulations using the widely supported modelling codes PHREEQC (Parkhurst and Appelo, 1999) and PHAST (Parkhurst et al., 2004) and conducted sensitivity analyses for variability in key uncertain parameters such as the biotite reactive surface area, rock porosity and diffusion coefficient, groundwater pH and its influence on dissolution rates, and the starting concentration of dissolved oxygen in the meltwater. As a final step, the modelling approach was linked to parameter values from SKB hydrogeological models for Forsmark so the oxygen ingress rates and concentrations could be related to recharge pathways for individual container locations in the repository.

The oxygen ingress model and its results were key to supporting the SKB conclusions about possible effects of oxygen ingress to repository depths for the reference evolution case and for analyses for the corrosion case. The review notes that two potential sources of uncertainty in the model are (i) the rate of ferrous iron release from biotite and (ii) F-factors taken from site hydrogeological models. In stating that an adequate amount of biotite would be present at depth to react with an oxygenated meltwater, even over the pessimistic timeframe of 1,000 years, Sidborn et al. (2010) explained that only about 20 percent of the ferrous iron in the matrix minerals that were part of the reaction flow and diffusion path would be depleted over 1,000 years by exposure to oxygenated water (1.5 mM O_2) in a flowing fracture. Nevertheless, the reviewers note that biotite grains in the Fennoscandian Shield have persisted for much longer than a few thousand years with little or no apparent alteration in shallow fractures, despite the likelihood that they have been exposed repeatedly to oxygenated water in meteoric recharge and during multiple past glaciations. SKB appropriately selected a biotite release rate for conditions that were generally comparable to those expected in Forsmark groundwaters, but the SKB arguments would be strengthened by investigating the sensitivity of the calculations to uncertainty for the release rate used by Malmström et al. (1997).

If future borehole drilling is conducted at Forsmark, SKB should plan to supplement the existing mineral data with more detailed mineralogical and geochemical analyses of shallow rock cores (within the first few meters below the surface) to determine whether oxidation reactions that are not evident at depth have occurred as expected where oxidizing groundwaters are more common. In particular, compositional and petrographic data for ferrous mineral oxidation in near-surface open fractures can provide useful information, as noted by near-surface investigations of individual biotite grains in open fractures at Laxemar (Drake et al., 2009; Sidborn et al., 2010) and in the Canadian Shield (McMurry and Ejeckam, 2002). Integration of the oxygen ingress model with site hydrogeological models introduced additional uncertainties about the length and hydrogeological properties of the modeled flow paths, as illustrated by SKB's use of two different hydrogeological models to calculate oxygen compositions at depth for the reference evolution case and the canister corrosion case.

This review also notes that in presenting results of the oxygen ingress calculations for the container corrosion case in the SR-Site main report (SKB, 2011, TR-11-01, Section 12.6.2) and in the supporting corrosion calculations report (SKD, 2010, TR-10-66, Section 5.2.3), SKB did not supply references to document the calculations. Given the relevance to canister safety functions, SKB should strengthen their discussion by providing sufficient information to allow a more detailed review of the appropriateness of the calculated estimates. For example, in the SR-Site main report (SKB, 2011, TR-11-01, Section 12.6.2), SKB described that F-factors for the corrosion case modelling were taken from an extended spatial variability case of the explicit discrete fracture network described by Joyce et al. (2010), but the text provided no reference or other information about the variant hydrogeological model or which results were integrated with the oxygen ingress model. In describing another set of the corrosion calculations, SKB stated that the advective conditions used in the calculations were taken from a separate corrosion model that SKB had used to estimate sulphide corrosion, but no reference for this model was provided, either. SKB should justify expressing these model results in such an atypical way, for example, stating in most cases that *x* number of canister positions would see a specified low oxygen concentration value of *y*, "*or higher*," instead of stating the actual maximum value outright (e.g., Sidborn et al., 2010, Section 9). Another example, in the SR-Site main report, states that 31 deposition holes would "experience oxygen concentrations above 10^{-7} M; and of these, the oxygen concentration is higher than ~ 1mM for 6 positions" (SKB, 2011, Section 12.6.2). In this example, SKB acknowledged a concentration difference of 4 orders of magnitude in the "maximum" results that were not being stated more clearly. In the interests of a complete review, SKB should provide the actual maximum concentration result for the calculation.

SKB acknowledged inherent uncertainties in the oxygen ingress calculations and identified that the results of the modelling were intended to be illustrative. SKB appropriately identified that numerous pessimistic assumptions in the conceptualization of the model excluded a number of other counterbalancing processes and conditions that are likely to be effective in preventing the ingress of oxygenated water along deep flow paths. In particular, the SKB analyses of depth-related fracture mineralization patterns indicate that low-temperature interactions with oxygenated water in flowing fractures (e.g., precipitation of goethite) appear to have been limited almost exclusively to the upper tens of meters of rock in the footwall segment of the Forsmark candidate rock volume. As noted by Sidborn et al. (2010), the preservation of unaltered pyrite and asphaltite in the upper 150 m of bedrock indicate that reducing conditions have prevailed in most parts of the fracture system at Forsmark for the past 250 million years. Despite uncertainties in the oxygen ingress model regarding the sensitivity of the model to the biotite dissolution rate and uncertainties from the integrated flow models about hydrogeological properties of the site, the evidence from the rock itself is compelling. Based on these observations, the reviewers agree with the Sidborn et al. (2010) conclusion that the oxygen ingress modelling and the pessimistic assumptions behind it were highly conservative, and reducing conditions will continue to prevail at repository depth.

4. Near Field Redox and Spent Fuel Solubility

For repository safety calculations in general, the dissolution rate of the uranium oxide fuel pellets controls the release rate of most of the other radionuclides in the inventory. Uranium oxide is thermodynamically stable under reducing conditions. In a geologic repository, the redox potential of the solution in contact with the spent fuel is a key variable because the solubility of UO_2 increases by many orders of magnitude under oxidizing conditions (Shoesmith, 2000). SKB considered the effect of groundwater redox conditions on radionuclide solubility only in terms of near-field (in-canister) conditions. SKB described that the spent fuel to be disposed will consist of enriched uranium oxide fuel from Sweden’s twelve nuclear power plants, with minor quantities of other oxide fuel types. The uranium oxide fuel pellets are a ceramic solid with a crystalline UO_2 matrix (SKB, 2011, Section 5.3.2). During its use in a nuclear power reactor, uranium oxide fuel acquires additional radionuclides (typically several percent of the total mass) by irradiation, fission, and radioactive decay. The specific inventory of radionuclides generated in a fuel assembly is determined by a number of factors such as the type of reactor, the amount of time the fuel was in the reactor, the specific location of the fuel assembly in the reactor core, and the energy produced by the fuel (burnup) during its time in the reactor. SKB identified that a minor fraction of the total radionuclide inventory, comprising species such as iodine or cesium that are gaseous or somewhat volatile under operating conditions in the reactor, is termed the instant release fraction (SKB, 2010, TR-10-52, Section 3.2). Relatively quick release rates also are assumed for another minor quantity of radionuclides that SKB termed the corrosion release fraction, which comprises radionuclides released by the corrosion of internal construction components such as fuel cladding, control rod cladding, and metal parts of the fuel assemblies. The remainder (and majority) of the spent fuel consists of (i) the fuel pellets’ UO_2 crystalline matrix; (ii) minor metallic phases such as molybdenum, palladium, and ruthenium that have a low solubility in UO_2 and have migrated under reactor operating conditions to UO_2 grain boundaries, where they exist as small discrete solids within the fuel pellets; and (iii) radionuclides such as plutonium, americium, and neptunium that can substitute chemically for uranium and are structurally bound as trace elements in the UO_2 crystal lattice itself (Johnson and Shoesmith, 1988).

4.1. Relevance to SR-Site

Before the long-term redox evolution of groundwater can affect the dissolution rate of spent fuel in a repository setting, other important barriers—particularly the barrier provided by the canister—must first be breached. In the SR-Site safety assessment, SKB identified two canister failure mechanisms that, though unlikely, could not be ruled out in the reference evolution: (i) canister failure due to corrosion and (ii) canister failure due to shear load. SKB identified that in the event of either of the canister failure mechanisms, the low solubility of spent fuel under reducing conditions would become an important contributor to repository safety (SKB, 2011, Sections 13.5.2. and 13.6.4).

SKB stated that the instant release fraction is assumed to be released instantly upon contact with water. SKB cautiously assumed that all construction materials containing the corrosion release fraction corrode completely, so the full inventory of the corrosion release fraction is released over a comparatively short time. Release rates for the corrosion release fraction were estimated for anoxic conditions, based on the assumption that corrosion of the cast iron insert and internal construction materials would assure a reducing capacity in the canister (SKB, 2010, TR-10-52, Section 3.2.5). SKB estimated the release rates of other radionuclides from either the dissolution rate or the conversion rate of the UO_2 fuel matrix. SKB described UO_2 fuel conversion as an oxidative dissolution process where, when the transport rate of mobilized uranium species out of the canister is low, the limited solubility of UO_2 causes the dissolved uranium species to reach a solubility limit so that the dissolution and precipitation of the uranium species as UO_2 occurs at a matching rate. SKB described that at a large scale, the mass of crystalline UO_2 is conserved, but that at a microscopic scale, the surfaces of the UO_2 crystals are reworked, so embedded radionuclides gradually are exposed at the crystal face and may be released from the UO_2 matrix and grain boundaries (SKB, 2010, TR-10-52, Section 3.3). If the transport rate of dissolved uranium species out of the canister is high, the embedded radionuclides are released at the oxidative dissolution rate of the UO_2.

SKB mainly considered oxidative conditions for the spent fuel solubility and radionuclide release rates as a function of radiolysis, which would be important primarily during the early history of a repository. For SR-Site, SKB based all fuel conversion and dissolution rates on reducing conditions, citing experimental and modelling studies on relatively fresh spent fuel and α-doped UO_2 in the presence of dissolved hydrogen or actively corroding iron as would be expected in the case of early canister failure (SKB, 2010, TR-10-52, Section 3.3.5). SKB identified that if the long-term evolution of repository conditions included the ingress of oxygenated glacial meltwater, the fuel might dissolve at a faster rate than expected for reducing conditions. SKB described that the spent fuel dissolution rate for oxidizing conditions (up to air saturation) for pH values between 7 and 9 would be in the interval of 10^{-4} to 10^{-5}/yr. With respect to the ingress of oxygenated water from glaciation, SKB stated that at most, such an event would occur only during short time periods when the ice front was directly above the repository, and its effect would be limited. SKB also noted that any dissolved oxygen in groundwater likely would be consumed by other reactions in the engineered barrier materials before it contacted the spent fuel.

SKB also considered the effect of near-field oxidative conditions on the solubility of radionuclides released into solution from the spent fuel (SKB, 2010, TR-10-52, Section 3.4). Thermodynamic solubility limits were assessed for groundwater compositions in terms of major ions, pH, and redox potential. However, SKB stated that for SR-Site, the corrosion products of the cast iron insert were expected to control the redox potential for all timescales, based on the magnetite-goethite equilibrium.

To model the effects of the dissolution of spent fuel for safety assessment calculations in SR-Site, SKB included the effect of an oxidizing capacity in the contact water by adopting a constant fractional dissolution rate with a triangular probability density function, expressed in $\log_{10}$, with a lower limit, best estimate, and upper limit of 10^{-8}, 10^{-7}, and 10^{-6} per year (SKB, 2011, Section 13.5.5). SKB noted that oxidizing conditions (about 4×10^{-3} moles of oxygen per year) would need to be supplied to the spent fuel , neglecting the consumption of oxygen by any other reducing materials in the canister, to support the largest of these dissolution rates (10^{-6} per year).

SKB identified that the potential for highly oxygenated glacial meltwater to penetrate to repository depth was a low probability event that was allowed only by a set of extreme pessimistic assumptions. SKB stated that even if the extreme case were to occur and oxygenated water entered a breached canister, the large reducing capacity of the copper and iron metals in the canister would continue to maintain reducing conditions locally within the failed canister. SKB provided no other considerations of groundwater redox evolution in terms of spent fuel solubility. SKB concluded that the suggested handling of, and data for, radionuclide solubilities in the SR-Site data report (SKB, 2010, TR-10-52) were sufficient to cover the safety assessment calculations for the canister shear failure case.

In considering the effect of redox conditions on spent fuel solubility, SKB noted that the ingress of oxygenated glacial meltwater to repository depth had been ruled out for the canister corrosion scenario in SR-Site, on the basis that even if such conditions were to occur, they would be insufficient to compromise the canister integrity (SKB, 2011, Section 12.6.2). SKB noted that other corrosion mechanisms besides oxygen ingress were responsible for canister failure in the alternate case. SKB stated that since the ingress of oxygenated waters to repository depth had been excluded from the reference evolution as a factor that would lead to the corrosion failure of a canister, any small amount of oxygen in groundwater that conceivably would recharge to the repository location would not significantly affect the solubility of the spent fuel inside a canister regardless of its failure mechanism (SKB, 2011, Section 13.5.5).

4.2. Technical Review of Redox Evolution and Spent Fuel Solubility

The reviewers examined the information about redox conditions and radionuclide solubility criteria that SKB presented in the SR-Site Main Report (SKB, 2011) and in the supporting Data Report (SKB, 2010, TR-10-52). To the extent that SKB has adequately supported the conclusion about oxygen ingress in glacial meltwater, as concluded by the review in Section 3 (i.e., that measureable amounts of dissolved oxygen will not penetrate to canister deposition positions in the target rock volume at the Forsmark site), this review concludes that SKB has adequately supported the assumption that oxidizing groundwater conditions will not significantly affect spent fuel dissolution rates or radionuclides solubilities in the near field under expected repository conditions. SKB also has conservatively included an upper-limit dissolution rate that addresses effects of potential oxidizing conditions besides that of oxygenated groundwater.

5. Migration of Redox-Sensitive Radionuclides

The rate at which radionuclides migrate through the geosphere is sensitive to a number of factors including the water flow rate, the nature of the geologic materials through which the water travels, the water chemistry, and the chemistry of the radionuclides themselves. The main retardation mechanisms considered in performance assessment models, including SKB the models of SR-Site performance, are diffusion of radionuclides into rock matrix and sorption of radionuclides onto rock surfaces (Crawford, 2010). Sorption includes surface adsorption and ion-exchange processes. Surface interactions, such as sorption, between dissolved constituents and solid phases can be complex, particularly in heterogeneous natural systems, and are sensitive to changes in the chemical and physical environment.

Varying groundwater redox conditions can alter valence states for some elements. In turn, these altered valence states can have a significant influence on sorption magnitude. Several radionuclides important to repository safety assessments are redox sensitive. These radionuclides include neptunium (Np), plutonium (Pu), selenium (Se), technetium (Tc), and uranium (U). Generally, lower redox potential (i.e., lower Eh) results in valence states that increase the magnitude of sorption for these redox-sensitive elements. As such, SKB identified that one safety function (R1a) of the geosphere in the SKB repository concept is the presence of chemically favourable reducing conditions (low Eh) and limited variation in Eh over the lifetime of the repository (SKB, 2011, TR-11-01).

5.1. Selection of Sorption Parameters Calculations

SKB acknowledged that the chemical composition of groundwater and the reactions between aqueous solutes are of great importance for understanding the processes that give rise to sorption as modeled in the SR‑Site (SKB, 2010, TR-10-50). Citing a lack of suitable mechanistic models to describe sorption of radionuclides in granitic rock, and the large spatial variation in groundwater compositions across the site at any given time, SKB elected to represent sorption processes in SR-Site by using equilibrium sorption partitioning coefficients (K_ds) with defined probability distributions (SKB, 2010, TR-10-50). Because of the influence of redox conditions on sorption, the selection of appropriate K_d values and probability distributions depends on an understanding of the evolution of groundwater redox over time. SKB accordingly considered the role of redox speciation as a separate factor when selecting K_d values for redox-sensitive elements (SKB, 2010, TR-10-50).

As described in Section 2, SKB developed geochemical models to assess the potential long-term redox evolution of the Forsmark area for SR-Site (Salas et al., 2010; Crawford, 2010). The data generated from these models were then used to calculate the aqueous speciation of redox sensitive radionuclides (Crawford, 2010). The speciation calculations were conducted for 20,000 randomly sampled groundwater compositions taken from the SR-Site temperate domain simulations (Salas et al., 2010). Additionally, sweep calculations were made for a range of hypothetical redox potentials in an effort to determine the aqueous chemical conditions (transition points) where reduced and oxidized radionuclide species were present in roughly equal concentrations (Crawford, 2010). These transition points were then used to evaluate the potential for a change in the redox state of the radionuclides during evolution of the system chemistry (Crawford, 2010; Salas et al., 2010). SKB determined that, with the exception of U, the modeled changes in redox were insufficient to result in a change in oxidation state for the redox sensitive elements (Crawford, 2010). Citing the sensitivity and associated uncertainty of U speciation with respect to modelled redox conditions and carbonate concentration in the Forsmark groundwaters, SKB propagated reduced as well as oxidized species of U in transport modelling for temperate and glacial periods (SKB, 2010, TR-10-50).

SKB also noted that the higher Eh conditions associated with redox evolution during glaciation events, and related changes in groundwater chemistry during those periods, could lead to the remobilization of sorbed redox-sensitive radionuclides (SKB, 2010, TR-10-50). SKB examined redox properties of key radionuclides and concluded that U and Tc were the radioelements that were most likely to experience a transition to oxidized species in such an event. SKB conducted sensitivity calculations to assess the possible role of redox effects on U sorption during a glacial cycle, in which SKB used transport conditions taken from the corrosion case scenario and used sorption K_d values for oxidizing conditions during the times when an ice front passed above the repository (SKB, 2010, TR-10-50).

5.2. Technical Review of Redox Evolution and Radionuclide Sorption

The reviewers examined the information about redox conditions and radionuclide sorption coefficients that SKB presented in the SR-Site Main Report (SKB, 2011, TR-11-01) and in supporting reports that described the SKB handling of radionuclide transport, selection of K_d values, and site evolution of groundwater chemistry (SKB, 2010, TR-10-50; Crawford, 2010; Salas, 2010). As discussed in Section 2, SKB modelling of the geochemical evolution of the Forsmark site groundwater is dependent on the initial input conditions and the inclusion within the model of redox reactions that minimize Eh excursions (Salas et al., 2010). Geochemical data that SKB collected for redox-sensitive elements during site characterisation activities provide reasonable support for the SKB conceptual model of site redox conditions (SKB, 2010, TR-10-50). In particular, the variations in U concentrations and U-series disequilibrium with depth are consistent with decreasing redox potential (Laaksoharju et al., 2008; SKB, 2010, TR-10-50).

Where significant uncertainty exists about redox-sensitive speciation, such as uncertainty about the speciation of U near the end of the temperate time domain, SKB has chosen to propagate both U(IV) and U(VI) oxidation states in its transport models (Crawford, 2010). This choice is appropriate because it addresses both the importance of the uncertainty in redox conditions and avoids the incorrect assumption that selection of lower sorption values is necessarily conservative with respect to dose (Crawford, 2010). Based on the current knowledge of the Forsmark site, this review considers that SKB’s redox evolution modelling results are acceptable as an evaluation of expected site-wide changes in redox conditions over broad time periods. The resulting selections of radionuclide sorption coefficients based on the predicted redox evolution are, therefore, reasonable and acceptable.

6. Conclusions

The objective of this review was to provide a comprehensive assessment of how and where SKB has addressed the effect of the long-term evolution of redox conditions at the Forsmark site in the context of the SKB safety functions for the SR-Site project, with a particular focus on how SKB assessed the potential influence of oxygenated waters on repository safety. Due to the importance of reducing conditions for maintaining canister integrity, SKB placed the greatest emphasis on the safety function that the geosphere should provide the reducing conditions. SKB also considered this safety function in the context of spent fuel dissolution rates and redox-sensitive radionuclide migration characteristics.

SKB has conducted a comprehensive site investigation, including groundwater redox characterization and an analysis of the spatial distribution of redox-sensitive fracture minerals, from which SKB identified that reducing groundwater conditions exist in all but the uppermost few meters of bedrock at the Forsmark site. In selecting ranges of K_d values to use for SR-Site radionuclide transport modelling, SKB has appropriately accounted for the range of redox conditions expected in the Forsmark site groundwaters over future times, including temperate and glacial periods. SKB included recharge and mixing of glacial meltwaters to depth in the development of the site flow models and hydrochemical evolution models (SKB 2011, Sections 10.4.1 and 10.4.6; Salas et al., 2010). SKB site investigations have found no chemical, isotopic, or mineralogical indicators that dissolved oxygen in such glacial waters has penetrated more than a few tens of meters in the target repository rock volume at Forsmark during previous glaciations (Sidborn, et al., 2010; Auqué et al., 2006). Even assuming that consumption of oxygen by various geochemical and microbial processes in the near-surface environment may or may not be diminished during a glaciation, SKB has cited reasonable observations from other studies in Sweden and elsewhere that microbial and mineral controls on redox conditions deeper in the geosphere at Forsmark are also likely to be sufficient to scavenge molecular oxygen from the water before it reaches depths of hundreds of meters below the surface.

SKB appropriately identified the risk significance of the potential ingress of oxygenated glacial meltwaters to depth with respect to SKB safety functions about canister integrity and radionuclide mobility, and SKB documented a thorough consideration of this topic in a supporting report for SR-Site (Sidborn et al., 2010). This review considers that overall, the information SKB has provided is an adequate exposition of the factors on which SKB based its conclusion that deep penetration of oxygenated glacial meltwaters is not expected to affect repository safety. Key supporting information from the SKB site characterization includes observations of (i) low-temperature goethite precipitation in the upper tens of meters of bedrock, where oxidizing conditions are most likely to occur or to have been present in under past conditions, and its scarcity in deeper fractures (ii) preservation of unaltered pyrite and asphaltite in the upper 150 m of bedrock for at least 250 million years.

SKB has supported key conclusions about the long-term evolution of redox conditions by a detailed characterization of site groundwater chemistry and mineralogy, by water-rock and mixing models that illustrate the expected changes under specified future conditions, and by identifying numerous additional controls on redox evolution that are observed under present-day conditions and are likely to persist in the future but were pessimistically excluded from SKB modelling calculations. SKB has appropriately interpreted and applied site characterization data to develop reasonable conceptual, analytical, and numerical models to represent the long-term evolution of redox conditions at the Forsmark site, including investigations of the potential ingress of oxygenated glacial meltwaters to a repository location at depth. Continued characterization of the distribution, composition, and alteration of redox-sensitive mineral phases at all depths, including baseline data from very near the surface, in future site characterization actions is recommended because the rocks themselves are among the best indicators of any past changes in redox.

This review concludes that SKB has appropriately identified the components of repository safety that are most sensitive to changes over time in groundwater redox conditions. SKB appropriately identified that the most safety-significant potential perturbation of the groundwater redox conditions is likely to be inflow of oxygenated water near canister deposition positions. SKB also identified and addressed the potential effect of changes in redox conditions on the oxidative dissolution of spent fuel, the solubility-controlled mobility of redox-sensitive radionuclides, and the sorption properties of redox-sensitive radionuclides. The review has not identified any significant factors that were not addressed by SKB that would alter the range of anticipated redox conditions in a way that would affect repository safety functions.

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The Swedish Radiation Safety Authority has a comprehensive responsibility to ensure that society is safe from the effects of radiation. The Authority works to achieve radiation safety in a number of areas: nuclear power, medical care as well as commercial products and services. The Authority also works to achieve protection from natural radiation and to increase the level of radiation safety internationally.

The Swedish Radiation Safety Authority works proactively and preventively to protect people and the environment from the harmful effects of radiation, now and in the future. The Authority issues regulations and supervises compliance, while also supporting research, providing training and information, and issuing advice. Often, activities involving radiation require licences issued by the Authority. The Swedish Radiation Safety Authority maintains emergency preparedness around the clock with the aim of limiting the aftermath of radiation accidents and the unintentional spreading of radioactive substances. The Authority participates in international co-operation in order to promote radiation safety and finances projects aiming to raise the level of radiation safety in certain Eastern European countries.

The Authority reports to the Ministry of the Environment and has around 270 employees with competencies in the fields of engineering, natural and behavioural sciences, law, economics and communications. We have received quality, environmental and working environment certification.

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