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Radionuclide Solubility Limits in SKB's Safety Case

Main Review Phase

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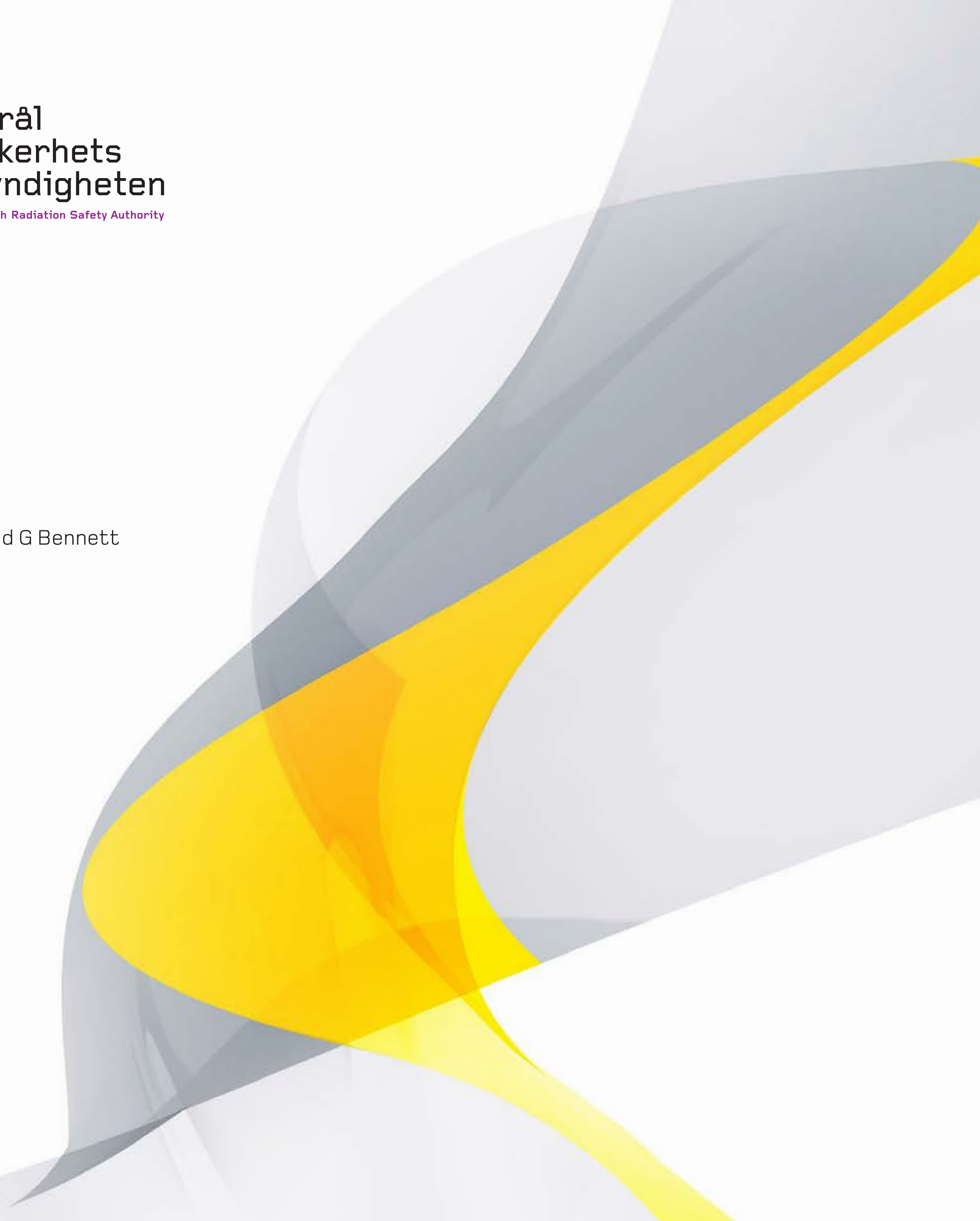

SSM perspektiv

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

Målet med detta uppdrag är att utvärdera SKB:s metod för beräkning av löslighetsgränser genom ytterligare granskning i förhållande det arbete som gjordes under den initiala granskningsfasen samt genom att reproducera specieringsberäkningar och bestämningar av löslighetsgränser för 2-3 radionuklider.

Författarens sammanfattning

Strålsäkerhetsmyndigheten (SSM) granskar för närvarande en tillståndsansökan som har lämnats in av Svensk Kärnbränslehantering AB (SKB) för ett slutförvar för använt kärnbränsle i Forsmark. Denna tekniska rapport dokumenterar resultaten från ett granskningsprojekt som ingår i huvudfasen av SSM:s granskning av SKB:s tillståndsansökan. Inom projektet genomfördes granskning av rapporter och oberoende modelleringsstudier för frågor som rör den potentiella lösligheten av radionuklider i grundvatten som kan komma in i slutförvaret. Projektet har genomförts av TerraSalus Limited på uppdrag av SSM.

SKB har presenterat en modell för beräkning av radionukliders löslighetsgränser i en serie av rapporter och dokument som har tagits fram under flera års tid. Modellen är vetenskapligt baserade och bygger på principerna i kemisk termodynamik. Spårbarheten i SKB:s dokumentation har dock varit en fråga som har hindrat denna och tidigare granskningar (Baldwin och Hicks 2012, Trivedi 2012). Det skulle vara bra om SKB kunde sammanställa ett enda öppet och uppdateradrat dokument som presenterade val och användning av termodynamiska data, identifiering och behandling av eventuella löslighetsbegränsande faser, samt uppskattning och användning av radionukliders löslighetgränserser i säkerhetsanalysen SR-Site.

Trots svårigheter med SKB: s dokumentation har det varit möjligt att förstå SKB:s konceptuella modell för begränsningarna i radionukliders löslighet, att fastställa att totalt sett de koder som används av SKB för att ta fram rekommendationer för löslighetsgränser är lämpliga, och att reproducera ett urval av SKB: s geokemiska modelleringsresultat med relativt små och förståeliga skillnader.

Olika vetenskapliga frågor och osäkerheter i samband med SKB:s modeller och data har identifierats inom denna granskning, till exempel korrosion och utvecklingen av redoxförhållanden i en slutförvarskapsel, eventuella effekter av mikrobiell aktivitet på radionukliders löslighet och stabilitet i alla radionuklidbärande fasta sulfatfaser, information om bildandet av plutoniumkolloider, samt den geokemiska utvecklingen av bufferten och dess interaktion med grundvatten. Detta är frågor för framtida forskning och säkerhetsanalysarbete som bör inriktas mot att förbättra realismen i säkerhetsanalysen, men det får ändå anses osannolikt att de skulle göra betydande förändringar på resultatet av säkerhetsanalysen.

Även om det har varit möjligt att förstå och kommentera i detalj SKB:s forskning och geokemiska modellstudier för beräkning av gränsvärden för radionukliders löslighet, har det inte varit möjligt att detaljerat spåra användningen av SKB:s löslighetsgränser inom säkerhetsanalysen. Den nivå av information som skulle krävas för att göra detta ingår inte i SKB:s rapporter. Den dokumentation som har granskats inom detta projekt är till exempel inte tillräckligt för att avgöra exakt vilka löslighetsgränser som har tillämpats för vilka grundvattensammansättningar och beräkningsfall.

Projektinformation
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Diarienummer ramavtal: SSM2011-4245
Diarienummer avrop: SSM2013-3217
Aktivitetsnummer: 3030012-4051

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 evaluate SKB's method for calculating solubility limits by additional review in relation to was accomplished during the initial review phase and by reproducing speciation calculations forming the basis for solubility limits covering 2-3 radionuclides.

Summary by the author

The Swedish Radiation Safety Authority (SSM) is reviewing a license application, which has been submitted by Svensk Kärnbränslehantering AB (SKB), for a spent nuclear fuel repository at Forsmark.
This technical note records the findings from a project that forms part of the main phase of SSM's license application review. The project involved review of reports and independent modelling studies on issues related to the potential solubility of radionuclides in waters that may enter the repository. The project was undertaken on behalf of SSM by TerraSalus Limited.

SKB has presented a conceptual model for calculating radionuclide solubility limits in a series of reports and papers that have been produced over several years. The model is scientifically based and founded on the principles of chemical thermodynamics. The traceability of SKB's documentation has, however, been an issue that has hindered this and previous reviews (Baldwin and Hicks 2012; Trivedi 2012). It would be helpful if SKB were to compile a single, fully transparent and up to date document that presented its work on the selection and use of thermodynamic data, the identification and treatment of possible solubility limiting phases, and the estimation and use of radionuclide solubility limits in the SR-Site assessment.

Despite the difficulties with SKB's documentation, it has been possible to understand SKB's conceptual model for radionuclide solubility limits, to determine that, overall, the codes used by SKB to develop recommendations for solubility limits are appropriate, and to reproduce a selection of SKB's geochemical modelling results with relatively small and understandable differences.

Various scientific questions and uncertainties associated with SKB's models and data have been identified, for example, relating to details of corrosion and the evolution of redox conditions within the waste canister, relating to the possible effects of microbial activity on radionuclide solubility and the stability of any radionuclide-bearing sulphate solid phases, relating to new data on the formation of plutonium colloids, and relating to the geochemical evolution of the buffer and its interactions with groundwaters. These are topics on which future research and assessment work could focus to improve the realism of the safety assessment, but it is considered unlikely that they would make significant changes to the outcome of the safety assessment.

Although it has been possible to understand and comment in some detail on SKBs research and geochemical modelling studies for the calculation of radionuclide solubility limits, it has not been possible to trace the use of SKB's solubility limits within the safety assessment in such detail. The level of information that would be required to do this is not included in SKB's reports. For example, the documentation reviewed in this project does not record exactly which solubility limits were applied for which groundwater compositions and calculation cases.

Project information

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Contents

1. Introduction

1.1. SSM's Review

The Swedish Radiation Safety Authority (SSM) is undertaking a formal review of a License Application, which has been submitted by Svensk Kärnbränslehantering AB (SKB) for construction, possession and operation of a spent nuclear fuel repository at Forsmark. SKB's Application includes a safety assessment known as SR-Site (SKB 2010a, TR-11-01 and supporting reports).

SSM is conducting its review in phases. The initial phase of SSM's review has been completed and SSM has concluded that SKB's reporting is sufficiently comprehensive and of sufficient quality to justify a continuation of SSM's review to the main review phase. Based on issues identified during the initial review phase, SSM has defined and prioritized a set of review assignments that will be undertaken during the main review phase. The intention is that these main phase review assignments should indirectly or directly support SSM's compliance judgements and the establishment of any necessary Licence Conditions.

SSM regards the main phase review assignments as an essential and necessary basis for the licensing review. It is not the role of individual review assignments, however, to explicitly evaluate compliance in relation to any part of SSM's regulations or guidelines, because the determination of compliance is one of SSM's key over-arching responsibilities in the licensing review.

This technical note records the findings from a main phase review assignment undertaken on behalf of SSM by TerraSalus Limited. The review assignment has focussed on the potential solubilities of radionuclides in waters that may enter the repository.

In more detail, the objectives of the review assignment included:

- Conducting a detailed assessment of SKB's method for calculating radionuclide solubility limits, building on and extending work done in the initial review phase in particular by Trivedi (2012).
- Attempting to reproduce the solubility limits calculated by SKB for two to four selected radionuclides, using if possible other software and thermodynamic databases.
- If possible within available resources following completion of the above objectives, undertaking additional calculations to further explore the sensitivity of the radionuclide solubility limits to relevant variations in groundwater composition as a basis for evaluating SKB's corresponding results.
- Considering the strengths and weaknesses of SKB's approach to representing co-precipitation of radionuclides, particularly radium, in the safety case.

The scope of the review assignment was defined in part by a list of key references that were identified for consideration, although other materials were also to be considered as relevant:

- Determination and assessment of the concentration limits to be used in SR-Can, Swedish Nuclear Fuel and Waste Management Company, SKB TR-06-32.
- Update of a thermodynamic database for radionuclides to assist solubility limits calculation for performance assessment, Swedish Nuclear Fuel and Waste Management Company, SKB TR-06-17.
- Assessment of the radium-barium co-precipitation and its potential influence on the solubility of Ra in the near-field, Swedish Nuclear Fuel and Waste Management Company, SKB TR-08-07.
- Experimental study on Ra^{2+} uptake by barite ($BaSO_4$). Kinetics of solid solution formation via $BaSO_4$ dissolution and $Ra_xBa_{1-x}SO_4$ (re) precipitation, Swedish Nuclear Fuel and Waste Management Company, SKB TR-10-43.
- Data report for the safety assessment SR-Site, Swedish Nuclear Fuel and Waste Management Company, TR-10-52, Section 3.4.
- Radionuclide transport report for the safety assessment SR-Site, Swedish Nuclear Fuel and Waste Management Company, SKB TR-10-50.

1.2. SKB's Disposal Concept

Based on several decades of research and development work, SKB is proposing to develop a repository for the final stage of spent nuclear fuel management according to the KBS-3 method. The purpose of the KBS-3 repository would be to isolate the nuclear waste from man and the environment for very long times. Around 12,000 tonnes of spent nuclear fuel is forecast to arise from the currently approved Swedish nuclear power programme, corresponding to roughly 6,000 canisters in a KBS-3 repository (SKB 2010a, TR-11-01).

In the KBS-3 method, spent nuclear fuel would disposed of within copper canisters, which would be placed within a bentonite clay buffer at approximately 500 m depth in groundwater-saturated, granitic rock. Inside the copper canister, the spent fuel would be supported by a cast iron insert.

A KBS-3 repository would include an array of horizontal waste deposition tunnels and according to the Licence Application the copper canisters containing the waste would be placed into vertical boreholes drilled in the floor of the tunnels. After waste canister and buffer emplacement, the tunnels would be backfilled with bentonite clay and then sealed with concrete plugs.

2. Motivation for SSM's Assessment

If the repository is to be licenced, constructed and used for waste disposal, it will be essential for there to be sufficient confidence in many aspects of the Licence Application and the associated safety assessment. Radionuclide solubility directly affects the 'source term' for the analysis of the consequences of canister failure and radionuclide transport leading to potential doses and risks to humans and impacts on other species.

SSM's preparation for the Licence Application review has necessarily included tracking SKB's research and development work, including the treatment of radionuclide solubility over several years (e.g., Dverstorp et al. 2008; Stenhouse et al. 2008; Brown et al. 2011; Trivedi 2012; Baldwin and Hicks; 2012; Pensado and Mohanty 2012). This research and review work has identified several issues relating to the radionuclide source term for SKB's safety assessments, including:

- Problems of traceability and inconsistencies within SKB's documentation, particularly between the safety assessment Data Reports and those from the supporting technical research.
- The need for greater conduct and visible reporting of sensitivity studies to provide support for key assumptions made during safety assessment.
- Considering errors and uncertainties associated with thermodynamic data.
- Taking account of the effect of temperature on radionuclide solubility.
- Considering the effects of phosphate on plutonium solubility.
- Considering the effects of colloids on plutonium (IV) solubility.
- The uncertainties associated with actinide complexation and the difficulties of defining a single value of the solubility product of a radioelement for use in safety assessment.
- The possible role of co-precipitation and solid solution processes on, for example, the solubilities of strontium, radium and barium.
- The effects of microbial activity (e.g., sulphate reduction) on the effective radionuclide solubilities used in performance assessments.
- The treatment of redox conditions in solubility conditions.
- The treatment of silver in solubility calculations.

In response to the previous regulatory research and more recent requests for further information during SSM's initial reviews of the Licence Application, SKB has provided more information on many of the topics and issues identified (e.g., Evins 2013a, b; Grivé et al. 2013).

The review of this new information and particularly the issues of traceability and consistency highlighted in Baldwin and Hicks (2012) motivate an attempt to clarify and increase understanding of SKB's work on radionuclide solubility. One approach to this has been by the reproduction of selected results from SKB's geochemical calculations.

In coming to a view on the level of confidence that exists, it is necessary to identify and consider the uncertainties that may affect radionuclide solubility, transport and the potential impacts from the repository, including the conditions (e.g. of chemistry and water flow) that may be experienced underground. These factors are also discussed in later sections of this report.

3. SKB's Assessment of Radionuclide Solubility

In preparation for the development of the Licence Application and SR-Site Safety Assessment, SKB has conducted several geochemical studies to evaluate the potential solubilities of radionuclides in waters that might enter the region close to the spent fuel after canister failure. These studies have been documented in a series of reports published in the period approximately between 2006 and 2010 (e.g. Duro et al. 2006a, b; Grandia et al. 2008; Bosbach et al. 2010; Grivé et al. 2010a, b). During this review SKB has provided further reports in this technical area (e.g. Grandia et al. 2013; Grivé et al. 2013a, b).

SSM's initial reviews of SKB's research and assessment work in the area of radionuclide solubility pointed out various apparent deficiencies in SKB's documentation (Baldwin and Hicks 2012; Trivedi 2012), but nevertheless concluded that it was appropriate to enter the main review phase. The following sub-sections of this main phase review report, therefore, summarise SKB's approaches to evaluation solubility limits (Section 3.1) and present an assessment of SKB's work, including results from independent geochemical modelling calculations (Section 4).

3.1. SKB's Presentation

3.1.1. Conceptual Model

SKB has evaluated "*concentration limits of the radionuclides in the vicinity of the spent nuclear fuel"* (Duro et al. 2006a, TR-06-32, page 11). Figure 1 illustrates SKB's conceptual model for the dissolution and release of radionuclides in waters that enter the region between the spent fuel and the cast-iron insert – further details are given below.

SKB argues that there will not be significant microbial activity in the region of interest as long as the buffer has a high enough density, but also recognises that if the density of the buffer was lower, for example as a result of erosion, then microbial activity might occur (SKB 2010d, TR-10-47, pages 164-170). Duro et al. (2006a, TR-06-32) discusses the potential effects of microbiologically-mediated reduction of sulphate on radionuclide solubility, but did not include the effects of this process when calculating and presenting recommended radionuclide solubility limits (Duro et al. 2006a, TR-06-32, page 52).

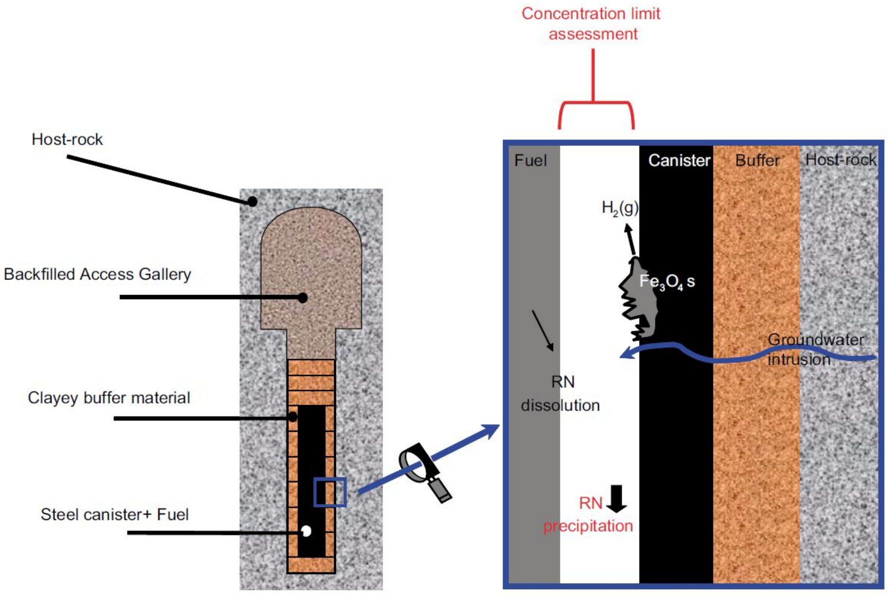


Figure 2.1 Schematic representation of the system for which SKB has assessed radionuclide solubility limits (Duro et al. 2006a, TR-06-32)

SKB emphasises that the solubility limits provided in Duro et al. (2006a, TR-06-32, page 11) are not intended to be used for representing the far-field of the repository, where radionuclides may interact with major minerals present in the host-rock.

3.1.2. Major Element Water Geochemistry

The solubilities of the radionuclides will be influenced by the composition of the waters that enter the canister. In its research programme, SKB has considered two cases. In a first case the waters that enter the canister are assumed to have flowed directly along fast-paths through the buffer and canister without interacting with the buffer and canister materials. In a second case the waters that enter the canister are assumed to have interacted with the buffer and/or the canister prior to contacting the fuel.

In the first case, SKB considered three different groundwater compositions:

- A deep Forsmark groundwater, described as the reference water.
- An ice-melting water derived from a glacial period.
- A saline water associated with regional uplift / glacial upconing.

In the second case, SKB considered a groundwater composition whose major cation and anion composition had been modified through interaction with the buffer and whose redox chemistry had been modified by interaction with the cast iron insert within the canister. It should be noted, however, that although this second case involving groundwater interaction with the buffer was considered in some of SKB's earlier research reports (e.g. Duro et al. 2006a, TR-06-32), it was not included in the SR-Site safety assessment on the basis that conditioning by accessory minerals (carbonates) in the buffer "*is expected to have relatively short duration*" (SKB 2010, TR-10-52, page 102).

3.1.3. Corrosion and Redox

To estimate the redox states of the waters, Duro et al. (2006a, TR-06-32) adopted the following approach:

- The reference redox state was represented by that of the reference Forsmark groundwater.
- Several other values of hydrogen or oxygen partial pressure, pH_2, pO_2, were also considered as a way of representing the effects of intrusion into the system of more oxic waters (Duro et al. 2006a, TR-06-32, Table 3-2).
- The redox state of waters that had interacted with the canister was assumed to be buffered by the corrosion of the cast iron insert and the production of magnetite in a first step and the production of hematite in a second step.

In more detail, Duro et al. (2006a, TR-06-32, page 16) assumed that under anoxic conditions magnetite and hydrogen gas would form as the main corrosion products according to the following reactions:

$$2FeOOH + Fe + 2H_2O = Fe_3O_4 \text{ (magnetite)} + 3H_2(g) \qquad (2.1)$$

$$3Fe + 4H_2O = Fe_3O_4 \text{ (magnetite)} + 4H_2(g) \qquad (2.2)$$

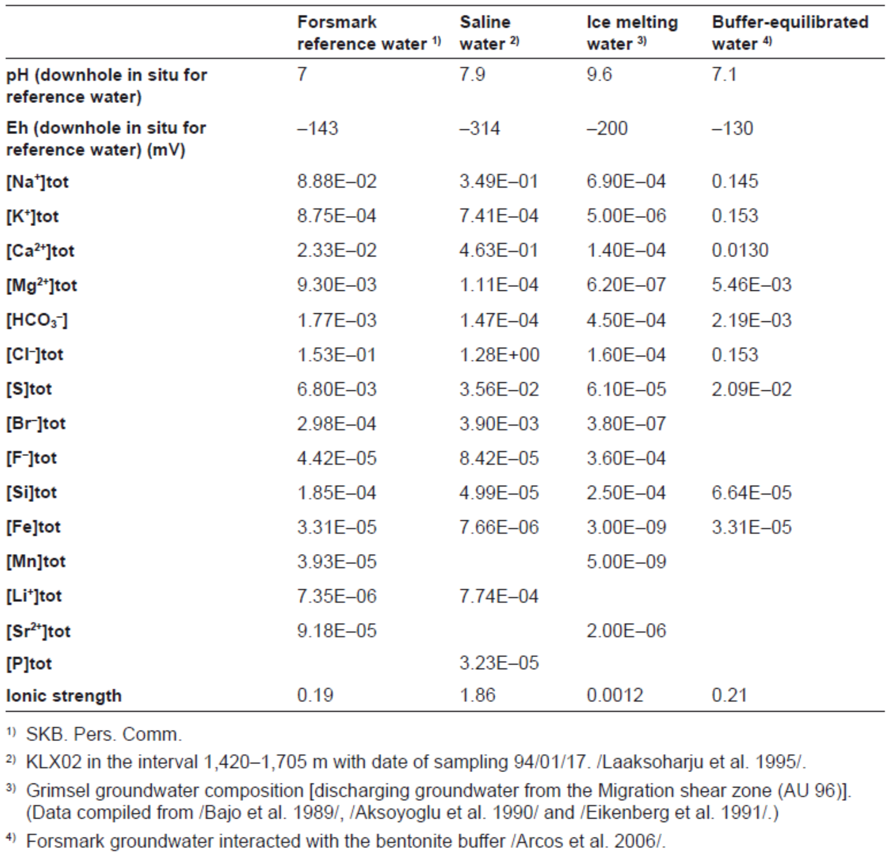
The maximum pressure of hydrogen gas that could form in the system was estimated based on the pressure at repository depth. Given the large availability of iron in the canister, a hydrogen overpressure can, theoretically, build up in the system, giving rise to a decrease in the redox potential of the environment. According to Duro et al. 2006a, TR-06-32, page 16), the maximum hydrogen overpressure will be limited by the maximum lithostatic pressure at repository depth, which has been taken to be 10 MPa (100 atm). Consequently, the minimum redox potential that the system can reach will correspond to $pH_2 = 10$ Mpa which, on a redox potential scale, implies an Eh = –476 mV at the pH of the reference groundwater (pH = 7.0).

Duro et al. (2006a, TR-06-32, page 16) assumed that further oxidation of the magnetite would cause the formation of Fe(III) oxides, and that amongst the possible Fe(III) solid phases, hematite (α-Fe_2O_3) would form in the long term as the most stable phase:

$$2Fe_3O_4 + H_2O = 3\alpha\text{-}Fe_2O_3 \text{ (hematite)} + H_2(g) \qquad (2.3)$$

The chemical compositions of the groundwaters considered by SKB in Duro et al. (2006a, TR-06-32, Table 3-1), including their Eh values are reproduced in Table 2.1.

Table 2.1 Selected composition of the Forsmark reference, saline, ice-melting and buffer-equilibrated waters. Concentrations are in mol/dm^3 (Duro et al. 2006a, TR-06-32, Table 3-1).



	Forsmark reference water [1]	Saline water [2]	Ice melting water [3]	Buffer-equilibrated water [4]
pH (downhole in situ for reference water)	7	7.9	9.6	7.1
Eh (downhole in situ for reference water) (mV)	–143	–314	–200	–130
$[Na^+]$tot	8.88E–02	3.49E–01	6.90E–04	0.145
$[K^+]$tot	8.75E–04	7.41E–04	5.00E–06	0.153
$[Ca^{2+}]$tot	2.33E–02	4.63E–01	1.40E–04	0.0130
$[Mg^{2+}]$tot	9.30E–03	1.11E–04	6.20E–07	5.46E–03
$[HCO_3^-]$	1.77E–03	1.47E–04	4.50E–04	2.19E–03
$[Cl^-]$tot	1.53E–01	1.28E+00	1.60E–04	0.153
[S]tot	6.80E–03	3.56E–02	6.10E–05	2.09E–02
$[Br^-]$tot	2.98E–04	3.90E–03	3.80E–07	
$[F^-]$tot	4.42E–05	8.42E–05	3.60E–04	
[Si]tot	1.85E–04	4.99E–05	2.50E–04	6.64E–05
[Fe]tot	3.31E–05	7.66E–06	3.00E–09	3.31E–05
[Mn]tot	3.93E–05		5.00E–09	
$[Li^+]$tot	7.35E–06	7.74E–04		
$[Sr^{2+}]$tot	9.18E–05		2.00E–06	
[P]tot		3.23E–05		
Ionic strength	0.19	1.86	0.0012	0.21

1) SKB. Pers. Comm.

2) KLX02 in the interval 1,420–1,705 m with date of sampling 94/01/17. /Laaksoharju et al. 1995/.

3) Grimsel groundwater composition [discharging groundwater from the Migration shear zone (AU 96)]. (Data compiled from /Bajo et al. 1989/, /Aksoyoglu et al. 1990/ and /Eikenberg et al. 1991/.)

4) Forsmark groundwater interacted with the bentonite buffer /Arcos et al. 2006/.

The SR-Site Data report (SKB 2010, TR-10-52, page 103) indicates that the magnetite/goethite equilibrium was used to calculate system Eh instead of the magnetite/hematite equilibrium. The treatment of redox in the SR-Site solubility calculations has been re-stated / clarified in a more recent SKB document (Evins 2013a, page 3). Evins (2013a, page 3) identifies α-FeOOH (goethite) as the most common and most stable oxyhydroxide. Any $Fe(OH)_3$ (ferrihydrate) formed is expected to transform rapidly into goethite Evins (2013a). Evins (2013a) notes that using the magnetite/goethite equilibrium to calculate system Eh instead of the magnetite/hematite equilibrium results in slightly higher Eh values and dissolved $Fe^{(III)}$ concentrations.

3.1.4. Geochemical Speciation-Solubility Models and Codes

With the aim of estimating radionuclide solubility limits, SKB has used standard thermodynamic geochemical approaches (e.g. based on equilibrium thermodynamics and the laws of mass balance and mass action) and recognised research models and computer codes (Phreeqc - Parkhurst and Appelo 2001; Hydra/Medusa - Puigdomènech 2002) to consider the speciation of the groundwaters and modified groundwaters discussed above.

When modelling the geochemistry of the groundwaters and estimating radionuclide solubility limits for use in safety assessments, SKB has over the years made minor changes to details of the water compositions considered, and in some instances has simplified the water chemistries by omitting some of the chemical components (compare Table 3-1 of Duro et al. 2006a, TR-06-32 with Table A-1 of Grivé et al. 2010a, R-10-50).

SKB has also developed and applied a relatively simplified spreadsheet-based tool for calculating radionuclide speciation and solubility limits which can be used "*in an agile and relatively fast manner*" (Grivé et al. 2010b, TR-10-61; Grivé et al. 2013b). One of the key simplifications adopted within this spreadsheet tool was that only a subset of the chemical reactions was included (Grivé et al. 2010b, TR-10-61, page 9).

On the basis of an analysis presented in Section F.3 of the Radionuclide Transport report (SKB 2010c, TR-10-50, page 275), SKB argues that uncertainty in thermodynamic data appears to have a larger impact on the radionuclide solubility limits than do variations in groundwater composition.

3.1.5. Thermodynamic Data

As SKB's studies have progressed over a period of several years, its data, models and recommended radionuclide solubility limits have been gradually revised and updated.

The thermodynamic data selected and used by SKB to model groundwater geochemistry and radionuclide solubility in the near-field have been discussed in several reports identified in the SR-Site Data Report (SKB TR-10-52). Key SKB references are Duro et al. (2006a, TR-06-32), Duro et al. (2006b, TR-06-17) and Grivé et al. (2010a, R-10-50).

In compiling and selecting thermodynamic data, the study of Duro et al. (2006a, TR-06-32) had as one of its aims to modify, update and/or complete the NAGRA-PSI thermodynamic database (TDB) (Hummel et al. 2002). Duro et al. (2006a, TR-06-32, page 19) notes that the data are also related "*to a previous database selection conducted by Enviros Spain on behalf of ANDRA (Bruno et al. 2001)*", but unfortunately the reference details for Bruno et al. 2001 are not provided.

The SR-Site Data Report tabulates the chemical reactions and equilibrium constants used in the SR-Site Simple Functions spreadsheet modelling (SKB 2010b, TR-10-52, Tables 3-29 to 3-32), but does not present the complete set of thermodynamic data used in the geochemical modelling studies that support the safety assessment.

Baldwin and Hicks (2012) began to trace the origins of the thermodynamic data selected and used by SKB in SR-Site but were unable to complete the task. Further comments on this aspect of SKB's work are provided in Section 4.1.5.

3.1.6. Solubility-Limiting Phases and Solubility Limits

Based on the results of thermodynamic modelling, the use of Pourbaix diagrams and expert judgement, SKB has identified which solid phases are likely to limit the solubilities of the relevant radionuclides under the geochemical conditions of interest (Section 6 of Duro et al. 2006a, TR-06-32 and Sections 2 and 3 of Grivé 2010a, R-10-50). With few exceptions (notably radium – see below), SKB has considered the solubility of 'pure' radionuclide solid phases, rather than of solid phases that contain only trace amounts of radionuclides (such as solid solutions or co-precipitates).

SKB's 2006 SR-Can safety assessment suggested that ^{226}Ra was one of the main radionuclides contributing to assessed dose. This finding is supported by the results of the SR-Site assessment (SKB 2010a, TR-10-11, page 45).

The assessed dose from ^{226}Ra is clearly dependent on the source term for this radionuclide, and this is directly related to the solubility behaviour of radium. In the 2006 SR-Can assessment, the source term calculations performed for ^{226}Ra assumed that its solubility would be controlled by the solubility of solid $RaSO_4$, but SKB (Grandia et al. 2008, TR-08-07, page 7) noted that information from radiochemical research, natural system studies and anthropogenic systems indicates that radium is often associated with the precipitation of barite, $BaSO_4$.

Bosbach et al. (2010, TR-10-43) undertook an experimental study on the uptake of Ra^{+2} by barite ($BaSO_4$) and studied the kinetics of solid solution formation via $BaSO_4$ dissolution and $Ra_xBa_{1-x}SO_4$ (re) precipitation. This study observed that the uptake of $^{226}Ra^{+2}$ and $^{133}Ba^{+2}$ were not limited to adsorption reactions, but proceed significantly into the bulk of the barite crystals. The observed $^{226}Ra^{+2}$ concentration in solution controlled by the solubility of a $Ra_xBa_{1-x}SO_4$ solid solution was several orders of magnitude below the solubility of Ra^{+2} that would be expected for pure $RaSO_4$.

In the SR-Site assessment, therefore, SKB's recommended approach was to take account of the co-precipitation of radium with barium sulphate (SKB 2010b, TR-10-52, page 116). The Ra/Ba ratio inside the canister was estimated from inventory data and radioactive decay calculations. The Ra/Ba ratio varies with time from extremely low values (~10^{-9} after about 40 years when the fuel is placed in the canisters) to a peak value of ~3 x 10^{-4} years after 100,000 years. For the assessment, a maximum value of the Ra/Ba ratio of 10^{-3} was assumed and applied throughout the entire repository evolution period. This ratio of 1 part in 1000 was then used as a correction factor with which to multiply the Ra^{2+} concentration calculated using the Simple Function spreadsheet tool with solid $RaSO_4$ as the solubility-limiting phase. The approach followed in SR-Site assumes that radium will be incorporated within a barium-radium solid solution or co-precipitate which will limit the solubility of radium. It also assumes that the solid solution can be represented as an ideal solid solution.

The set of radionuclide solubility-limiting phases and the corresponding radionuclide solubility limit values calculated for the 2006 SR-Can safety assessment was published in Table 8.1 of Duro et al. (2006a, TR-06-32). These data were later updated in Table 3.4 of Grivé et al. (2010a, R-10-50).

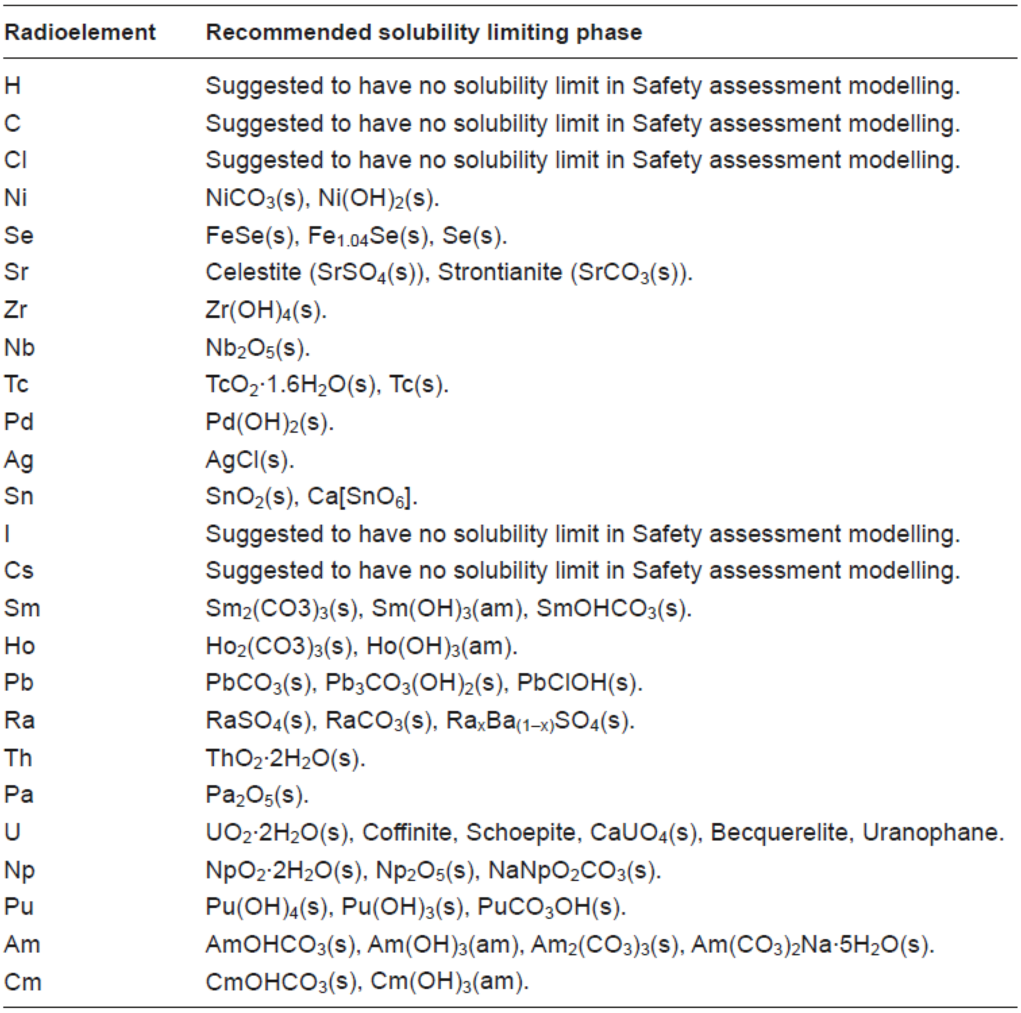
The Data Report for the SR-Site safety assessment (SKB, 2010b, TR-10-52) cites the same information on the identity of radionuclide solubility-limiting phases as documented in Grivé et al. (2010a, R-10-50) – Table 2.2.

The SR-Site Data Report (SKB 2010b, TR-10-52) does not document the calculated radionuclide solubility limit values, but an appendix to the Radionuclide Transport Report presents frequency-solubility histograms (Figures F-17 to Figure F-28 of SKB 2010c, TR-10-50) plotted using the results from probabilistic solubility calculations made using the Simple Functions spreadsheet tool in conjunction with the @Risk spreadsheet add-in, to illustrate the impact on solubility limits of variations in groundwater composition and uncertainties in thermodynamic data. Table 3-4 of the Radionuclide Transport Report (SKB 2010c, TR-10-50) presents median values of the radionuclide solubilities for temperate climate conditions used in SKB's deterministic transport calculations. SKB's approach to the treatment of uncertainty in thermodynamic data is described more fully in Grivé et al. (2013).

Tables of radionuclide solubility limit values calculated by SKB for un-interacted water compositions (the Forsmark Reference, Saline, and Ice-Melting waters) are presented in Table 3-4 of Grivé et al. (2010a, R-10-50) and Table B-1 of Grivé et al. (2010b, TR-10-61). Selected values from SKB's tables are reproduced below (Table 2.3) to allow comparison with independently calculated solubility limit values (see Section 4.3).

In SR-Site, calculations of radionuclide transport rely on three primary computer codes, COMP23, FARF31 and MARFA. COMP23 (e.g. Cliffe and Kelly 2006, R-04-64) is a compartment code used for radionuclide migration calculations in the near field (the canister and the engineered systems). Because COMP23 does not allow changes in solubility limits with time, SKB has used a mixture of groundwater compositions representing the entire assessment period to calculate a single set of solubility limits for the safety assessment: "*The solubility limits for the safety assessment were, thus, calculated with a groundwater composition consisting of 25% of groundwater compositions representing the temperate climate, 25% representing the permafrost climate, 25% representing glacial climate and 25% representing submerged climate"* (SKB 2010c, TR-10-50, page 283).

Table 2.2 SKB's recommended solubility limiting phases (SKB 2010b, TR-10-52, page 110). All data are from Duro et al. (2006a, TR-06-32), except that data for lead (Pb) is from Grivé et al. (2010a, R-10-50).



Radioelement	Recommended solubility limiting phase
H	Suggested to have no solubility limit in Safety assessment modelling.
C	Suggested to have no solubility limit in Safety assessment modelling.
Cl	Suggested to have no solubility limit in Safety assessment modelling.
Ni	$NiCO_3(s)$, $Ni(OH)_2(s)$.
Se	$FeSe(s)$, $Fe_{1.04}Se(s)$, $Se(s)$.
Sr	Celestite ($SrSO_4(s)$), Strontianite ($SrCO_3(s)$).
Zr	$Zr(OH)_4(s)$.
Nb	$Nb_2O_5(s)$.
Tc	$TcO_2 \cdot 1.6H_2O(s)$, $Tc(s)$.
Pd	$Pd(OH)_2(s)$.
Ag	$AgCl(s)$.
Sn	$SnO_2(s)$, $Ca[SnO_6]$.
I	Suggested to have no solubility limit in Safety assessment modelling.
Cs	Suggested to have no solubility limit in Safety assessment modelling.
Sm	$Sm_2(CO3)_3(s)$, $Sm(OH)_3(am)$, $SmOHCO_3(s)$.
Ho	$Ho_2(CO3)_3(s)$, $Ho(OH)_3(am)$.
Pb	$PbCO_3(s)$, $Pb_3CO_3(OH)_2(s)$, $PbClOH(s)$.
Ra	$RaSO_4(s)$, $RaCO_3(s)$, $Ra_xBa_{(1-x)}SO_4(s)$.
Th	$ThO_2 \cdot 2H_2O(s)$.
Pa	$Pa_2O_5(s)$.
U	$UO_2 \cdot 2H_2O(s)$, Coffinite, Schoepite, $CaUO_4(s)$, Becquerelite, Uranophane.
Np	$NpO_2 \cdot 2H_2O(s)$, $Np_2O_5(s)$, $NaNpO_2CO_3(s)$.
Pu	$Pu(OH)_4(s)$, $Pu(OH)_3(s)$, $PuCO_3OH(s)$.
Am	$AmOHCO_3(s)$, $Am(OH)_3(am)$, $Am_2(CO_3)_3(s)$, $Am(CO_3)_2Na \cdot 5H_2O(s)$.
Cm	$CmOHCO_3(s)$, $Cm(OH)_3(am)$.

Table 2.3 Solubility limit values from Table 3-4 of Grivé et al. (2010a, R-10-50).

Radioelement	**Forsmark Reference Water**	**Saline Water**	**Ice-melting Water**
	Solubility limiting phase and log solubility (mol/dm^3)	Solubility limiting phase and log solubility (mol/dm^3)	Solubility limiting phase and log solubility (mol/dm^3)
Ag	AgCl -5.11	AgCl -5.79	AgCl -4.04
Am	$Am(CO_3)_2Na:5H_2O$ -5.57	$Am(OH)_3$ -7.16	$AmCO_3OH$(am) -5.63
Cm	$Cm_2(CO_3)_3$ -5.46	$Cm(OH)_3$ -7.16	$CmCO_3OH$(am) -5.63
Ho	$Ho_2(CO_3)_3$ -5.64	$Ho(OH)_3$(am) -5.66	$Ho_2(CO_3)_3$ -5.19
Nb	Nb_2O_5 -4.51	Nb_2O_5 -2.54	Nb_2O_5 -3.97
Ni	$Ni(OH)_2$(beta) -2.81	$Ni(OH)_2$(beta) -6.87	$Ni(OH)_2$(beta) -4.25
Np	$NpO_2:2H_2O$ -8.96	$NpO_2:2H_2O$ -8.99	$NpO_2:2H_2O$ -9.11
Pa	Pa_2O_5 -6.52	Pa_2O_5 -6.5	Pa_2O_5 -6.62
Pb	Cerussite -5.97	Hydrocerussite -6.55	PbClOH -5.13
Pd	$Pd(OH)_2$ -5.46	$Pd(OH)_2$ -5.4	$Pd(OH)_2$ -5.46
Pu	$Pu(OH)_4$(am) -7.57	$Pu(OH)_4$(am) -9.3	$Pu(OH)_4$(am) -6.24
Ra	$RaSO_4$(cr) -6.62	$RaSO_4$(cr) -5.82	$RaSO_4$(cr) -6.53
Se	$FeSe_2$ -10.74	Se -10.42	$FeSe_2$ -6.39
Sm	$SmOHCO_3$ -6.84	$SmOHCO_3$ -8.59	$SmOHCO_3$ -7.37
Sn	SnO_2(am) -7.23	SnO_2(am) -5.57	SnO_2(am) -7.07
Sr	Celestite -3.01	Strontianite -4.95	Celestite -2.82
Tc	$TcO_2:1.6H_2O$ -8.37	$TcO_2:1.6H_2O$ -8.35	$TcO_2:1.6H_2O$ -8.39
Th	ThO_2(am, aged) -8.05	ThO_2(am, aged) -8.62	ThO_2(am, aged) -8.94
U	UO_2(am, aged) -6.38	Bequerelite -7.22	UO_2(am, aged) -8.61
Zr	$Zr(OH)_4$(am, aged) -7.76	$Zr(OH)_4$(am, aged) -7.74	$Zr(OH)_4$(am, aged) -7.85

4. Assessment

Based on review of SKB's reports and other published materials (e.g., in the scientific literature), as well as SSM's experience of tracking SKB's programme for the last decade or more, this section presents the findings of the review assignment, including results from the independent calculations performed.

The following subsections address:

- SKB's model for evaluating radionuclide solubility limits.
- SKB's use of solubility limits in the SR-Site safety assessment.
- Independent calculations of solubility limits for selected radionuclides.
- Redox conditions and uncertainties.
- The co-precipitation of barium.
- Thorium solubility.

The section also comments on SKB's reporting and discusses various other uncertainties.

4.1. SKB's Model for Evaluating Solubility Limits

The following observations can be made regarding SKB's model for the evaluation of radionuclide solubility limits.

4.1.1. Conceptual Model

SKB's conceptual model for calculating recommended radionuclide solubility limits assumes that after canister failure, there will always be sufficient water present within the canister to allow radionuclide dissolution. SKB's model of radionuclide solubility does not quantify the amounts of water or gas that may move in or out of the canister. In reality, the amount of radionuclide dissolution that can occur may be limited by the supply of water to the canister interior.

In its modelling to evaluate radionuclide solubility limits, SKB assumes that for all of the reference cases leading to recommended solubility limit values there will not be significant microbial activity within the region of interest (Figure 2.1). No arguments are given in Duro et al. (2006a, TR-06-32) or Grivé et al. (2010a, R-10-50) to support SKB's expectation that there will not be any significant microbial activity; instead the possible effects of microbial activity in terms of sulphate reduction on radionuclide speciation and solubility are estimated and discussed in the relevant sections of the reports. The SR-Site Data report (SKB 2010, TR-10-52, page 104) argues that there would be a limited supply of electron donors (e.g. methane, hydrogen) for microbes to use in reducing sulphate. However, since hydrogen is one of the primary products of insert corrosion, this argument does not seem immediately convincing.

Section 3.5.14 of the buffer process report (SKB 2010d, TR-10-47, page 164) summarises various experimental results on microbial activity in bentonite including those of Masurat et al. (2010) and argues, on the basis of these experiments, that there will not be significant microbial activity in the region of interest, as long as the buffer has a high enough density. Considerably less microbial activity was observed in experiments with bentonite densities of 2,000 kg/m^3 than with bentonite densities of 1,800 kg/m^3 and 1,500 kg/m^3 (see Figure 3-3 of SKB 2010d, TR10-47). The buffer process report recognises that if the density of the buffer was lower, for example following erosion, more microbial activity might occur, but argues that this would still not produce enough sulphide to cause significant corrosion of the copper canister (SKB 2010d, TR-10-47, pages 164-170).

The SR-Site Data report confirms, however, that microbial activity and sulphate reduction is not taken into account in the radionuclide solubility limits used in the SR-Site assessment, and notes this as a relevant uncertainty for Sr, Ra, Sn, Pb, Se, Ni, Ag and Pu (SKB 2010, TR-10-52, Table 3-25). The implication of some of the text in the SR-Site Data report (SKB 2010, TR-10-52, page 104) is that excluding sulphate reduction when setting radionuclide solubility limits is a conservative approach, but this is not clearly the case for all radionuclides. For example, if microbes were active and reduced sulphate to sulphide, they might affect the stability of any radium-barium solid solutions / co-precipitates that formed. The treatment of co-precipitation is discussed further in Section 4.5.

4.1.2. Major Element Water Geochemistry

In calculating radionuclide solubility limits, SKB has considered several groundwater types and compositions (Table 2.1 above which is reproduced from Duro et al. 2006a, TR-06-32; Table A-1 in Grivé et al. 2010a, R-10-50, and Appendix 1 in Grivé et al. 2013) and has performed sensitivity studies on the effect on radionuclide solubility of varying groundwater chemistry. However, it is not obvious how these groundwater compositions and the radionuclide solubility limits calculated from them relate to the recommended end-member water compositions in the Data Report, (SKB 2010b, TR-10-52, Table 6.6), which were adopted based on work by Salas et al. (2010, TR-10-58).

The omission from the SR-Site assessment of water compositions resulting from chemical interactions between groundwaters and the buffer (SKB 2010, TR-10-52, page 102) does not, however, seem well justified. The Data Report argues that accessory minerals in the buffer will be removed from the buffer by dissolution relatively rapidly, *"Conditioning of the groundwater by accessory minerals (carbonates) in the buffer is expected have relatively short duration, or to have small impact on the overall composition"* (SKB 2010b, TR-10-52, page 102), but the report does not present or reference calculations to quantify the duration for which carbonates in the buffer may persist and influence the chemistry of the waters reaching the spent fuel. Given that the Site Descriptive Model (SKB 2008, TR-08-05, page 316) indicates that groundwaters at the Forsmark site are often close to being at equilibrium with calcite, it may be that there is little potential for dissolution of calcite in the buffer. According to SKB (2010d, TR-10-47, Table 2.1), MX-80 and Deponit-CAN bentonites contain 0 to 1, and 10 ± 1 wt % calcite and siderite. Depending on the amount of carbonate initially present in the buffer material, therefore, some carbonate may be present in the buffer after long periods (possibly many thousands of years). This idea is supported by the modelling results of Arcos et al. (2006, TR-10-16, page 39) whose calculations suggest that after an initial ~10,000-year period of dissolution, calcite may later re-precipitate in the buffer and then persist for several tens of thousands of years. Ultimately, the omission of water compositions resulting from chemical interactions between groundwaters and the buffer may not be significant to the results of the safety assessment but, even if this is the case, it seems questionable from the perspective of demonstrating understanding and assessing the possible range of system behaviour.

It is also noted that the composition of the ice melting water considered in calculating radionuclide solubility limits (Table 2.1) is quite extreme (e.g., in terms of being rather dilute). Based on a review of the composition of glacial waters, Arthur (2010) identified two main types of sub-glacial melt water:

- Those like the ice melting water considered in Duro et al. (2006a, TR-06-32) from valley glaciers, which are extremely dilute Ca-HCO_3-SO_4 type solutions (< 500 mg/L TDS).
- Those from larger ice sheets, which are more concentrated (<10,000 mg/L TDS) Na Ca-SO_4-HCO_3 type solutions.

There is also significant potential for the compositions of glacial waters to be modified by geochemical and microbiological reactions *en route* to repository depths – such changes do not seem to have been considered within SKB’s determination of radionuclide solubility limits; they may in some sense have been captured within SKB’s sensitivity studies (e.g. in Appendix F of the Radionuclide Transport report, SKB 2010c, TR-10-50, pages 275 to 283), but this is not explicit.

As noted above, SKB suggests that the effect of uncertainty in thermodynamic data is greater than that associated with water chemistry. However, it is suspected that SKB’s assessment of the relative importance of these factors in Section F.3 of the Radionuclide Transport report (SKB 2010c, TR-10-50, pages 275 to 283), overstates the importance of the uncertainty in the thermodynamic data. This is because in an internally-consistent thermodynamic database, the values of the individual equilibrium constants are correlated with one another, and the strategy used in SKB’s assessment for sampling values for each of the equilibrium constants from within their estimated ranges of uncertainty may not have preserved these correlations properly. Incorrect pairing of data values would mean that at least part of the broad spread of the data shown in the histograms on the left of figures F-1 to F-16 would represent an artefact of the modelling approach, rather than a true measure of uncertainty deriving from the thermodynamic data.

Further comments on SKB’s assumptions regarding water geochemistry are given below in Section 4.2.

4.1.3. Corrosion and Redox

Duro et al. (2006a, TR-06-32, page 16) assumed that the solid phase products formed during insert corrosion would be the thermodynamically most stable solid minerals in the iron-water system (initially magnetite, later magnetite and hematite). As a result, their model of the redox conditions within the region of interest was essentially fixed; the redox potential of the system was set for the pH of interest from the relevant equilibrium amongst the stable corrosion products. Although some calculation cases were made at different assumed system redox potentials (Table 3-1 of Duro et al. 2006a, TR-06-32), the uncertainties associated with redox conditions and their evolution were not explored or evaluated in detail.

Evins (2013a, page 3) argued that using the magnetite/goethite equilibrium to calculate system Eh instead of the magnetite/hematite equilibrium results in slightly higher Eh values, but does not document any analyses that quantify this or its effects on the radionuclide solubility limits.

Many solubility-controlling phases, especially at low temperature, are metastable. Aqueous systems also often display redox disequilibrium. Such disequilibrium may be caused by various effects, including radioactive decay (e.g. Wolery 1992). In addition, the stability of some redox-controlling phases may be variable due to factors such as crystallinity (i.e., crystal size), order/disorder, ionic substitution, or, in the case of fresh precipitates, aging (e.g. Helgeson et al. 1978). SKB's documentation does not seem to discuss or evaluate the possibilities of redox disequilibria, of further possible alternative corrosion products (e.g. green rusts) or of alternative reactions pathways. This topic is discussed further in Section 4.4.

4.1.4. Geochemical Speciation-Solubility Models and Codes

The Phreeqc code used by SKB for evaluating radionuclide solubility limits is a widely used code that has been tested in many studies and can be regarded as well verified and tested. Phreeqc is essentially a model of inorganic chemistry, although it can be used to represent chemical reactions involving some relatively simple organic molecules. Phreeqc was not, however, designed to represent the more complex microbiologically-mediated that often occur in natural systems although, again, some researchers have extended versions of the code in this direction. The possible effects of microbial activity are discussed further in Section 4.5.

It is general good practice when performing speciation-solubility calculations to include rather than exclude aqueous components and species in the model, even when the existence or thermodynamic data for a component or species are uncertain. Taking this inclusive approach allows investigation of the possible significance of a component or species through the use of sensitivity studies. In the end, it is necessary to have confidence that all of the significant species are included in the model (e.g. Wolery 1992).

The results presented by Grivé et al. (2010b, TR-10-61, Tables B-1 to B-6) indicate that, for most of the problems of interest, the Simple functions spreadsheet reproduces the solubility of the solubility limiting phase calculated by Phreeqc to within half an order of magnitude. However, the output from the Simple functions spreadsheet differs more significantly from the Phreeqc output (by 1 to 2 orders of magnitude) for a few species, e.g. AgCl, $AmCO_3OH_{(am)}$. The differences appear to be greater for saline waters than for dilute waters. It is noted that the latest versions of Phreeqc, which were not available when SKB's calculations were conducted, allow use of the Specific Interaction Theory (SIT) ionic strength correction method, which has greater applicability to saline waters than the more traditional approaches (versions of the Extended Debye-Hückel or Davies equations) used in earlier versions of Phreeqc and the Simple functions spreadsheet.

For the relatively simple speciation-solubility calculations required for determining radionuclide solubility limits, the Phreeqc code runs in under a second on an average personal computer. Phreeqc can be run either from an interactive user interface or in a 'batch mode' that can be used to perform many code runs in rapid succession. It would also be relatively straightforward to run the code within a probabilistic harness.

Given these various points, we are not fully convinced of the benefits of using the spreadsheet approach for speciation-solubility calculations. Nevertheless, it is considered that, overall, the codes used by SKB to develop recommendations for solubility limits are appropriate.

4.1.5. Thermodynamic Data

Baldwin and Hicks (2012) recommended that SSM's main review phase should include further checking to trace the origin of the thermodynamic data used by SKB. In particular, they recommended further checking of the data in Tables 3.29 to 3.32 of the SR-Site Data report that they had been unable to trace to determine if it derived from Hummel et al. (2002).

This project has looked briefly into this suggestion and has found that many of the data that Baldwin and Hicks (2012) were not able to trace in their initial review come from the "*Chemical Thermodynamics*" series of reports produced by the OECD NEA (e.g., NEA 2001, 2003, 2007), rather than from Hummel et al. (2002). Notwithstanding this, there are still some data values that it has not been possible to trace. It is concluded, therefore, that SKB has used thermodynamic data from sensible sources, but that it has not presented these data or the reasons for their selection in a complete or traceable way.

4.2. SKB’s Use of Solubility Limits in SR-Site

Based on the range of SKB documentation that has been examined in this project (Appendix 1), it has not been possible to trace in detail how solubility limits have been used in the SR-Site safety assessment. A principle difficulty with SKB’s documentation is the opaqueness of statements such as “*The solubility limits for the safety assessment were, thus, calculated* with *a groundwater composition consisting of 25% of groundwater compositions representing the temperate climate, 25% representing the permafrost climate, 25% representing glacial climate and 25% representing submerged climate”* (SKB 2010c, TR-10-50, page 283). How the water compositions mentioned in this statement relate to the waters considered in the thermodynamic modelling conducted to determine recommended radionuclide solubility limits (Duro et al. 2006a, TR-06-32; Grivé et al. 2010a, R-10-50; Grivé et al. 2013) is unclear. The justification for assuming an equal split (presumably in time) amongst the four water compositions mentioned is also unclear.

Although it is generally cautious (conservative) to use pure radionuclide phases (rather than e.g. solid solutions) to determine solubility limits, it has not been possible to trace how uncertainties in the identity of the radionuclide solubility-limiting phases have been considered or quantified in the SR-site safety assessment calculations. There may be considerable and potentially significant uncertainty in the identity of radionuclide solubility-limiting solid phases for some radionuclides (e.g. americium, uranium - Table 2.2), from SKB’s reports (e.g. Grivé et al. (2010b, TR-10-61, page 10) but it appears that only one such solid phase has been considered per radionuclide for each of the groundwater composition selected (Table 2.3). The expert judgements described in Duro et al. (2006a, TR-06-32) and Grivé et al. (2010a, R-10-50) for identifying possible solubility limiting solid phases under particular chemical conditions are considered to be rational and appropriate, but there may still be additional factors (e.g. uncertainty associated with the concentrations of certain species in groundwaters, uncertainty associated with thermodynamic data for further possible solubility-limiting solid phases, effects of nucleation, kinetics, particle size and crystallinity) that mean uncertainty remains over which solids could form under any particular set of conditions. Grivé et al. (2010b, TR-10-61, page 10) acknowledges that it is not always the most stable solid phase which is more likely to precipitate. This, therefore, questions the consideration of only one solubility limiting solid phase for each water composition.

Grivé et al. (2013) provides a useful description and examples of how uncertainty in SKB’s selected thermodynamic data has been handled using the Simple Functions spreadsheet and this gives confidence that the effects of uncertainties associated with the stability constants for particular chemical species can be traced and quantified. However, once again, exactly how these uncertainties are treated in the safety assessment calculations remains unclear.

Finally, it is noted that although precipitation, co-precipitation and solubility limitation processes may occur for some radionuclides at locations in the disposal system outside the region inside the canister close to the spent fuel, SKB has not explicitly quantified such processes. SKB’s reports acknowledge that such processes may occur and mention, for example, the coprecipitation of thorium in the bentonite buffer (SKB 2010a, TR-10-11, page 653). The potential implications of such processes are discussed in Section 4.5.

4.3. Independent Solubility Limit Calculations

As noted above, one of the objectives of this project was to attempt to reproduce the solubility limits calculated by SKB for two to four selected radionuclides. The reproduction of parts of a licence applicant’s work can clarify and increase understanding of their work, as well as providing a degree of independent verification and scrutiny of the basis for the Application.

To this end, this section of the report presents results from speciation-solubility calculations conducted during this study. The calculations have been made using Phreeqc (Parkhurst and Appelo 2001) together with Release 20 of the Hatches thermodynamic database (Bond et al. 1997; Baston et al. 2008; Heath et al. 2011; Hunter 2013).

The calculation cases were selected in order to include a range of radionuclides with differing complexity in their chemical speciation behaviour, and a range of different groundwater compositions. A third factor in the selection of calculation cases was the availability within SKB’s documentation of clearly presented data and results that could be compared with the results produced in this project.

The calculations were made by determining the speciation of the relevant water and then increasing the concentration of the radionuclide in question until the solubility of the solubility limiting phase was reached. To avoid unintentional changes to the water speciation, the Phreeqc EQUILIBRIUM_PHASES and REACTION functions were not used.

In order to reproduce the main features of SKB’s conceptual model and modelling, the redox conditions were fixed at the start of the simulations using an input pe value, rather than being calculated within the Phreeqc code, for example, from equilibrium with magnetite, goethite or hematite. Also, the reduction of sulphate to sulphide species and the reduction of carbonate species to methane were prevented in the calculations. Ionic strength corrections were made using the Extended Debye-Hückel / Davies equations rather than SIT.

4.3.1. Solubility Limits for Selected Radionuclides in Forsmark Reference Groundwater

Table 4.1 presents results from a set of speciation-solubility calculations made to allow examination of radionuclide solubility limits in the Forsmark reference groundwater composition as documented in Grivé et al. (2010a, R-10-50 and 2010b, TR-10-61). The radionuclide solubility limiting phases considered were those recommended by Grivé et al. (2010b, TR-10-61).

Where direct comparisons of the radionuclide solubility limit values determined using Phreeqc are possible, these lie generally within a factor of two. Exact agreement would not be expected because of the differences in the thermodynamic databases used.

For some radioelements the databases contain different solid phases (e.g. zirconium) and the differences highlight the potentially very significant uncertainty for the calculated solubility limits of the choice of solubility limiting solid phase.

The 4th column in Table 4.1 shows the median values of the solubility limits used by SKB to represent temperate climate conditions (from SKB 2010, TR-10-50, Table 3-4). It can be seen that the median values used in SKB's transport calculations are in broad agreement with the other values (approximately within an order of magnitude) for Sr, Ra, Zr, Th and Np, but that the value used for U in the transport calculations seems very low and the value used for Pu in the transport calculations seems very high. No explanations have been found for these features of SKB's data.

Table 4.1 Comparison of solubility limits for a selection of radionuclides calculated by SKB and in this project for the Forsmark reference water (columns 2, 3 and 6) and values used by SKB to represent temperate climate conditions in the Radionuclide Transport Report (column 4). The composition of the Forsmark reference water was from Grivé et al. (2010a, b). Radionuclide solubility limiting phases were from Grivé et al. (2010b).

SKB (TR-10-61)			**SKB (TR-10-50)**	**This project**		**Factor Difference**
SKB selected thermodynamic data Solubility limiting solid phase	**Phreeqc**[a] concentration (mol/dm^3)	**Simple functions spreadsheet** concentration (mol/dm^3)	**Median solubility for temperate climate conditions** concentration (mol/dm^3)	**Hatches 20** Solubility limiting solid phase	**Phreeqc**[b] concentration (mol/dm^3)	**b/a**
Celestite, $SrSO_4$	9.8E-04	9.8E-04	3.7E-03	Celestite, $SrSO_4$	1.4E-03	1.38
$RaSO_4$	2.4E-07	3.1E-07	9.1E-07	$RaSO_4$	1.2E-07	0.49
$Zr(OH)_4$ (am, aged)	1.7E-08	1.8E-08	1.8E-06	not in database	-	-
-	-	-	-	$Zr(OH)_4$ (am, fresh)	1.4E-04	-
$ThO_2.2H_2O$ (am, aged)	8.9E-09	7.9E-09	2.6E-09	$ThO_2.2H_2O$ (am, aged)	2.1E-09	0.23
$UO_2.2H_2O$	4.2E-07	6.8E-07	9.5E-10	not in database	-	-
-	-	-	-	UO_2 (am)	8.0E-06	-
-	-	-	-	UO_2 nea)	5.0E-08	-
$Pu(OH)_4$ (am)	2.7E-08	1.4E-08	4.8E-06	$Pu(OH)_4$	5.8E-09	0.22
$NpO_2.2H_2O$	1.1E-09	1.1E-09	1.0E-09	not in database	-	-
-	-	-	-	NpO_2 (am)	2.0E-10	-

4.3.2. Radionuclide Speciation in Forsmark Reference Groundwater

In order to examine and understand the similarities and differences in the representation of the chemical systems of interest in greater detail, Figures 4.1 and 4.2 allow comparison of the calculated distributions of aqueous species for two example radionuclides in the Forsmark reference groundwater.

Figure 4.1 shows the calculated aqueous speciation of plutonium in the Forsmark reference groundwater as a function of water pH. Figure 4.2 shows the equivalent results for americium. SKB's results are shown on the left and the corresponding results obtained in this project are shown on the right.

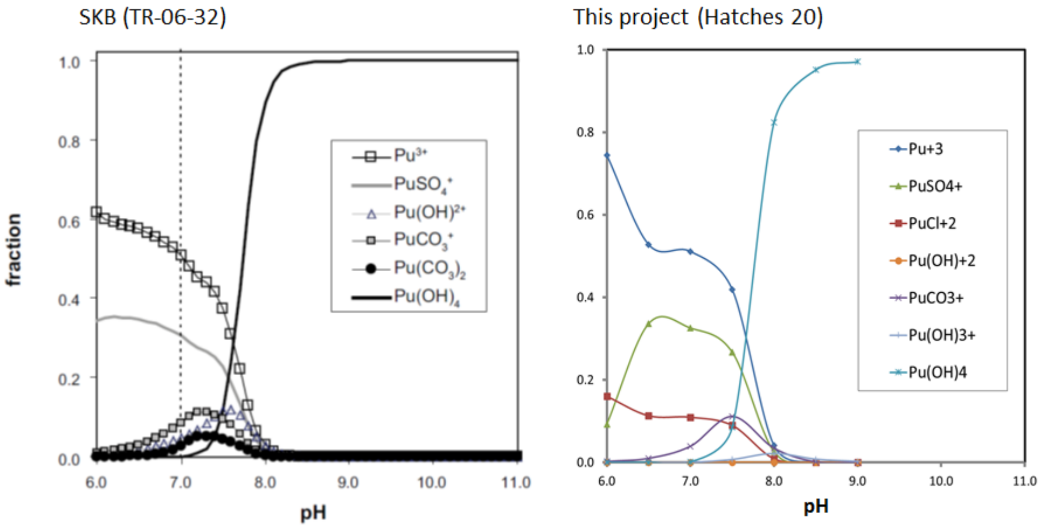
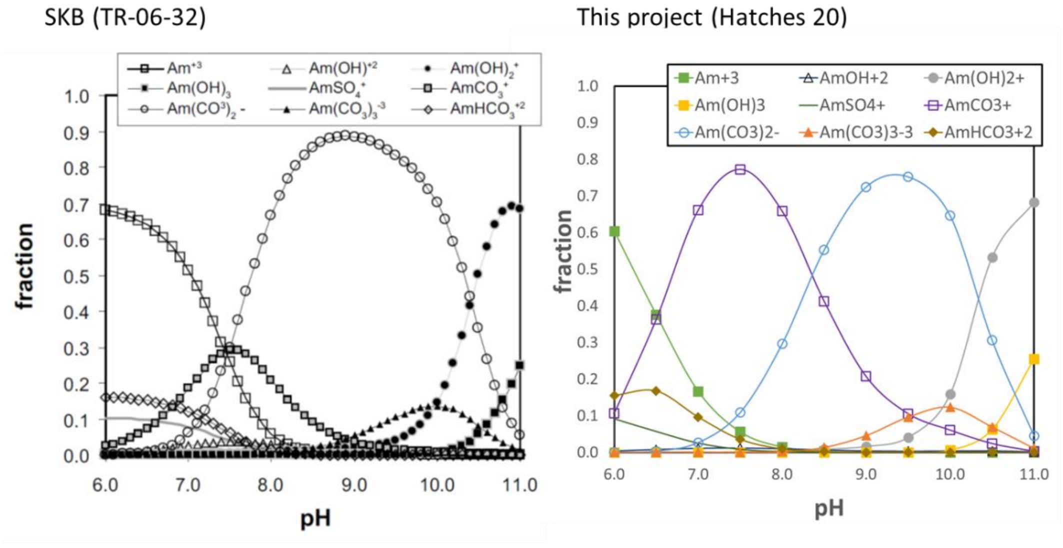


Figure 4.1 Comparison of the calculated speciation of plutonium in the Forsmark Reference Water as a function of pH calculated in Duro et al. (2006a, TR-06-32, page 85) and in this project using Release 20 of the Hatches thermodynamic database


SKB (TR-06-32)

This project (Hatches 20)

Figure 4.2 Comparison of the calculated speciation of americium in the Forsmark Reference Water as a function of pH calculated in Duro et al. (2006a, TR-06-32, page 88) and in this project using Release 20 of the Hatches thermodynamic database

For plutonium the comparison is generally good, with both sets of calculations exhibiting the same main features. Pu^{+3} is the predominant aqueous species at pH values below approximately 7.5; above this pH, the Pu(OH)$_4$ species dominates. The dominance of Pu(III) species at lower pH and of Pu(IV) species at higher pH does not reflect a change in system Eh (redox potential), which was kept constant throughout these simulations but, rather, reflects the relative strengths of the aqueous Pu species as a function of system hydrolysis. Some relatively minor differences can be observed between the two sets of simulations, however, such as the higher proportion of the PuCl^{+2} species in the calculations made using the Hatches database, a species that is not included in the table of reactions and equilibrium constants recommended for use in the SR-Site assessment (Table 3-31 of the SR-Site Data report SKB (2010b, TR-10-52). Although it lists a selected $\Delta_f G_m^o$ value for PuCl^{2+}, NEA (2003) rejected the value for the formation constant of PuCl^{2+} that had been derived and selected by the earlier NEA review (NEA 2001). Release 20 of the Hatches database, however, retains the PuCl^{2+} species and the formation constant value from the earlier NEA (2001) review.

Altmaier et al. (2013) discuss various studies have been conducted into the speciation and solubility of plutonium since the review of NEA (2003). They note studies that suggest the data selected in NEA (2003) may over-estimate the strength of Pu(IV) hydrolysis, although the data they present is mainly for Pu(OH)$^{+3}$ and Pu(OH)$_2^{+2}$ and may not, therefore, affect the distribution of species illustrated in Figure 4-1 very significantly. Of potentially greater significance, however, is that Altmaier et al. (2013) suggest that recent studies support a concept in which Pu(IV) intrinsic colloids represent equilibrium species that are an integral part of the thermodynamic system and which can increase total plutonium solubilities by ~2 orders of magnitude in neutral to alkaline waters. Brown et al. (2011) discuss the likely form of such Pu(IV) colloids. Such concepts are not explicitly included in

SKB's approach to determining radionuclide solubility limits for the SR-Site assessment and so the recommended solubility limits calculated on the basis of the data and reactions in the Data Report (SKB 2010b, TR-10-52, Tables 3-29 to 3-31) may, from a geochemical perspective, be incorrect (too low). This may not make a significant difference to the overall results from the SR-Site assessment, however, because the case of an intact buffer SKB assumes that colloidal species will be effectively filtered by the bentonite and their transport will be prevented. For the case of an eroded buffer, SKB does not apply solubility limits and so in this case the assessment models transport of both aqueous and colloidal species.

For americium there are also obvious similarities between the calculation results (e.g. the distributions of Am^{3+} and $Am(OH)_2^+$ shown in Figure 4.2), but there is an obvious difference in the calculated proportion of the $AmCO_3^+$ species. In the results from the calculations made using Release 20 of the Hatches database, the $AmCO_3^+$ species is more dominant (reaching ~75% at pH=7.5 as compared with ~30% in the results of Duro et al. (2006a, TR-06-32, page 85)) and this shifts the peak of the $Am(CO_3)_2^-$ curve to a higher pH value at ~pH = 9.5 as compared with ~pH = 9.0 in SKB's results. It also reduces slightly the fraction of Am^{+3} at lower pH. The differences suggest that although the thermodynamic data recommended in the SR-Site Data report (SKB 2010, TR-10-52, Tables 3-29 to 3-31) include the values for the formation constants of $AmCO_3^+$ and $Am(CO_3)_2^-$ given in NEA (2003), which were also used in the Hatches calculations made in this project, older data probably from (NEA 1995) may have been used in the calculations made by Duro et al. (2006a, TR-06-32).

Since the review of NEA (2003), a more recent re-interpretation of the americium-carbonate system has been made (Reiller et al. 2012), which includes the suggestion that the $Am(CO_3)_3^{-3}$ species maybe relatively less significant than indicated previously. The re-interpretation by Reiller et al. (2012) post-dates the data recommendation made in the SR-Site Data report (SKB 2010, TR-10-52, Tables 3-29 to 3-31) and was probably not, therefore, considered in the SR-Site assessment.

Although these calculations have been performed for just two radionuclides, plutonium and americium, they illustrate the types of uncertainties that exist. The comparisons highlight the need for full and transparent documentation of the thermodynamic data used at each stage of the process, of the reasons for the selection of data, and for clear recognition of the uncertainties.

4.3.3. Effect of Water Composition on Radionuclide Solubility

Tables 4.2 and 4.3 allow comparison of calculated solubility limits for strontium and thorium in different water compositions.

For strontium, the calculated solubility limits are within a factor of two, although it is notable that the SKB values are consistently higher than those calculated using the Hatches database. For thorium, the calculated solubility limits are, with one exception, within a factor of approximately five. Again it is notable that the SKB values are consistently higher than those calculated using the Hatches database.

The exception is the solubility limit for thorium in the buffer-equilibrated water, where the difference between the calculated solubility limits is much larger and approaches a factor of 500. Examination of the data highlights a relatively high solubility value for thorium of 1.0E-06 mol/dm^3 in the buffer-equilibrated water given in Duro et al. (2006a, TR-06-32, page 98). It is unclear exactly why this value is so high. SKB reports published after ~2006 and the update to SKB's thermodynamic database (Grivé et al. 2010a, R-10-50, page 23), report lower solubility limits for thorium, but these reports do not consider a buffer-equilibrated water composition.

The lower solubility limits for thorium given in SKB's later reports presumably reflect the changes made to SKB's thermodynamic data for thorium (Grivé et al. 2010a, R-10-50, pages 9-10), but unfortunately the justifications for these changes are reported in a rather vague way, "*Thorium data have been mainly selected from the Thorium book of the NEA chemical Thermodynamics Series*". Grivé et al. (2010a, R-10-50, pages 9-10) specifically identify two thorium hydroxide-carbonate species that were not selected by NEA (2009), but which may be relevant under the conditions of interest in the disposal system. However, the SR-Site data report (SKB 2010b, TR10-52, Table 3-31) includes only one of these two thorium hydroxide-carbonate species; no explanation has been found in SKB's reports to justify the selection of the recommended thermodynamic data.

Quite apart from the issue of data traceability and justification, the solubility of thorium in the buffer could have effects on the calculated impacts form the disposal facility – this is discussed further below in Section 4.6.

Table 4.2 Comparison of calculated solubility limits for strontium in a range of groundwater compositions. SKB's water compositions, radionuclide solubility limiting phases and calculated solubility limits are from Grivé et al. (2010a, b), except for those relating to the buffer equilibrated water which are from Duro et al. (2006a).

Water	**Solubility Limiting Solid Phase**	**SKB, Phreeqc**[a]	**SKB, Simple functions spreadsheet**	**This Project, Phreeqc & Hatches 20**[b]	**Factor Difference**
		concentration (mol/dm^3)	concentration (mol/dm^3)	concentration (mol/dm^3)	b/a
Forsmark Reference Water	Celestite, $SrSO_4$	9.8E-04	9.8E-04	1.4E-03	1.38
Buffer-Equilibrated Water	Celestite $SrSO_4$	2.3E-04	-	4.6E-04	2.00
Ice Melting Water	Strontianite, $SrCO_3$	1.1E-05	7.9E-06	1.3E-05	1.16
Saline Water	Celestite, $SrSO_4$	1.5E-03	2.7E-03	2.6E-03	1.68

Table 4.3 Comparison of calculated solubility limits for thorium in a range of groundwater compositions. SKB's water compositions, radionuclide solubility limiting phases and calculated solubility limits are from Grivé et al. (2010a, b), except for those relating to the buffer equilibrated water which are from Duro et al. (2006a).

Water	**Solubility Limiting Solid Phase**	**SKB, Phreeqc**[a]	**SKB, Simple functions spreadsheet**	**This Project, Phreeqc & Hatches 20**[b]	**Factor Difference**
		concentration (mol/dm^3)	concentration (mol/dm^3)	concentration (mol/dm^3)	b/a
Forsmark Reference Water	$ThO_2.2H_2O$ (am, aged)	8.9E-09	7.9E-09	2.1E-09	4.3
Buffer-Equilibrated Water	$ThO_2.2H_2O$ (am, aged)	1.0E-06	-	2.1E-09	476.2
Ice Melting Water	$ThO_2.2H_2O$ (am, aged)	2.4E-09	2.7E-09	4.7E-10	5.1
Saline Water	$ThO_2.2H_2O$ (am, aged)	1.1E-09	1.3E-09	2.4E-10	4.9

4.4. Redox Conditions and Uncertainties

SKB's conceptual model for evaluating radionuclide solubility limits considers that the chemical system of interest near the spent fuel will, initially, on the entry of water to the copper canister, be strongly reducing, but that as waters enter the system it will gradually become more oxidised (Duro et al. 2006a, TR-06-32; Evins 2013a). The redox evolution of the iron system, thus, begins with metallic iron, $Fe^{(0)}$ and progresses towards an assumed equilibrium amongst ferrous, $Fe^{(II)}$ and ferric, $Fe^{(III)}$, species. Duro et al. (2006a, TR-06-32) assumed that the solid phase products formed during corrosion of the insert would be the thermodynamically most stable solid minerals in the iron-water system Any $Fe(OH)_{2(s)}$ formed was assumed to convert to magnetite, $Fe_3O_{4.}$ Later, on further oxidation, magnetite and hematite, Fe_2O_3 (Duro et al. 2006a, TR-06-32, page 16) or magnetite and goethite (Evins 2013a, page 3) were assumed to form.

The iron-oxygen-water-carbon dioxide system is a complex chemical system in which a range of aqueous species and solids can form (e.g. Langmuir 1969; Navrotsky et al. 2008). Several of the possible solid phases have similar Gibbs free energies of formation with the result that kinetics, surface energies and crystal size can be important factors affecting the phases that form. Microbial activity can also influence the evolution of some systems (e.g. Ruby et al. 2009; Larese-Casanova et al. 2010).

Oxidation and corrosion of the cast iron insert may lead to a variety of solid products; in addition to magnetite and hematite, various other iron oxyhydroxides may be formed. According to Langmuir (1969), goethite and amorphous ferric oxyhydroxide are the most often precipitated forms in ambient temperature geologic systems. Amorphous ferric oxyhydroxide has a tendency to convert slowly to goethite. Lepidocrocite, maghemite and hematite are relatively uncommon direct precipitates, but lepidocrocite does precipitate at pH values between 2 and 6.5 from the oxidation of solid ferrous iron species. Maghemite usually forms from by the oxidation of magnetite or the dehydration of lepidocrocite. Hematite usually crystallizes from amorphous ferric oxyhydroxide by dehydration or by long-term ageing in solution.

Navrotsky et al. (2008) note that although hematite is the most stable Fe_2O_3 polymorph and goethite is the most stable FeOOH phase[1], some of the other polymorphs (e.g., lepidocrocite, akaganeite) have only slightly higher Gibbs free energies and, therefore, being only slightly metastable, are kinetically accessible when precipitated from aqueous solution. In addition, iron oxide phases that are thermodynamically metastable as micrometer-sized or larger crystals can often be thermodynamically stabilized at the nanoscale (Navrotsky et al. 2008).

Other recent studies (e.g. Chaves 2005; Davesne et al. 2010; Bruggeman et al. 2012; Guilbaud 2013) have identified and characterised several forms of green rusts and these might also be formed during corrosion of the cast iron insert. Green rusts contain a mixture of ferrous and ferric iron and structurally belong to a family of minerals known as layered double hydroxides. They comprise alternating layers of positively-charged hydroxide and hydrated anions. Some of the $Fe^{(II)}$ in the octahedral sheets of $Fe(OH)_2$ is replaced by $Fe^{(III)}$. This results in a positive layer charge that is balanced by the anions between the layers. The exact nature of a green rust depends on the interlayer anion. However, the results of many studies

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[1] For coarse iron oxide particles under ambient conditions (Navrotsky et al. 2008).

have shown that GRs have a specific chemical composition that can be represented with the general formula:

$[Fe^{II}_{(6-x)}Fe^{III}_{x}(OH)_{12}]^{x+}[(An)_{x/n}.yH_2O]^{x-}$

Where: x = 0.9 to 4.2,
An is an n-valent anion (typically CO_3^{-2}, Cl^- or SO_4^{-2}), and
y is the amount of interlayer water (typically y = 2 to 4).

The literature distinguishes between:

GR1 ($An^- = F^-, Cl^-, Br^-, I^-$),
GR2 or $GRSO_4$ ($An^- = SO_4^{-2}$), and
$GRCO_3$ ($An^- = CO_3^{-2}$).

Green rusts are known to be formed by a number of abiotic and biotic processes under near-neutral to alkaline conditions in sub-oxic environments, and have been identified as products of both abiotic and microbially-induced corrosion of iron and steel (e.g. Chaves 2005).

During the gradual corrosion-oxidation process in the repository, therefore, the surface of the insert may become covered by a spatially inhomogeneous corrosion product layer comprising magnetite, various iron-oxyhydroxides, green rusts, goethite and hematite, with some of these intermediate phases converting slowly towards the thermodynamically more stable forms.

Based on studies conducted within the European Commission FUNMIG project, Bruggeman et al. (2012) concluded that *"it has now been established that green rust reactivity must be incorporated into geochemical speciation and transport calculations in subsurface groundwater whose composition spans the Fe(II)/Fe(III) redox boundary. Both thermodynamic considerations and experimental evidence show that this mineral may be present in such environments. Green rust has also been shown to reduce* $Np^{(V)}$*,* $Se^{(VI)}$ *and* $Se^{(IV)}$*, although the pathways and resulting reaction products are diverse and demonstrate the complexity of heterogeneous reduction processes in which both the solution composition and the mineral assemblage is changing as a function of reaction parameters."*

Figure 4.3 shows two Pourbaix diagrams that show the stability fields of carbonate green rust, $Fe^{(II)}_4Fe^{(III)}_2CO_3$ (Ruby et al. 2009) and of sodium-bearing and sodium-free sulphate green rust (Davesne et al. 2013), in geochemical conditions not too dissimilar to those that might occur near a corroding cast iron insert in a KBS-3 repository.

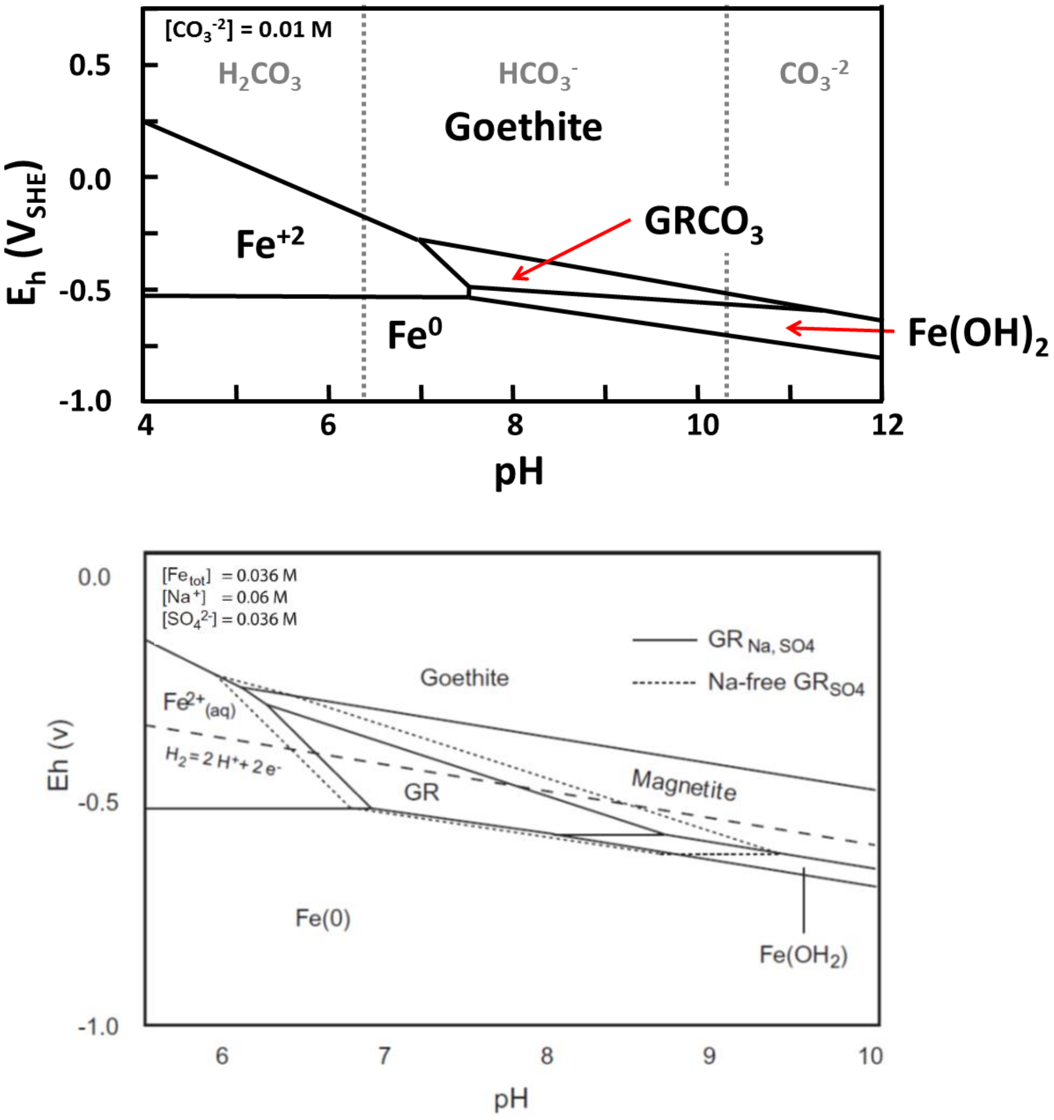

Figure 4.3 Eh-pH diagram showing (top) the stability field of carbonate green rust (GRCO$_3$, Fe$^{(II)}_4$Fe$^{(III)}_2$CO$_3$ (re-drawn from Ruby et al. 2009) and (bottom) the stability fields of sodium-bearing and sodium-free sulphate green rusts (Davesne et al. 2013).

To further investigate the possibility of green rust formation in a KBS-3 repository at Forsmark, a series of trial Phreeqc calculations were made using the Hatches thermodynamic database with the following reactions involving green rusts:

GreenRustCO$_3$, (Trolard and Bourrié 2012)

$Fe_6(OH)_{12}CO_3 = 4Fe^{+2} + 2Fe^{+3} + 12OH^- + CO_3^{-2}$, log k = -135.52

GreenRustSO$_4$, (Davesne et al. 2013)

$Fe_6(OH)_{12}SO_4 = 4Fe^{+2} + 2Fe^{+3} + 12OH^- + SO_4^{-2}$, log k = -139.2

The calculations were made to simulate the interaction between a buffer-equilibrated water and the cast iron insert. The buffer-equilibrated water composition of Duro et al. (2006a, TR-06-32 – see also Table 2.1 above) was used as a starting point and was brought to equilibrium with calcite and gypsum present as accessory minerals in the buffer. The speciation of this water was then calculated. The total iron concentration was then increased to simulate interaction with the cast iron insert and, in different simulations, the resulting waters were brought to equilibrium with green rust-sulphate and green rust-carbonate. Selected results from these calculations are given in Table 4-4.

Aqueous components	**Concentration mol/dm^3**	**Concentration mol/dm^3**
C	4.50E-03	4.50E-03
Ca	1.33E-02	1.33E-02
Cl	1.56E-03	1.56E-03
Fe	5.11E-03	1.02E-02
K	1.56E-01	1.56E-01
Mg	5.58E-03	5.58E-03
Na	1.48E-02	1.48E-02
S	5.62E-02	5.62E-02
Si	6.78E-05	6.79E-05
Water characteristics		
pH	7.2	7.2
pe	-3.424	-2.616
Eh (mV)	-202	-154
Activity of water	0.991	0.991
Ionic strength	0.33	0.34
Solid phase	**Saturation Index**	**Saturation Index**
Green Rust SO_4	0.00	3.42
Green Rust CO_3	-3.42	0.00
Magnetite	3.58	6.10
Hematite	2.35	4.57
Goethite	1.00	2.11

Table 4.4 Results from trial Phreeqc calculations to investigate the possibility of green rust formation in a KBS-3 repository at Forsmark. The two columns show the compositions of waters resulting from the interaction between a buffer-equilibrated water and the cast iron insert, and assuming equilibrium with green rust SO_4 (left column) and with green rust CO_3 (right column).

These modelling studies are described as trial calculations because it was not possible to ensure complete consistency with the data in the Hatches database when estimating and applying the equilibrium constants for the green rust reactions given above. Nevertheless, the calculations are taken to indicate further support for the idea that green rusts may form in the repository as metastable phases, possibly together with magnetite, if/where corrosion leads to increased dissolved iron concentrations. The formation of green rusts might be favoured if the groundwaters are poor in calcium (e.g. the glacial water of Table 2.1) and/or if ion exchange processes in a sodium bentonite buffer were to lower aqueous calcium concentrations and, thereby, cause calcite and gypsum dissolution to supply elevated levels of carbonate and sulphate to the canister.

The SKB reports reviewed during this project (Appendix 1) do not discuss the processes described above in any detail or clearly link the complexities and uncertainties associated with the insert corrosion process to evaluations of redox evolution or radionuclide solubility limits.

4.5. The Co-Precipitation of Radium with Barium

The SR-Site safety assessment was the first of SKB's assessments to take quantitative credit for the co-precipitation of radium.

SKB (2008, TR-08-07) reviewed the state of the art with respect to thermodynamic modelling of the dissolution/precipitation behaviour of solid solutions in aqueous systems, and such models have been applied, albeit sometimes in simplified form, to model the potential behaviour of radium in the near-field of the KBS-3 repository.

Figure 4.4 from SKB (2008, TR-08-07) shows SKB's conceptual model for the formation of a radium-barium sulphate co-precipitate / solid solution.

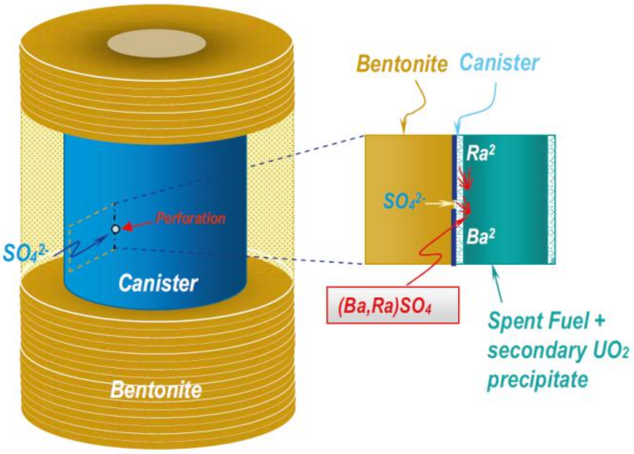

Figure 4.4 SKB's conceptual model of radium co-precipitation with barium sulphate. SO_4^{-2} ions from porewater contact spent fuel through a perforation in the canister. Barium and radium in the fuel are leached and subsequently immobilised via solid solution formation SKB (2008, TR-08-07, page 27).

In principle, the thermodynamic approaches followed by SKB for modelling co-precipitation are applicable and appropriate. For example, at the low levels of radium incorporation into the barium sulphate host phase expected, it is appropriate to represent the solid solution that may be formed as approximating an ideal solid solution.

The available literature, including that reviewed in (SKB 2008, TR-08-07) and the experimental study of Bosbach et al. (2010, TR-10-43), provides clear evidence for the incorporation of radium into the structure of solid barium sulphate in many natural systems and experiments. The studies also provide evidence for the substantial lowering of dissolved radium concentrations in waters in contact with such co-precipitates or solid solutions, as compared with the dissolved concentrations that would occur if they were buffered by equilibrium with a pure radium sulphate solid phase. Notwithstanding these findings, it is noted that further experiments could usefully be conducted, in particular to investigate the extent of equilibrium during uptake of radium by pre-existing solid barium sulphates, but also to extend the results obtained by Bosbach et al. (2010, TR-10-43) to pH values spanning the near-neutral range expected in the repository and further investigate the competing influences on barium uptake of ions such as Sr^{+2}.

There are, however, uncertainties when moving from modelling relatively simple experimental systems, such as those considered in Bosbach et al. (2010, TR-10-43), and attempting to apply the models to the repository situation:

- **The timing of radium and barium release**. SKB indicates that the inventories of barium and radium grow with time after waste deposition. Most of the barium will be produced in the initial 500 years after waste deposition, whereas the production of ^{226}Ra reaches its peak some 300,000 years after waste deposition. Grandia et al. (2013, page 20) notes that the release of barium and radium is considered to occur congruently with the dissolution of the spent fuel at rates between 10^{-6} and 10^{-9} per year, and that the rate of barium transport away from the canister would be limited by slow diffusion rates. SKB has considered two potential scenarios for the relative timing of barium and ^{226}Ra release:
  - Simultaneous release of radium with barium in which ^{226}Ra will be readily incorporated into the precipitating $BaSO_{4(s)}$ to build a radium-barium sulphate co-precipitate or solid solution,
  - The case when ^{226}Ra is released after barium. SKB (2008, TR-08-07, page 39) noted that for this case there was not at that time sufficient experimental information to establish whether and how the system would reach equilibrium.

- **The availability of sulphate.** A sufficient supply of sulphate is necessary if precipitation of a radium-barium sulphate is to occur. Initially the principal source of sulphate to the location where SKB envisages that radium may co-precipitate (i.e. near the canister) is likely to be gypsum within the bentonite buffer, but groundwater may also supply sulphate at rates depending on transport properties (e.g. diffusivities) of the buffer. According to SKB (2010d, TR-10-47, Table 2.1), MX-80 and Deponit-CAN bentonites contain approximately 0.7 and 1.8 ± 0.2 wt % gypsum and anhydrite. The range of sulphate concentrations in natural groundwaters in the Fennoscandian shield is quite variable, with sulphate concentration from 1×10^{-6} to 9×10^{-3} mol/dm^3. SKB (2008, TR-08-07, pages 26 to 28) summarises modelling work by Arcos et al. (2006, TR-06-16) that considered the dissolution of gypsum in the buffer caused by interaction with groundwaters. It is clear from that work and the related discussion in SKB (2008, TR-08-07) that the supply of sulphate to the canister could be quite variable in time. Depending on the precise location in the buffer relative to a fracture supplying groundwater, the models of Arcos et al. (2006, TR-06-16) suggested time periods of ~600 to ~3,000 years for the effective removal of sulphate by dilute glacial waters SKB (2008, TR-08-07, page 28). For interactions with more typical, non-glacial groundwaters, the removal of gypsum from the buffer might take on the order of ~15,000 to perhaps ~20,000 years (Arcos et al. 2006, TR-06-16, page 33)[2].

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[2] Incidentally, these modelling results also seem to show some possible inconsistency in SKB's assumptions for the SR-Site assessment regarding geochemical evolution within the buffer. On one hand, SKB argues that accessory minerals in the buffer will be removed from the buffer by dissolution relatively rapidly - *"Conditioning of the groundwater by accessory minerals (carbonates) in the buffer is expected have relatively short duration, or to have small impact on the overall composition*" (SKB 2010b, TR-10-52, page 102), while on the other, SKB cites the modelling study of Arcos et al. (2006, TR-06-16) as evidence that gypsum,

- **Microbial sulphate reduction**. As discussed above, under some circumstances (e.g. if buffer density decreases during erosion) microbial activity close to the canister might reduce some sulphate to sulphide. Studies such as the MINICAN experiments (Smart et al. 2012) indicate that microbes can be active in low density bentonite and that the sulphide they produce can have significant effects on corrosion. The reduction of sulphate might also affect the stability of any radium-barium sulphate solid solutions formed, although to our knowledge this has not been investigated experimentally and the extent of sulphate reduction in a solid phase might be expected to be less and may also occur more slowly than reduction of dissolved sulphate. The studies of Masurat et al. (2010) and Pedersen and Hallbeck (2013), however, indicate that microbial sulphate reduction will cease if the buffer bentonite is compacted to a wet density of somewhere between 1,900 and 2,000 kg/m^3, although that the exact density at which this occurs is still under investigation.

In view of the uncertainties, in the SR-Site assessment, SKB included a probabilistic calculation case in which no credit was taken for the co-precipitation of radium, i.e. in which the solubility of Ra was a factor of 1,000 higher than the recommended value. According to SKB, this case showed an increase in the release rate of Ra by a factor of about 1.5 (SKB 2010a, TR-10-11, page 694).

Notwithstanding the uncertainties associated with radium co-precipitation in a sulphate solid phase under reducing conditions, the consideration of co-precipitation and solid solution processes in general is a sensible move towards a more realistic representation of the radionuclide source term.

4.6. Thorium Solubility

As noted above, radionuclide solubility could be relevant in parts of the disposal system other than immediately next to the spent fuel.

SKB (2010a, TR-10-11, page 653) states that, "*It cannot be excluded that co-precipitation processes and sorption/immobilisation in the remaining bentonite in the deposition hole could confine Th-230 to the near field. If this is the case, its daughter nuclide, the considerably more mobile Ra-226, would be released. The so generated Ra-226 is assumed to be released to the flowing groundwater in the fracture intersecting the deposition hole. This causes higher releases of Ra-226, since there is a contribution not only directly from the fuel dissolution, but also from the confined Th-230. Since Ra-226 is often the main contributor to dose, this also causes higher total doses. Sorption of Th in the near field is thus assumed. The effect of disregarding Th sorption is analysed as a separate calculation case.*"

The key issue here is whether the precipitation of thorium in the buffer could lead to greater retention of the thorium than has been modelled by SKB using sorption coefficients. This is conceptually possible and might occur, perhaps on a local scale, particularly if thorium precipitate dissolution was slower than thorium de-sorption. However, it has not been possible within the scope of this project to quantify the

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which is more readily soluble than calcite, may persist in the buffer for several thousands of years.

transport of thorium into the buffer and compare this to SKB's sorption coefficients for thorium, which range quite widely from 4 to 700 m^3/kg (Tables 5-16 and 5-17 of the Data Report SKB 2010b, TR-10-52).

5. Overall Assessment

SKB has presented a conceptual model for calculating radionuclide solubility limits in a series of reports and papers that have been produced over several years. The model is scientifically based and founded on the principles of chemical thermodynamics. The traceability of SKB's documentation has, however, been an issue that has hindered this and previous reviews. It would be very helpful if SKB were to compile a single, fully transparent and up to date document that presented its work on the selection and use of thermodynamic data, the identification and treatment of possible solubility limiting phases, and the estimation and use of radionuclide solubility limits in the SR-Site assessment.

Despite the difficulties with SKB's documentation, it has been possible to understand SKB's conceptual model for radionuclide solubility limits, to determine that, overall, the codes used by SKB to develop recommendations for solubility limits are appropriate, and to reproduce a selection of SKB's geochemical modelling results with relatively small and understandable differences.

Various scientific questions and uncertainties have been identified associated with SKB's models and data, including:

- There may be greater uncertainty than appears to be recognised in SKB's reports associated with the complexities of the corrosion processes that may affect the cast iron insert and the corrosion products that may form. For example, green rusts may form in the repository as metastable phases, possibly together with magnetite, if/where corrosion leads to increased dissolved iron concentrations. More work would be needed to develop a detailed conceptual model of such processes and to evaluate the evolution of redox conditions within the system. The uncertainties associated with the evolution of redox conditions over time have implications for the calculated solubility limits – it is not clear whether the ranges of solubility limits used in the SR-Site safety assessment capture these uncertainties. Having said this, plots such as those shown in Figure 4.3 suggest that green rusts may be unlikely to buffer near-field redox potentials that are very different from those assumed by SKB in the SR-Site assessment.

- With regards to groundwater chemistry, there is a question relating to the justification for SKB's use in the SR-Site safety assessment of recommended radionuclide solubility limits which were calculated on the basis of one set of groundwater compositions, when a different set of end-member groundwater compositions was recommended from the data selection process for geosphere data. This is not to say that there is necessarily an incompatibility between the data sets used, but that this is not clearly shown in the reports examined by this project.

- The omission from the SR-Site assessment of water compositions resulting from chemical interactions between groundwaters and the buffer does not seem well justified. This is potentially important because, for example, buffer-equilibrated waters with elevated carbonate and or sulphate concentrations might promote the formation of green rusts, which would in turn affect the redox conditions near the spent fuel and influence radionuclide solubilities. There may also be some inconsistencies in the assumptions made in the SR-site assessment regarding the geochemical evolution of the buffer. Ultimately, the omission of water compositions resulting from chemical interactions between groundwaters and the buffer may not be significant to the results of the safety assessment but, even if this is the case, it seems questionable from the perspective of demonstrating understanding and assessing the possible range of system behaviour. The development of a realistic, consistent model of the geochemical behaviour of the buffer would seem to be an essential part of the support for the safety case.

- Recent thermodynamic studies support a concept in which Pu(IV) intrinsic colloids represent equilibrium species that are an integral part of the thermodynamic system and which can increase total plutonium solubilities by ~2 orders of magnitude in neutral to alkaline waters. SKB has not included the effects of such colloidal species in its solubility limits and so the recommended solubility limits for plutonium may be incorrect (too low), although this may not make a significant difference to the overall results from the SR-Site assessment because of the way in which SKB has treated colloid transport.

- SKB has described and applied a reasonable inorganic geochemical model of the co-precipitation of radium with barium, which leads to a 1,000-fold reduction in the recommended solubility limit for radium as compared with the solubility limit that would be calculated considering a pure radium solid phase. This 1000-fold reduction in the radium solubility limit has the potential to reduce calculated potential doses and risks from the repository, but its validity depends on an assumption that microbial activity will not lead to sulphate reduction and, thereby, some destabilisation of the radium-barium sulphate co-precipitate. SKB has, however, included a calculation case in the SR-Site assessment in which no credit was taken for the co-precipitation of radium. Notwithstanding the uncertainties associated with the particular case of radium co-precipitation in a sulphate host phase, the consideration of co-precipitation and solid solution processes more generally, where this is possible, would be a sensible move towards a more realistic representation of the radionuclide source term and a more realistic safety assessment in which solubility considerations might play a more significant role.

- Precipitation or co-precipitation could occur for some radionuclides at locations in the disposal system outside the region inside the canister close to the spent fuel. SKB has not explicitly modelled such processes in its safety assessment, but has considered radionuclide sorption. The consistency of the sorption parameter values used by SKB and the possible effects of chemical processes (e.g., co-precipitation) that might occur in the buffer has not been thoroughly checked by this review.

Although it has been possible to understand and comment in some detail on SKB’s research and geochemical modelling studies for the calculation of radionuclide solubility limits, it has not been possible to trace the use of SKB’s solubility limits within the safety assessment in such detail. The level of information that would be required to do this is not included in SKB’s reports. For example, the documentation reviewed in this project does not record exactly which solubility limits were applied for which groundwater compositions and calculation cases.

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APPENDIX 1

Coverage of SKB reports

Table A.1: Coverage of SKB Reports

Reviewed report	Reviewed sections	Comments
Arcos D, Grandia F, Domènech C, 2006. Geochemical evolution of the near field of a KBS-3 repository. Swedish Nuclear Fuel and Waste Management Company, SKB Report SKB TR-06-16.	Relevant parts	
Bosbach D, Böttle M, Metz V, 2010. Experimental study on Ra^{2+} uptake by barite ($BaSO_4$). Kinetics of solid solution formation via $BaSO_4$ dissolution and $Ra_xBa_{1-x}SO_4$ (re) precipitation, Swedish Nuclear Fuel and Waste Management Company, SKB Report TR-10-43.	All	
Duro L, Grivé M, Cera E, Gaona X, Domènech C, Bruno J, 2006a. Determination and assessment of the concentration limits to be used in SR-Can, Swedish Nuclear Fuel and Waste Management Company, SKB Report TR-06-32.	All	
Duro L, Grivé M, Cera E, Domènech C, Bruno J, 2006b. Update of a thermodynamic database for radionuclides to assist solubility limits calculation for performance assessment, Swedish Nuclear Fuel and Waste Management Company, SKB Report TR-06-17.	Relevant parts	
Evins L, 2013a. Treatment of redox in SR-Site solubility calculations, SKBdoc id 1396559.	All	
Evins L, 2013b. Treatment of silver in solubility calculations, SKBdoc id 1396561.	All	
Grandia F, Merino J, Bruno J, 2007. Assessment of the radium-barium co-	All	

precipitation and its potential influence on the solubility of Ra in the near-field, Swedish Nuclear Fuel and Waste Management Company, SKB Report TR 08-07.	
Grivé M, Domènech C, Montoya V, García D and Duro L, 2010a. Determination and assessment of the concentration limits to be used in SR-Can, Supplement to TR-06-32. Swedish Nuclear Fuel and Waste Management Company, SKB Report R-10-50.	All
Grivé M, Domènech, C, Montoya, V, Garcia, D, and Duro, L, 2010b. Simple Functions Spreadsheet tool presentation, Swedish Nuclear Fuel and Waste Management Company, SKB Report TR-10-61.	Relevant parts
Grivé M, Idiart A, Colàs E and Duro L, 2013. Handling of uncertainty in thermodynamic data, SKBdoc id 1396560.	All
Grandia F, Grivé M and Bruno J, 2013. Reply to comments and questions from SSM concerning Ba-Ra sulphate co-precipitation in canister, Amphos21 Report No. 2518_13.	All
SKB, 2010a. Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main report of the SR-Site Project, Swedish Nuclear Fuel and Waste Management Company, SKB Report TR-11-01.	Relevant parts
SKB, 2010b. Data report for the safety assessment SR-Site, Swedish Nuclear Fuel and Waste Management Company, SKB Report TR-10-52.	Section 3.4
SKB, 2010c. Radionuclide transport report for the safety assessment SR-Site, Swedish Nuclear Fuel and Waste Management Company, SKB Report TR-10-50.	Section 3, Appendix F
SKB, 2010d. Buffer, backfill and closure	Sections on

process report for the safety assessment SR-Site, Swedish Nuclear Fuel and Waste Management Company, SKB Report TR 10-47.	microbial activity

2014:11

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 315 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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