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Technical Note

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Use of Solubility Limits in the SR-Site Safety Assessment

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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

De flesta radionuklider som frigörs från använt kärnbränsle i en trasig kapsel har en låg löslighet i grundvatten och kan uppnå kemisk jämvikt med sekundära faser. Denna egenskap innebär potentiellt ett kvarhållande av radionuklider frigjorda från använt kärnbränsle och en reduktion av högsta radionuklidutflöde från närområdet av ett slutförvar.

Syftet med detta projekt är att analysera SKB:s användning av löslighetsgränser i säkerhetsanalysen SR-Site. Fördelningen av radionuklider i olika förekomstformer behöver analyseras med perspektiven fullständighet och osäkerheter i termodynamiska data och grundvattenkemiska betingelser.

Författarens sammanfattning

En kapsel innehållande använt kärnbränsle kan i en slutförvarsmiljö för vissa framtida scenarier brista och det använda bränslet kommer därefter i kontakt med grundvatten. Koncentrationen av radioaktiva grundämnen som uran kan då stiga till en nivå där lösningen blir mättad. Efter att detta inträffat kommer ingen mera upplösning ske och en utfälld fas kommer att bildas. I en sådan situation är det radioaktiva ämnet löslighetsbegränsat, vilket påverkar dess frigörelse med grundvattenrörelser från närområdet av ett slutförvar.

Hanteringen av löslighetsgränser i SKB:s säkerhetsanalys SR-Site har blivit granskad som en del av den inledande granskningsfasen. Syftet har varit att utröna om granskningen kan anses vara vetenskapligt sund, om den täcker in tillräckligt många nyckelaspekter av analysen, om den använder ändamålsenliga modeller och data samt om den har tillräcklig kvalitet.

I hjärtat av SKB:s metod finns kalkylbladsverktyget som kallas enkla funktioner (eng. Simple Functions) som beräknar löslighetsgränser för radioaktiva ämnen vid en viss given grundvattensammansättning. Löslighetsgränserna tas sedan över av SKB verktyget COMP23 som en av många parametrar och koden beräknar den resulterande risken som funktion av tiden för olika slutförvarsscenarier.

Efter granskningen av löslighetsgränser kan konstateras att den kemiska grunden för hur löslighetsgränser har tagits fram är generellt beskriven på ett bra sätt, att metoden för att beräkna löslighetsgränser är överlag i enlighet med dagens vetenskapliga förståelse samt att stickprov kring hur data har förts över mellan olika beräkningar antyder att kvalitetskontrollen har varit tillräcklig.

Vissa frågor kräver förtydliganden så som hur beräkningarna fungerar i en situation där grundvatten med mycket hög salthalt. Dessutom behövs ett mera robust fall för medfällning av radium med stabil bariumsulfat i närområdet, speciellt för det fall mikrobiell sulfatreduktion kan förekomma. Dessutom behöver tidsberoendet användas för beräkningar kring löslighetsgränser över tidsskalan 1 miljon år.

Projektinformation
Kontaktperson på SSM: Bo Strömberg
Diarienummer ramavtal: SSM2011-4266
Diarienummer avrop: SSM2012-144
Aktivitetsnummer: 3030007-4032

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

Most radionuclides released from spent nuclear fuel in a failed copper canister are only sparingly soluble in groundwater and may reach saturation with respect to the solubility of secondary phases. This feature has the potential to retain radionuclides released from spent nuclear fuel and reduce peak releases from the near-field.

The objective of this project is to analyse SKB's use of radionuclide solubility limits in the SR-Site safety assessment. The speciation of radioelements shall be addressed in the perspective of completeness and uncertainties in thermodynamic data and groundwater chemical conditions.

Summary by the author

In a radioactive waste disposal environment, in some potential situations (scenarios) a disposed canister containing spent fuel may be breached and the fuel may come into contact with groundwater. The concentration of a radioactive element such as uranium may rise to a level where the solution is saturated. No more of the radioactive element may dissolve and a precipitated solid may be formed. In this situation the radioelement is solubility limited, affecting the groundwater flux of the radioelement leaving the near field.

As part of the SSM's Initial Review phase, the treatment of solubility limits in SKB's SR-Site safety assessment has been reviewed to understand: if the treatment is scientifically sound, has a sufficiently wide coverage of key aspects of the assessment, uses adequate models and data and is of appropriate quality.

At the heart of the SKB approach is a spreadsheet tool called Simple Functions that calculates the solubility limit of radioactive elements given the groundwater chemistry. The SKB tool COMP23 takes the supplied solubility limits as one of many parameter values and calculates the resultant risks over time for alternative disposal scenarios.

This review of solubility limits has concluded that, in general, the chemical basis of the derived solubility limits is well described, that the way in which solubility limits have been calculated is broadly in line with current scientific understanding, and spot checks of how data has been transferred between different calculations indicates adequate control of quality in this case.

Some issues require further clarification, including: how well the calculations perform in a situation when water with high dissolved salts content is encountered; making a more robust case for co-precipitation of radium with stable barium sulphate in the near field, especially if sulphate could be microbially degraded; improving the description of how solubility limits are used in assessment calculations; and making full use of the time dependency of solubility limits over a 1 million year timescale.

Project information

Contact person at SSM: Bo Strömberg
Framework agreement number: SSM2011-4266
Call-off request number: SSM2012-144
Activity number: 3030007-4032

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Contents

1. Introduction

The safety assessment SR-Site by the Swedish Nuclear Fuel and Waste Management Company (SKB) will be reviewed by SSM in a stepwise and iterative fashion. The first step is called the Initial Review. The overall goal of the Initial Review Phase is to achieve a broad coverage of SR-Site and its supporting references, in particular to identify the need for complementary information and clarifications to be delivered by SKB.

This document reviews SKB's use of radionuclide solubility limits in the SR-Site safety assessment. Guidance from SSM [1] is that the review should consider the:

- Completeness of the safety assessment
- Scientific soundness and quality of the SR-Site
- Adequacy of relevant models, data and safety functions
- Handling of uncertainties
- Safety significance (although this will be more elaborately dealt with during the Main Review Phase)
- Quality in terms of transparency and traceability of information in SR-Site and in the associated references.

To elucidate the responses to these topics, the following questions were applied to SKB's documentation:

1. Are there any obviously missing pieces of information in the SR-Site and its supporting references?
2. Are key scientific conclusions adequately supported and justified? Are the necessary references provided and are they sufficiently specific?
3. Are there any alternative results or alternative scientific explanations published in the open scientific literature which have not been addressed or mentioned by SKB?
4. Is the source information of key datasets related to the assignment sufficiently described and referenced? Is any data treatment explained and justified (e.g. derivation of effective parameters)?
5. Are mathematical models including utilised assumptions related to the assignment sound and sufficiently explained and justified?
6. Has SKB defined any safety function(s) concerning solubility? If so are safety functions and their associated safety function indicators and criteria adequately explained and justified in the SR-Site?
7. Are all known and relevant uncertainties identified, analysed and discussed in sufficient detail?
8. Is the overall safety relevance of the specific review assignment within its scientific area explained and justified?
9. Is the safety assessment strategy for the handling of issues related to a specific review assignment explained in a clear manner?
10. Is information at different levels in the safety assessment consistent and logically subdivided (e.g. main SR-Site report, main supporting references and other references)?

Additionally, this review is guided by Swedish Regulations. For instance the Swedish Radiation Safety Authority's General Recommendations concerning the Application of the Regulations concerning Safety in connection with the Disposal of Nuclear Material and Nuclear Waste (SSMFS 2008:21) [2] includes:

"The assumptions and calculation models used should be carefully selected with respect to the principle that the application and the selection should be justified through a discussion of alternatives and with reference to scientific data. In cases where there is doubt as to a suitable model, several models should be used to illustrate the impact of the uncertainty involved in the choice of model" and

"The validity of assumptions used, such as models and parameter values, should be supported, for example through the citing of references to scientific literature, special investigations and research results, laboratory experiments on different scales, field experiments and studies of natural phenomena (natural analogues)."

Specifically concerning the use of solubility, this review has followed the process concerning the derivation of solubility limits for use in assessment calculations.

Firstly the derivation of groundwater chemistry ranges which form the chemical setting for solubility calculations has been reviewed. Then the chemical speciation of radioelements has been reviewed in terms of the completeness and uncertainties in thermodynamic data. As described below, SKB use the Simple Functions spreadsheet tool to calculate solubility limits; this has been reviewed by comparison to comprehensive speciation calculations. The treatment of co-precipitation, which is important for Ra-226, has been specifically reviewed. Finally, the methodology and utilisation of solubility data within assessment calculations has been reviewed.

Appendix 1 outlines the documents that have been reviewed. Appendix 2 outlines the need for complementary information from SKB. Appendix 3 lists review topics that might be considered by SSM for the next phase of the review of SR-Site.

Note that in this review the solubility of key radioelements is considered excluding the solubility of the spent fuel itself. The spent fuel matrix is predominantly UO_2, and its dissolution is controlled by complex oxidative/dissolution processes [3]; this is a speciality technical area that will be reviewed separately by SSM.

2. Technical review

2.1. Groundwater chemistry

The solubility of radionuclides is critically dependent upon the ambient chemistry of the ambient water. Solubility is typically an issue appropriate for consideration in the near field environment where, due to close contact with the spent fuel source term, concentrations may be high enough to exceed the solubility of a radioelement[1]. Given this context it is important to assess the adequacy of SKB's assessment of the near field chemical setting for solubility calculations.

A key starting point in SKB's development of a conceptual approach to solubility is that there is no near field safety function concerning chemical conditioning of the near field. A safety function that includes specific referral to aqueous chemical conditions concerns the geosphere safety function R1, defined as follows [4]:

R1: Provide chemically favourable conditions

a) Reducing conditions; Eh limited
b) Salinity; TDS limited
c) Ionic strength; > 4 mM charge equiv.
d) Concentrations of HS^{-}, H_2, CH_4 organic C, K^{+} and Fe limited
e) pH; pH < 11
f) Avoid chloride corrosion; pH > 4 and $[Cl^{-}] < 2$ M

As outlined in section 10.3.7 of [4], the SKB approach is to assume that in the base case, near field aqueous chemical conditions are restored to those resembling a meteoric-origin water; particularly important are safety functions R1c: ionic strength > 4mM, and R1d: limited sulphide concentrations. These limit buffer colloidal generation (R1c) and copper canister corrosion due to sulphide attack (R1d). While not directly a safety function, and not considered in the main corrosion case, solubilities are required for alternative safety assessment calculations. Figure 1 shows how SR-Site requires groundwater chemistry data to feed into the calculation of solubilities.

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[1] The term radioelement is used here as it better encompasses the sum mass effect of the key radioisotopes of an element, such as Th-230, Th-232 etc.

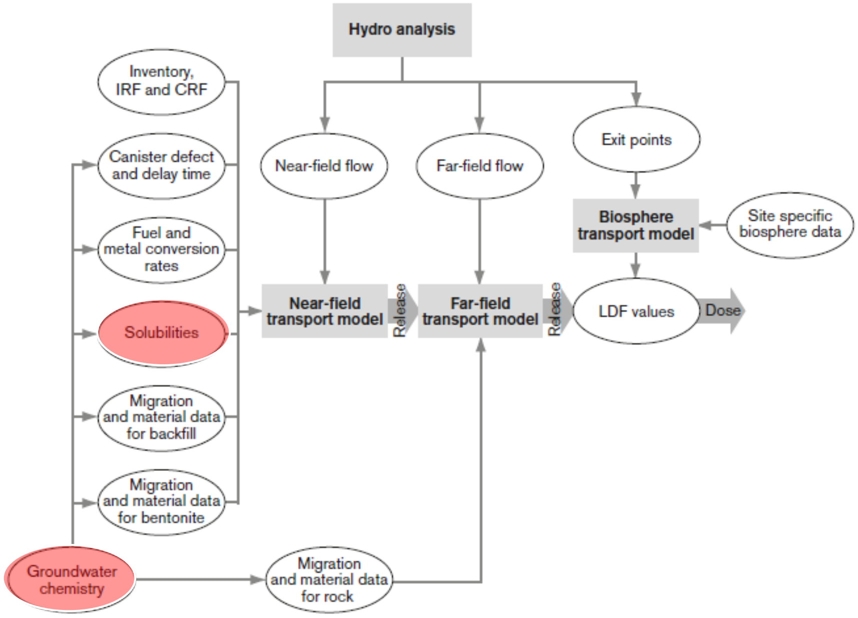

Figure 1. Relationship of groundwater chemistry to solubility. Modified from [4].

The chemical compositions of groundwaters at repository depth have been calculated from a comprehensive study using a combination of hydrological modelling followed by mixing calculations using end-member groundwaters and the geochemical code PHREEQC [5] to simulate chemical reactions. Deep waters were simulated using a Deep Saline Water end-member, and less saline waters derived using mixtures of Deep Saline, Old Meteoric, Glacial Littorina, and Altered Meteoric end-members [6].

The end-members are derived from present day waters which take into account water rock interactions such as reactions with iron minerals and sulphide etc.

An example showing calculated pH and calcium concentrations given the present day hydrogeology of Forsmark as a benchmark is given in Figure 2.

Figure 2, from Section 10.3.7 of [4], shows that pH in measured present day waters are broadly comparable to the simulated values, while the modelling of dissolved calcium values under-predicts concentrations by about a factor of 2 in the repository zone and by about an order of magnitude nearer the surface. It is important to obtain a good conceptual model for calcium as it is chemically more likely to form complexes with anions in solution than sodium and potassium.

In terms of the consequences for safety calculations, solubility limits given alternative hydrogeological conditions are calculated given mixtures of component groundwaters. If a mixture under-predicts values of cations such as calcium, then complex formation of calcium with anions in solution will be under-predicted. These anions are then available to form complexes with radioelements.

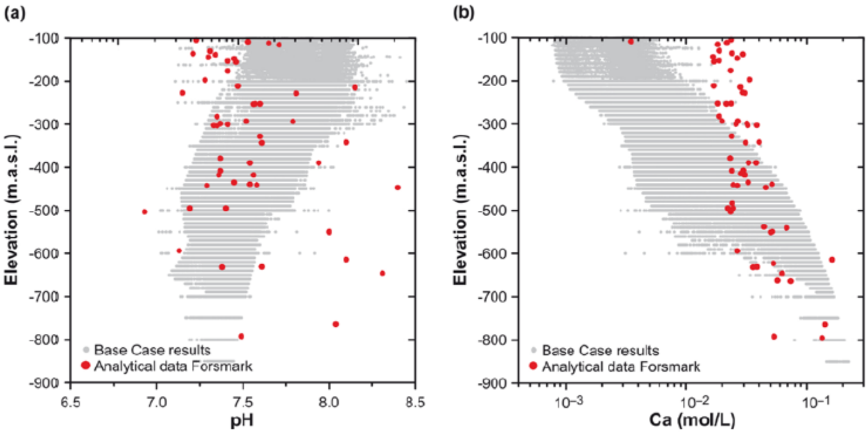

Figure 2. Modelled compared to measured pH and calcium concentrations for present day conditions, reproduced from [4].

Using carbonate as an example, predicting less calcium will over-predict the availability of HCO_3^- and CO_3^{-2} in solution. Radioelements such as uranium form complexes with carbonate ions in neutral to alkaline conditions. Thus formation of uranium carbonato complexes will be over-predicted in the Simple Functions calculations, making uranium more soluble.

The consequence is that for some radioelements, solubilities will be over-predicted. This may be optimistic for human intrusion scenarios in the near field, where transport of uranium from the near field will result in less formation of Ra-226 and its daughters. However it may be pessimistic for exposure in the biosphere where more Ra-226 and its daughters will be generated.

SKB recognise this, and in Section 10.3.7 of [4] say that “A full propagation of uncertainties, from the hydrogeological modelling into the geochemical calculations, has not been performed”. The example given here is just for one solute, calcium. Clearly a fuller assessment of the impact of hydrochemical conceptual uncertainties upon calculated solubilities should be addressed in future safety case iterations.

For redox sensitive radioelements such as U, Np, Pu, Tc etc., solubility is strongly affected by the redox state of the water used in the calculations. The SKB approach is to utilise the Fe^{+2}/Fe^{+3} couple as a control upon redox [6]. Given the presence of large amounts of iron in the canisters, the field observations of iron oxides in fracture coatings and also field measurements of redox and relatively low values of sulphide analysed in groundwater samples [7], this is appropriate. The Safety Function BUFF2 also requires the buffer to be designed to exclude microbes, so limiting sulphide reduction [4].

In the erosion/corrosion case where, upon canister breach, there is no longer an intact microbial excluding buffer, it is appropriate to consider the effect of the generation of sulphides (due to microbial reduction of sulphate upon solubility). This could be as an indirect effect, by controlling the solution redox chemistry, or a direct effect upon reduction of barites (barium sulphate), which is postulated as a co-precipitation driven solubility control for radium.

Note that SKB also considers cases where a number of canisters will fail due to mechanical loading in connection with large earthquakes. In this case, as the canister will be breached while it is still surrounded by compacted bentonite clay, it is entirely appropriate to exclude the effect of sulphide reduction.

In order to be used for solubility calculations, the ambient chemical compositions must contain all ligands capable of forming solid phases and complexes with radioelements. The solid phases and complexes considered in SR-Site are discussed more thoroughly below. Speciation in solution of some radioelements is sensitive to the solution pH and the redox state. However, in general terms and as examples, radioelements that can be expected to form cations in solution such as UO_2^{+2}, Pu^{+4}, NpO_2^{+}, Ra^{+2} etc., could form complexes with major and trace element anions such as OH^-, Cl^-, CO_3^{-2}, SO_4^{-2}, etc. Anionic form radioelements such as TcO_4^-, I^- (I-129), Cl^- (Cl-36) and CO_3^{-2} (C-14) can form complexes with major and trace element cations such as Ca^{+2}, Mg^{+2}, H^+, K^+ etc.

In terms of coverage of these potentially complexing anions and cations, for complex formation and solubility, SR-Site considers species such as Ca^{+2}, H^+, OH^-, Cl^-, CO_3^{-2} and SO_4^{-2}. It does not consider some components in solution such as the major component Mg and minor phosphate. A similar approach to the calculation of solubility was adopted in SR-CAN [8]. Review of SR-CAN commented that the Mg and phosphate could affect the speciation and solubility of radioelements and should therefore be included in the assessment of solubility [9].

While Mg is considered during the derivation of the geochemical setting and evolution of the disposal facility, this review did not find evidence that the effects of Mg and phosphate have been considered when groundwater data is used to calculate solubilities for SR-Site using the Simple Functions spreadsheet tool [10]. As an indicative scoping study appropriate for the preliminary nature of this review, this study undertook some speciation modelling using PHREEQC, the same tool that has been used in SR-Site for supporting calculations. The purpose of this was to form an opinion as to whether or not Mg and phosphate could form complexes in solution that could affect SR-Site solubility calculations.

For Mg, simple scoping calculation were undertaken using the composition of Forsmark groundwater as defined in Table A1, Appendix A of Grivé et al. (2010) [13]. For illustrative purposes a nominal amount of Pu was added, to the value of 8E-11M, simply to see if the complexation of Pu could be affected by the presence of Mg. No precipitation of solid phases was assumed as the intent was to look at only the speciation in solution. The outcome is presented in Table 1.

Table 1 shows that <5% of Mg forms a complex with SO_4^{-2}, and >1% forms a complex with carbonate. Looking at the inventory of sulphate, 8.5% of the inventory of SO_4^{-2} is in the form of the $MgSO_4$ complex.

On its own this data could be taken to suggest that some of the aqueous sulphate inventory is taken up by Mg and hence not available to form complexes with radionuclides.

However the extent of formation of an aqueous complex by a radioelement is dependent upon the thermodynamic stability of a complex compared to other species in solution that could form. The nominal amount of added Pu in solution in this simulation predominantly forms Pu^{+4} hydroxide complexes. Less than 0.1% of the Pu inventory is in the form of a sulphate complex. For Pu this indicates that, under the simulated conditions, competition for sulphate species with Mg does not affect speciation in solution, and hence is unlikely to affect solubility.

Table 1. Speciation of Mg, SO_4^{-2} and Pu in Forsmark water as defined in [10].

Species	Molarity	%
Mg species (total 9.3E-03M)		
Mg^{+2}	8.80E-03	94.62
$MgSO_4$	4.43E-04	4.76
$MgHCO_3^-$	5.72E-05	0.62
Sulphate species (total 5.2E-03M)		
SO_4^{-2}	3.03E-03	58.27
$CaSO_4$	1.25E-03	24.04
$NaSO_4^-$	4.72E-04	9.08
$MgSO_4$	4.43E-04	8.52
Plutonium species (total 8E-11M)		
$Pu(OH)_4$	6.63E-11	82.88
$Pu(OH)_3^+$	9.73E-12	12.16
$Pu(OH)_2(CO_3)_2^{-2}$	8.96E-13	1.12
Pu^{+3}	7.42E-14	0.09
$PuSO_4^+$	5.46E-14	0.07

This type of scoping calculation should be considered by SKB for other conditions and other radionuclides in order to close out the issue of the absence of Mg from solubility assessment calculations.

The effect of phosphate upon the solubility of radionuclides has been considered in spent fuel disposal safety cases, for instance in Canada [11]. In that case the assessment said: “In several cases, the presence of phosphate and sulphide ions can have a very important effect on the assessed solubility” [11]. For Pu in particular, under neutral to alkaline reducing conditions which lead to Pu(IV) reduction to Pu(III), the Canadian calculations have shown that for their groundwater the solubility of Pu is controlled by the solid $PuPO_4$. A phase diagram illustrating the dominating effect of phosphate upon Pu solubility is shown in Figure 3.

Based upon the impact of dissolved phosphate upon solubility in the Canadian study, which is also for disposal of spent fuel, at least some scoping calculations should enable SKB to understand the impact of dissolved phosphate and determine whether or not it should be considered further in disposal calculations.

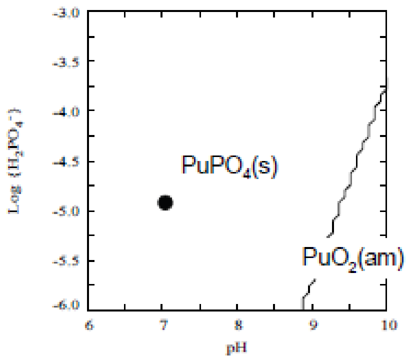

Figure 3. Phase diagram for Pu in the presence of phosphate for the Canadian CR-10 groundwater. Reproduced from [11].

In the introduction to this document, seven criteria were given with which to assess the appropriateness of the explanation of SR-Site issues. Addressing these questions for groundwater data used in solubility calculations:

1. Are there any obviously missing pieces of information in the SR-Site and its supporting references? *No, the referencing to data sources has been comprehensive.*
2. Are key scientific conclusions adequately supported and justified? *The explanation of how groundwater data has been derived for use in simulations was provided in detail that allowed the user to follow the arguments presented*.
3. Are there any alternative results or alternative scientific explanations published in the open scientific literature which have not been addressed or mentioned by SKB? *The SKB text mentions additional reactions that could be considered such as ion-exchange, which covers what could be expected. Further studies to obtain data and assess the impact of sulphate reduction and the presence of phosphate may be warranted. The impact of ignoring the presence of Mg should be assessed through scoping calculations*.
4. Is the source information of key datasets related to the assignment sufficiently described and referenced? *Groundwater data are sufficiently well described for a reviewer to trace the original source references*.
5. Are mathematical models including utilised assumptions related to the assignment sound and sufficiently explained and justified? *Cannot comment in this report about hydrological modelling, but geochemical modelling assumptions, and gaps in the analysis, have been outlined*.
6. Has SKB defined any safety function(s) concerning solubility? If so are safety functions and their associated safety function indicators and criteria adequately explained and justified in the SR-Site? *No direct safety functions are described*.
7. Are all known and relevant uncertainties identified, analysed and discussed in sufficient detail? *Uncertainties in the derivation of the groundwater end-members and in the subsequent geochemical calculations have been explained. A robust and consistent approach to defining sulphide levels is required. SKB themselves have described data and conceptual model gaps, which presumably will be addressed in the next stage of the safety case process. An analysis of the consequences of conceptual uncertainties in the hydrochemical model upon*

consequent safety case solubility limit values should be undertaken.

8. Is the overall safety relevance of the specific review assignment within its scientific area explained and justified? *See comments about how solubility is described in the safety case in Section 3.6.*
9. Is the safety assessment strategy for the handling of issues related to a specific review assignment explained in a clear manner? *The Data Report [6] references the use of groundwater data to provide the background chemical context for the derivation of chemical data for use by the Simple Functions spreadsheet.*
10. Is information at different levels in the safety assessment consistent and logically subdivided (e.g. main SR-Site report, main supporting references and other references)? *The Data Report [6] clearly and logically references the underlying studies. However the high level Main Report [4] does not include any details or summary concerning the calculation of solubilities.*

2.2. Thermodynamic speciation

In most radioactive disposal safety case calculations, solubility limits are calculated either by direct equilibrium thermodynamic speciation modelling or by experimental data that have been assessed and supported by such calculations [12]. In SR-Site solubility limits have been calculated through chemical thermodynamic modelling using the Simple Functions spreadsheet tool, which is discussed in the next section. Such calculations require chemical thermodynamic data for the formation of complexes in solution and for the dissociation constants for solid phases.

In this section, the adequacy of SKB's studies to derive a self consistent and appropriate dataset of equilibrium constants, which are then input into the Simple Functions spreadsheet and enable solubility constants to be calculated, is discussed.

The approach of using the Simple Functions spreadsheet for calculating solubilities given the underpinning groundwater chemistry is the same in both SR-Can to SR-Site. Additional work has been undertaken [13][2] to:

1. Update the thermodynamic databases for Ni, Se, Zr and Th as the NEA Database Project has reviewed and updated data for these radioelements [14, 15, 16, 17].
2. Include chemical data for the radioelement Pb.

For Ni, Se, Zr and Th, the NEA reviews are very comprehensive. The key issues are: (a) have the complex association constants and the solid phase dissociation constants

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[2] Note that this reference apparently addresses solubility in SR-Can, although being issued in 2010 it clearly addresses the needs of SR-Site and refers to updates from the SR-Can calculations to those for SR-Site.

been correctly transcribed, and (b) are there any missing data given the SKB site specific context.

In this preliminary review, as appropriate to the scope and scale of this study, the logic of the addition of species and, in some cases, the transcription of database values from the NEA data reviews to the SR-Site programme has been checked. These are discussed below.

For Ni, the aqueous species $Ni(OH)_2^0$ is included by SKB whereas the NEA review [14] screens this out. From page 99 onwards of [14], the NEA review concludes that there is insufficient direct evidence (e.g. spectroscopic) to confirm the presence of $Ni(OH)_2^0$. However, as the SKB review correctly concludes [13], this does not mean that the species cannot exist, and therefore the species is included in SKB calculations. This is sound reasoning, particularly as the dihydro complex is more likely to be present at neutral to alkaline pH values.

Selenium is mentioned at the start of TR-10-50 as being reviewed within the document, but this is not the case (unless it has been assessed but is not reported in the document). Therefore it is concluded that this is a typographic error in the SKB report.

For Zr, the solubility of an aged hydroxide, $Zr(OH)_4$(am, aged) was selected as the solubility limiting phase. Excluded was a higher solubility limiting phase associated with fresh $Zr(OH)_4$. This is reported in the NEA review on page 126 [16] with a $\log_{10}K$ value of $^-5.55 \pm 0.20$.

For Th, SKB include the species $Th(OH)_2(CO_3)$ and $Th(OH)_3(CO_3)^-$ even though they are excluded from the NEA review on the grounds of insufficient confidence for the complex association values [17]. As these species could form under near neutral low carbonate conditions, which might be found in the repository near field, the inclusion of these species is plausible for SR-Site calculations, although in reality their significance is likely to be low.

Apart from determining the status of the missing review of Se, the update of thermodynamic data for Ni, Zr and Th is suitable for use and does not require more detailed review.

In SR-Site, Pb is included for the first time in SKB calculations. An extensive review was undertaken of the original data and is reported [13]. A key source of reference data was a review undertaken by Blanc et al. [18]. This was not a public domain document but had been produced by BGRM for an Andra waste disposal study. The document has now been obtained from SKB through SSM.

The scope of this assessment did not allow for a thorough review of the assessment of Pb thermodynamic data as discussed in [13]. However, spot checks of the transcription of key Pb data from Blanc et al. [18] to SKB [13] were undertaken.

For aqueous species, Table 2-1 of SKB [13] gave association constant values ($\log_{10}K$) of:

Table 2. Values of association constants for selected aqueous species of Pb from SKB R-10-50 [13].

Species	Log_{10} K (association constant value)
$PbOH^+$	-7.51
$Pb(OH)_2$ (aq)	-16.95
$Pb(OH)_3^-$	-27.20
$Pb(OH)_4^{-2}$	-38.90
$PbCO_3$ (aq)	7.00

These corresponding values were found on page 112-113 of Blanc et al. [18] and were found to be exactly the same constants.

Note that on page 20, Section 3.1.2 of SKB [13], conceptual uncertainties associated with the assessment of Pb chemistry are discussed. This mentions issues raised in this review in previous sections, including the presence of sulphide (which for Pb is an important precipitant, producing the solid galena) and the potential importance of phosphate as a precipitant due to the formation of very low solubility lead phosphates.

In Section 3.7.3 p55 of the Radionuclide Transport Report [19], SKB reported an issue with the plutonium thermodynamic data as follows:

“The solubility limits for plutonium are too high because of an incorrect value for the associated error in an equilibrium constant used in the calculations. Figures in Appendix F have been corrected but incorrect solubility limits for plutonium have been used in all calculation cases. No recalculations were made since the fault was found at a very late stage of the SR-Site project, during the review of this report”

At the initial assessment level of this review, the full set of thermodynamic data used in SR-Site could not be reviewed. However if SKB have themselves identified this issue it should be followed through and corrected in future safety case iterations.

Specifically concerning the inclusion of thermodynamic data in SKB calculations, below are answers to the questions that this review is required to address:

1. Are there any obviously missing pieces of information in the SR-Site and its supporting references? *In terms of referencing to data sources, SKB documentation has been comprehensive. It is not clear from the documentation if selenium data has been reviewed.*
2. Are key scientific conclusions adequately supported and justified? *The explanation of how thermodynamic data have been selected for inclusion in SKB calculations has been provided in detail that allowed the user to follow the arguments presented.*
3. Are there any alternative results or alternative scientific explanations published in the open scientific literature which have not been addressed or mentioned by SKB? *The SKB assessment of chemical data has discussed the appropriateness of the chemical species and*

solid phases and alternative reactions, which given the initial status of this review appears to be adequate.

4. Is the source information of key datasets related to the assignment sufficiently described and referenced? *The majority of additional sources of the chemical data considered by SKB are NEA reviews which are very comprehensive. Additional data concerning the chemistry of Pb were less accessible but have been obtained from SKB by SSM. SKB have identified numerical errors in Pu data that should be corrected.*
5. Are mathematical models including utilised assumptions related to the assignment sound and sufficiently explained and justified? *Use of models is discussed in the assessment of the Simple Functions spreadsheet tool which is reviewed in the next section.*
6. Has SKB defined any safety function(s) concerning solubility? If so are safety functions and their associated safety function indicators and criteria adequately explained and justified in the SR-Site? *No direct safety functions are described*.
7. Are all known and relevant uncertainties identified, analysed and discussed in sufficient detail? *Uncertainties in the derivation of chemical data have been discussed in detail for each radioelement. The potential impact of sulphide and phosphate as missing species has been discussed.*
8. Is the overall safety relevance of the specific review assignment within its scientific area explained and justified? *See comments about solubility described in the safety case in Section 3.6.*
9. Is the safety assessment strategy for the handling of issues related to a specific review assignment explained in a clear manner? *The Data Report [6] clearly states the approach to the derivation of chemical data for use by the Simple Functions spreadsheet and also the use of that tool and its underlying uncertainties.*
10. Is information at different levels in the safety assessment consistent and logically subdivided (e.g. main SR-Site report, main supporting references and other references)? *The Data Report [6] clearly and logically references the underlying studies that supported the use of the Simple Functions spreadsheet. However the high level Main Report [4] does not include any details or summary concerning the calculation of solubilities.*

2.3. Simple Functions spreadsheet

The Simple Functions spreadsheet is a means of producing computationally efficient solubility limit values for radionuclides, given chemical thermodynamic data and groundwater chemistry, without resorting to the use of complex thermodynamic speciation codes which are computationally intensive, such as PHREEQC. The Simple Functions spreadsheet has been described in detail by SKB [10]. This computational efficiency means that the tool can be linked to batch processing tools and run many hundreds of times, in terms of SR-Site sampling from a large parameter space of groundwater chemistries, to derive solubility limit distributions for use in safety case calculations.

The reader should be aware that there are two alternative approaches that have been utilised elsewhere:

- Firstly, solubility limit distributions may be derived through elicitation by expert judgment [20], and
- Secondly, directly using experimentally measured solubility limits [21].

The SKB approach has been reviewed previously as part of the regulatory assessment of SR-Can [9], so an in-depth assessment is not repeated here.

However it is worthwhile pointing out that in Section 4.1, p55 of the Simple Functions description [10], the tool is described as being validated by comparison with the PHREEQC model and with the MEDUSA code. This could be contentious as validation ensures that a software tool is fit for its intended purpose. It could be argued that the Simple Functions tool is validated because it reproduces very similar output to programs such as PHREEQC, that it is intended to mimic. It could also be argued that the intended use for Simple Functions is to simulate the solubility of radionuclides, in which case a more appropriate validation would have been comparison against experimental and analogue data appropriate to SR-Site.

Note that for SR-Can, the Simple Functions report outlining how the tool had been utilised in that assessment had undertaken a thorough comparison of simulations by the tool compared to experimental and analogue data [22].

For this initial review, this section investigates if, given the SR-Site calculational cases to which it has been applied, the Simple Functions tool is conceptually appropriate. The conceptual basis of the Simple Functions tool is described in Grivé et al. [10].

A key uncertainty issue is that of the treatment of saline conditions. There is no direct safety function considering the maintenance of specific ranges of solubilities. The salinity of groundwaters in the proposed repository zone varies with time as a result of changes in hydrogeology during glaciation cycles. A total of eight cycles of glacial advance and retreat are simulated over 1 million years. Each glacial cycle has a duration of 120k years. Figure 4 is reproduced from Figure 10.151 of [4]: taking the sum of cation equivalents to be an indicator of how salinity will increase, then up to 0.3M of cations could occur as a result of upconing of saline groundwater during glacial cycles.

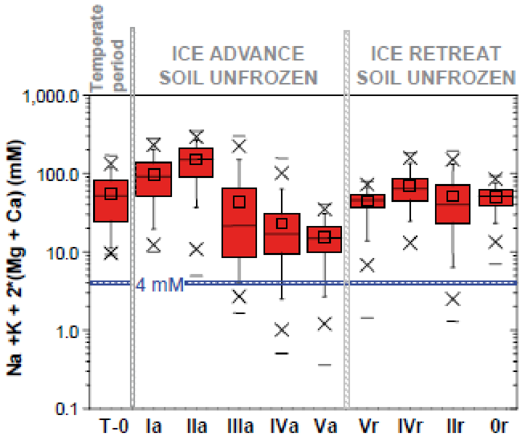


Figure 4. Change in the cation safety function in Forsmark groundwater at the proposed repository depth over one climate cycle. Reproduced from Figure 10.151 in [4].

Taking account of the effect of salinity is important in speciation calculations due to the effect it has upon dissolved ion activity coefficients. Activity coefficients describe the non-ideal nature of the interactions between ions in solution. The chemically effective concentration of an ion in solution is called the activity, expressed as follows:

$$a_i = m_i * \gamma$$

where a_i is the activity coefficient of species i, m_i is its concentration and γ_i is the activity coefficient.

Instead of salinity, the ionic strength in solution is used in activity coefficient calculations to express the average effect of other ions in solution upon the reactivity of a dissolved species. The ionic strength I is expressed as:

$$I = \frac{1}{2}\sum_i q_i * m_i$$

where q represents the charge of the ith species and m its molality.

The Simple Functions tool uses a formulation proposed by Oelkers and Helgeson [23], which is similar in form to the Davis equation to calculate activity coefficients.

According to the description of the Simple Functions spreadsheet [10], this is adequate to simulate the effect of ionic strength up to 0.2M concentrations of ions in solution, although the accuracy of this statement could not be tested in this preliminary study.

As shown in Figure 4, and discussed above, over 0.3M of the sum of cation molarities (and to balance, the same molarity of anions) could be reached for short periods during glacial cycles due to saline groundwater upconing. This is effectively greater than the 0.2M ionic strength limit for the Simple Functions spreadsheet [10].

For this study, a limited assessment was undertaken to understand what might be the consequences of using low ionic strength activity corrections in high ionic strength situations. As the Simple Functions tool was not available for use, PHREEQCv2 was used with the Davis equation to simulate speciation in solution with activity coefficients treated in a similar manner to the Simple Functions approach. This was compared to a full Pitzer calculation of speciation in solution. The Pitzer approach to calculation of activity coefficients takes into account second and higher virial coefficients for the interactions between specific ions in solution, compared to the average ion-atmosphere approach used in low ionic strength approaches such as the Davis equation. Comparing the Pitzer and Davis equation approaches rather than the Oelkers and Helgeson approach used in the Simple Functions tool is acceptable as the *validation* (see comments at the start of this section) of Simple Functions satisfactorily compared the tool with PHREEQC calculations using the Davis equation.

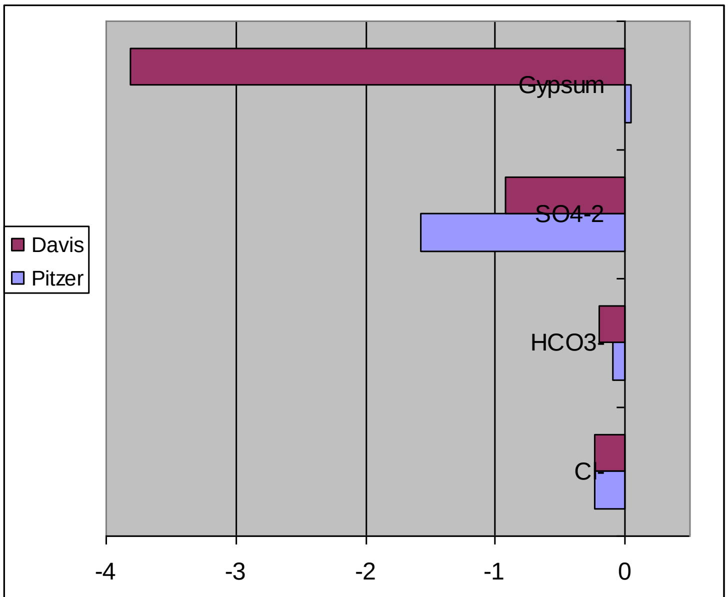
For this very simple calculation, a high salinity Laxemar groundwater of composition outlined in Table A1, p32 of [13], was utilised for the simulations. This water has an ionic strength of 1.75M, chosen to illustrate what the maximum possible impact of salinity might be given SR-Site conditions.

Given the initial assessment nature of this review, the objective of the calculations was to compare the activity coefficients and the solubilities of key major elements. The pitzer.dat and phreeqc_v2.14.3v2.dat databases provided with PHREEQC were utilised for this assessment without modification [5]. The outcome for key species is shown in Figure 5.

The log10 of the activity coefficients of the aqueous species Cl^-, HCO_3^- and SO_4^{-2} and the saturation indices of the solid gypsum (also on a log10 scale) are shown. For the aqueous species there is a small difference between Pitzer and Davis approaches for the monovalent ions, but more pronounced for the -2 charged sulphate species. For these species, the method of activity coefficient correction causes significantly different values to be generated only if the species charge is greater than one.

The solid gypsum is chemically $CaSO_4$. Both component species are double charged. The Davis approach results in gypsum having a very strongly negative saturation index: i.e. being very soluble in solution. However the Pitzer approach is rather different: the solid is predicted to be at saturation, i.e. likely to precipitate. Data were not available for the barium content of this water, as it would have been useful to look at the solubility of barites ($BaSO_4$) which, as discussed below, is a potential control limiting the solubility of Ra-226 through co-precipitation.

This simple illustrative calculation shows that for those calculations considering upconing of saline water, using the Simple Functions approach may not give appropriate solubility limits. As upconing of saline waters only occurs for a brief period during glacial cycles, this outcome is not likely to have a major impact on the assessment outcome over the entire 1 million year simulation. However as it is important to record and discuss key uncertainties, the difference in solubilities during upconing could be explored in illustrative side calculations to the main assessment to further clarify the consequences for key radionuclides.



	Cl-	HCO3-	SO4-2	Gypsum
■ Davis	-0.24	-0.2	-0.921	-3.81
□ Pitzer	-0.24	-0.09	-1.58	0.04

Figure 5. Log10 Activity coefficients for Cl^-, HCO_3^- and SO_4^{-2} and gypsum saturation indices calculated using Pitzer and Davis activity coefficient corrections. Analysis based upon Laxemar most saline groundwater.

Version B of Simple Functions has been developed to allow the inclusion of the effect of iron corrosion upon aqueous chemistry in the tool. This simulates the effect of corrosion by taking into account chemical equilibria between magnetite and goethite [10] through reactions as follows:

$Fe_3O_4 + 1.5H_2O + 0.25O_2(g) = 3FeOOH$

A description of the derivation of the appropriate equations is included on page 19, Section 3.2 of [10]. The derivation is terse but accurate, as checked by this study, if it is assumed that goethite and magnetite are the key corrosion controlling phases. It is noticeable that this description does not reference other documents in SR-Site.

There is a conceptual consistency issue. Section 3.5.1 page 97 of the Fuel and Canister Process Report [24], discusses *anaerobic* corrosion of the iron inserts through reactions such as:

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$

In the Fuel and Canister Report SKB says: “The corroding iron insert will influence the water chemistry in the void in the canister by generating high concentrations of dissolved hydrogen gas and small concentrations of dissolved Fe(II).”

This is different to the approach that includes reactions with oxygen (through ingress? Not explained) outlined in Section 3.2 of [10]. This suggests that either the Simple Functions approach should be updated to maintain consistency throughout the assessment, or that an explanation should be given that explains the reason why the adopted approach is suitable but different to that in other areas of SR-Site.

In terms of the questions posed by SSM, for this Section the answers are:

1. Are there any obviously missing pieces of information in the SR-Site and its supporting references? *The reason why corrosion including oxygen is included in Model B calculations is not explained. In addition validation should include comparison against measured/analogue data not just other modelling tools.*
2. Are key scientific conclusions adequately supported and justified? *The use of a magnetite/goethite couple to calculate the effect of key variables such as redox and* Fe^{+2} *content is well described but needs to be consistent with other SR-Site descriptions.*
3. Are there any alternative results or alternative scientific explanations published in the open scientific literature which have not been addressed or mentioned by SKB? *These are not discussed in SR-Site but documentation in SR-Can discusses analogues and experimental solubility results, which should be more clearly referenced in the validation section of [10].*
4. Is the source information of key datasets related to the assignment sufficiently described and referenced? *The methodology is comprehensively and appropriately described.*
5. Are mathematical models related to the assignment sound and sufficiently explained and justified? *The Simple Functions spreadsheet tool is adequately explained.*
6. Has SKB defined any safety function(s) concerning solubility? If so are safety functions and their associated safety function indicators and criteria adequately explained and justified in the SR-Site? *No direct safety functions are described.*
7. Are all known and relevant uncertainties identified, analysed and discussed in sufficient detail? *The effect of high salinity (due to upconing of saline groundwater) upon radioelement solubility should be discussed as a conceptual and numerical model uncertainty and explored in side calculations.*
8. Is the overall safety relevance of the specific review assignment within its scientific area explained and justified? *See comments about solubility described in the safety case in Section 3.6.*
9. Is the safety assessment strategy for the handling of issues related to a specific review assignment explained in a clear manner? *The Data Report [6] clearly states the approach to the derivation of chemical data for use by the Simple Functions spreadsheet and also the use of that tool and its underlying uncertainties*

10. Is information at different levels in the safety assessment consistent and logically subdivided (e.g. main SR-Site report, main supporting references and other references)? *The Data Report [6] clearly and logically references the underlying studies that support the use of the Simple Functions spreadsheet. However the high level Main Report [4] does not include any details or summary concerning the calculation of solubilities*.

2.4. Intrinsic colloids

Intrinsic colloids are those produced directly by radioelements as opposed to waste generated or naturally occurring colloidal particles which sorb radionuclides and are then transportable in groundwater. The potential for formation of intrinsic colloids was raised during the SSM review of Sr-Can [9].

The potential for the formation of intrinsic colloids is particularly an issue for actinide species such as Pu^{+4}, which due to their high charge will readily hydrolyse in solution as a precursor step towards polymerisation and formation of intrinsic colloids.

The review of SR-Can quotes recent studies that have shown that intrinsic Pu colloids are nanoclusters of PuO_2, and requests information concerning how SKB will treat such colloids.

During this initial review, although the potential for formation of pseudocolloids is discussed in many places within SR-Site, no explicit mention of the formation of intrinsic colloids was found. However in the main SR-Site report, Section 13.5.2 on page 652 [4] the following is mentioned concerning the reason why imposing a solubility limit may be optimistic upon container breach:

"…since it cannot be excluded that the solid particles formed by various radionuclides reaching saturation would leave the canister and migrate further."

From this statement it could be inferred that those calculations where:

- The buffer is eroded,
- The container is breached,
- With advective flow,
- There is no barrier to radionuclide transport out from the container, and
- There is no consideration of radionuclide solubility,

therefore represent a pessimistic situation equivalent to the formation of intrinsic colloids in which transport of radioelements is not hindered by processes such as sorption onto corrosion products, backfill or buffer.

As this inference is made by this review and is not stated by SKB, this issue cannot be discussed any further until SKB clarify if this scenario addresses the comments raised by the SR-Can review.

2.5. Co-precipitation

Solubility is considered in variant calculations to the central corrosion main scenario [4]. Within these calculations Ra-226 is identified as one of the key risk affecting radionuclides. The solubility of Ra-226 is solubility constrained by $RaSO_4$ [10].

The main corrosion scenario considers breach of the canisters by corrosion after the buffer and backfill have been removed by erosion in an advective flow environment. Corrosion is described as a process involving sulphide attack and is one of the main reasons why a buffer safety function, BUFF2, has been defined in which buffer density is designed to reduce microbial access to canisters. This safety function is described in Section 8.3.2 p55 of the Main Report [4]. However if the buffer has been eroded resulting in corroding water access to the canister, then this safety function will have been breached and the sulphide present in groundwater at repository depths will be augmented and maintained by microbial reactions. Concerning canister corrosion scenarios, Section 10.4.9, page 532 of the Main Report [4] says:

“In the combined erosion/corrosion calculations the time to canister failure is calculated by adding the corrosion time to the erosion time for each deposition hole with its specific flow and for a sulphide concentration randomly sampled from the sulphide distribution.”

Therefore canister breach calculations assume that conditions favour sulphide based corrosion mechanisms. However, calculations considering radioelement solubility after canister breach assume that Ra-226 solubility is controlled by co-precipitation with $BaSO_4$. This indicates a potential conceptual mismatch.

Radium is well known to almost qualitatively co-precipitate with barium sulphate, and was one of the first co-precipitation processes to be mechanistically investigated [25]. The $(Ba, Ra)SO_4$ co-precipitate is observed in nature, such as the cause of high gamma doses from precipitates on pipework carrying some types of oil-field brines.

SKB has produced a detailed review outlining the plausibility of radium co-precipitation within the context of Swedish spent fuel disposal [26]. This is not a new topic within the context of Swedish disposal studies: studies for the Stripa site in the 1980s investigated naturally occurring radium concentrations and concluded that dissolved Ra-226 was controlled more by chemical processes such as co-precipitation and less by radioactive disequilibrium processes, although barium groundwater concentrations were not measured in that study [27].

The description of the Simple Functions tool [10] does not include radium co-precipitation as it is not in-built into the tool, but provides solubility limits for $RaSO_4$. The SKB review of radium co-precipitation compared the solubility of radium as $RaSO_4$ and as $(Ba, Ra)SO_4$. Figure 6 is reproduced from [26] and shows that in theory the solubility of Ra-226 is reduced by a factor of 1000 as $(Ba, Ra)SO_4$ compared to $RaSO_4$.

This assessment has been supplemented by further SKB studies that have experimentally investigated $(Ba, Ra)SO_4$ co-precipitation [28], which showed that radium approached concentrations that could be considered as equilibrium between radium and barium sulphate over 100 days.

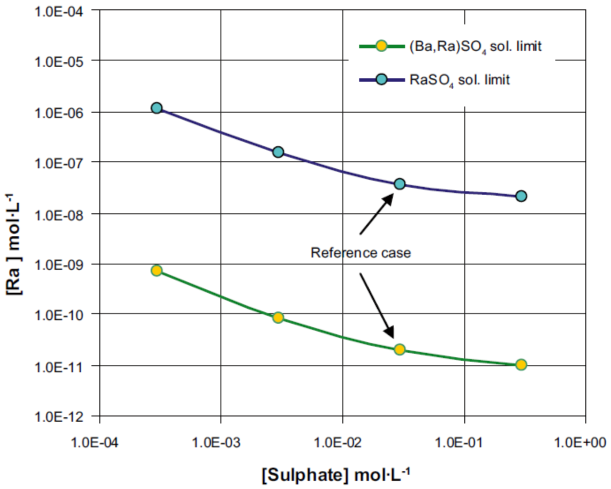


Figure 6. Solubility of Ra-226 due to RaSO4 compared to (Ba, Ra)SO4. Reproduced from Figure 4.11 in [26].

A discussion of the underlying conceptual model for co-precipitation is also included in Appendix H of the Radionuclide Transport Report [19].

The SKB Data Report [6] outlines that (Ra, Ba)SO_4 co-precipitation was included as a solubility limiting feature for Ra-226, and that as a consequence the solubility of Ra-226 was lower by a factor of 1000 from the solubility limit for $RaSO_4$.

According to SKB, the consequence of radium co-precipitation and of the solubility of radium in general, on the main assessment calculations is minimal. Section 5.2.2 of SKB’s Radionuclide Transport Report [19] says:

“Solubilities of neither Th nor Ra (taking into account co-precipitation with Ba) significantly limit the mean release rate of Ra-226.”

This is further supported by Section 13.6.2 page 694 of the Main Report [4] which says:

“As an illustration, a probabilistic case where no credit was taken for co-precipitation of Ra/Ba was calculated, i.e. where the solubility of Ra was increased by a factor of 1,000. This led to an increase of the release rate of Ra by only a factor of about 1.5”

However, the assessment also includes additional hypothetical cases, for instance where there is a large canister opening with low flow rates (Section 13.7.3 of the Main Report). In cases C, C*, D, D*, E and E*, radium is a key dose contributing radionuclide, in which case radium co-precipitation could be important. Irrespective of which calculational cases are being considered, as far as can be ascertained this is the first time that co-precipitation has been utilised numerically in a Swedish safety case and so sets a precedent. Finally, it is important to engender confidence in the science underpinning the assessment.

Figure 7 and Figure 8 compare the correlations between naturally occurring radium with barium and calcium in groundwater relevant to SR-Site; the diagrams are originally from the SKB Retardation Report [29].

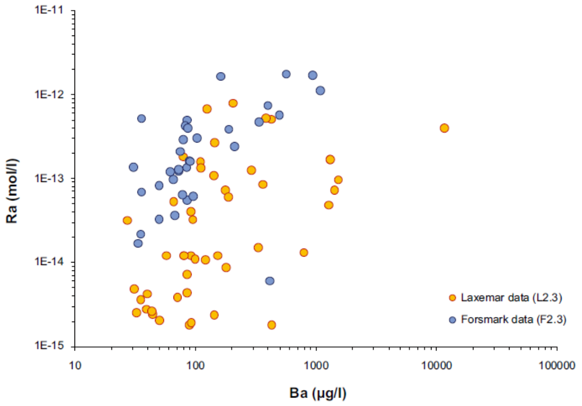


Figure 7. Correlation between Ra and Ba in Forsmark and Laxemar groundwaters, reproduced from [29]

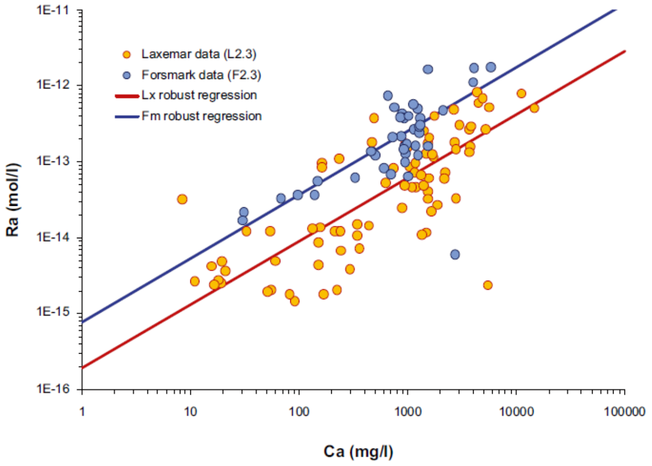


Figure 8. Correlation between Ra and Ca in Forsmark and Laxemar groundwaters, reproduced from [29]

Calcium is correlated with radium while the same cannot be said for barium. It is entirely possible that radium is solubility limited by co-precipitation with barium sulphate in the repository near field but not related to barium in the geosphere. However it is striking that radium and calcium are correlated in present day groundwaters. This correlation could be completely unrelated to co-precipitation, but it would be useful for SKB to consider and explain all lines of evidence to increase the robustness of the case for using co-precipitation.

In terms of the questions posed by SSM, in this section:

1. Are there any obviously missing pieces of information in the SR-Site and its supporting references? *The discussions are quite comprehensive.*
2. Are key scientific conclusions adequately supported and justified? *The justification for the inclusion of co-precipitation may require a consideration of wider issues such as consistency with other aspects of the assessment.*

3. Are there any alternative results or alternative scientific explanations published in the open scientific literature which have not been addressed or mentioned by SKB? *Alternative co-precipitation models have been discussed by SKB, but other solid phases, such as carbonates like $CaCO_3$ have not been considered.*
4. Is the source information of key datasets related to the assignment sufficiently described and referenced? *The methodology is comprehensively described, but at this initial assessment level it has not been possible to review in detail the derivation of the $RaSO_4$ solubility enhancement factor of 1000.*
5. Are mathematical models related to the assignment sound and sufficiently explained and justified? *The model for co-precipitation is based upon an ideal solid solution model which is explained at length but could not be assessed within this initial assessment. It is important to check whether or not alternative solid-solution models have been assessed and selection based upon experimental and field evidence.*
6. Has SKB defined any safety function(s) concerning solubility? If so are safety functions and their associated safety function indicators and criteria adequately explained and justified in the SR-Site? *No direct safety functions are described*.
7. Are all known and relevant uncertainties identified, analysed and discussed in sufficient detail? *The numerical uncertainties associated with the factor of 1000 should be outlined. Conceptual uncertainty, such as why radium correlated with calcium and not barium in present day groundwaters, should be addressed.*
8. Is the overall safety relevance of the specific review assignment within its scientific area explained and justified? *See comments about solubility described in the safety case in Section 3.6. Radium co-precipitation is discussed in terms of when it was excluded, on page 694 of the Main Report [4], but not where it was included. On page 117 of the Radionuclide Transport Report [19] the consequences of co-precipitation are discussed in depth.*
9. Is the safety assessment strategy for the handling of issues related to a specific review assignment explained in a clear manner? *The derivation of a factor of 1000 reduction in Ra solubility due to co-precipitation is documented.*
10. Is information at different levels in the safety assessment consistent and logically subdivided (e.g. main SR-Site report, main supporting references and other references)? *The Data Report [6] logically references the underlying studies that led to co-precipitation of radium being included.*

2.6. Utilisation of solubility data within assessment calculations

All of the discussions provided earlier in this report concern the process leading to the derivation of solubility limits for use in SR-Site assessment calculations.

In order to derive distributions for use in assessment calculations, the Simple Functions spreadsheet tool is linked to an Excel add-in application called @risk and the combined tool then run for 6916 “iterations”. The tool used latin hypercube sampling to pick data within uncertainty ranges in groundwater chemical data and uncertainties in underlying thermodynamic data in order to calculate data sets of solubility distributions for each radioelement. The data distributions so derived were then utilised within the transport calculation codes COMP23 and FARF31. This process is described in Section 3.7.1 page 50 of the Radionuclide Transport Report [19].

Note that the Fuel and Canister Report [24] describes a different approach, saying:

“Solubility limits are defined for three different water compositions resulting from geochemical processes and climate changes” (para 1, page 67 of [24]), and

“Concentration limits used in the calculations will be based on the results reported in /Duro et al. 2006b, Grivé et al. 2010/. The solubilities and the speciation recommended in /Duro et al. 2006b/ pertain to reducing conditions in the canister cavity, but for redox-sensitive radionuclides, calculations for a range of redox conditions have also been carried out” (para 4, page 68 of [24]).

This is a discrepancy. It may be speculated that the Fuel and Canister Report [24] relates to the Sr-Can assessment where this approach was adopted [8]. However it does not describe the actual approach taken in SR-Site.

The Radionuclide Transport Report [19] says 6916 iterations were actually sampled from 50,000 potential combinations of uncertainties within parameter values and climate conditions. SKB has outlined the key chemical components that are likely to affect radionuclide solubility limits, for each radioelement considered in transport calculations [19]. This highlights for instance that the solubilities of some radionuclides are sensitive to the values of certain dissolved solutes. For instance, uranium speciation is sensitive to dissolved CO_3^{-2} levels.

As all potential combinations of conditions were not sampled and it is difficult to trace what conditions were sampled and which were not, it is not possible to know if some combinations of conditions to which solubilities were sensitive have been missed.

The presentation of calculated distributions in [19] is not very detailed. To gain confidence that there has been reasonable coverage of the sensitivity of radioelement solubility to input chemical conditions, it is suggested that the discussion of distributions could be enhanced to demonstrate that the values are within the chemical behaviour expected for each radioelement, given the parameter space that has been sampled. An example of the SKB data for radium is shown in Figure 9.

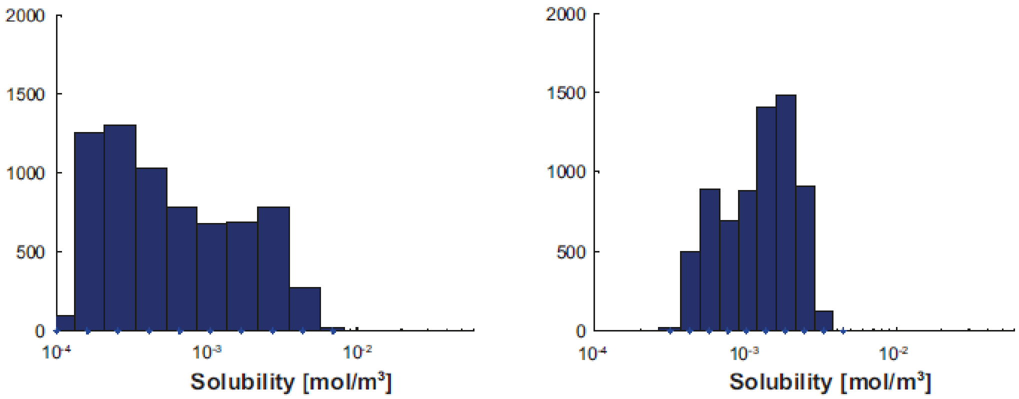


Figure 9. Solubility limit distribution of radium under temperature conditions (LHS) skewed compared to permafrost conditions groundwater (RHS). Reproduced from [19].

No explanation was given as to the cause of the skewed distribution under temperate conditions.

There are also some statements that must be typographical errors or open to interpretation. In discussing the relative effects of thermodynamic uncertainty compared to gross chemical changes caused by groundwaters arising from different climatic states, SKB say in Section F4 of [19]:

“Since the uncertainty in thermodynamic data appears to have a larger impact on the solubility limits than variations in groundwater composition, the choice of groundwater should be of less importance.”

This is open to discussion. The SKB approach was to fix the groundwater composition (e.g. fixed at a temperate composition) and vary thermodynamic data uncertainty, and vice-versa: fix thermodynamic data and vary the chemistry around uncertainties in temperate data compositions.

At first sight this seems to be a logical approach. In high quality groundwater analysis, chemical data are measured to at least a precision of +/- 5%, so the amount of chemical variation will not be large over a single groundwater composition.

However, within the assessment there are very different groundwater chemistries, ranging from altered meteoric water to saline deep groundwater. The true test of chemical variability is the sensitivity of the solubility limits to the range of alternative groundwater chemistries. No calculations were undertaken for this study but it can be postulated that the variability could be significant.

A more difficult issue to reconcile is that of the derivation of the final distributions used in transport calculations. In Appendix F of [19], SKB says that distributions were obtained by sampling:

"25% of groundwater compositions representing the temperate climate, 25% representing the permafrost climate, 25% representing glacial climate and 25% representing submerged climate.."

This approach makes sense if indeed it has been demonstrated that solubilities were insensitive to groundwater chemistry. However that demonstration, as discussed above, may not have covered the actual chemical variability given climate driven changes to groundwater chemistry.

For example: uranium solubility in existing slightly reducing temperate groundwater conditions is surely going to be different from that in more oxidising glacial meltwaters? To be indistinguishable over all chemical conditions, the solubilities of uranium would have to be similar despite possibly uranium existing in either the U(IV) or U(VI) oxidation states.

If solubilities are sensitive to the gross chemical differences between different waters then this must also imply that solubilities will vary as a function of time as different groundwater chemistries have an impact upon the facility at different times within the glacial cycle. The Fuel and Canister Report [24] supports this, saying "For redox-sensitive radionuclides, redox conditions in the groundwater are extremely important, and their variation can cause several orders of magnitude difference in the radionuclide concentration in some cases".

If this is the case then it is uncertain how random samples from four different chemical conditions to produce"average" groundwater solubilities for each radionuclide is a robust and defensible approach.

Rather than a conceptual issue, it may be simply the case that SKB has not documented the derivation of average solubilities in sufficient detail to enable the reader to have confidence in the methodology. Whatever the reason, SKB will need to update this area so that readers of SR-Site to have confidence in the calculations.

In terms of the questions posed by SSM, in this section:

1. Are there any obviously missing pieces of information in the SR-Site and its supporting references? *There are possibly several stages in the derivation of average solubilities that have not been documented.*
2. Are key scientific conclusions adequately supported and justified? *If the SKB approach is taken at face value then there are conceptual issues such as the sensitivity of solubility to different groundwater compositions.*
3. Are there any alternative results or alternative scientific explanations published in the open scientific literature which have not been addressed or mentioned by SKB? *Solubilities should be a function of chemistry which should lead to time dependent solubilities across glacial cycles within the assessment period.*
4. Is the source information of key datasets related to the assignment sufficiently described and referenced? *The underlying*

thermodynamic dataset was comprehensively described elsewhere.

5. Are mathematical models related to the assignment sound and sufficiently explained and justified? *The use of the @risk macro tool should be explained in sufficient detail for the reader to have confidence in the latin hypercube/Monte Carlo type sampling approach (e.g. what is the consequence of sampling 6916 times from 50,000 groundwater combinations?).*
6. Has SKB defined any safety function(s) concerning solubility? If so are safety functions and their associated safety function indicators and criteria adequately explained and justified in the SR-Site? *No direct safety functions are described.*
7. Are all known and relevant uncertainties identified, analysed and discussed in sufficient detail? *Uncertainties were described such as the thermodynamic database and effect of chemical variability, indicating that sufficient underpinning studies could have been undertaken, but the discussions were terse and limited in terms of the chemical behaviour of radioelements, which does not help the reader become fully confident in the conclusions.*
8. Is the overall safety relevance of the specific review assignment within its scientific area explained and justified? *The safety relevance of solubility limits is very clearly discussed in general terms in the Radionuclide Transport Report [19], but it was difficult to track that solubility was not used in many calculations but only in some alternative calculations (stated for instance in Table 3.2 of [19] but not in the text of the Main Report [4]). The first mention of exclusion of solubility from calculations was on page 653 where it is reported "demonstrated in section 13.5.6 by analysing a case where solubility limits are included".*
9. Is the safety assessment strategy for the handling of issues related to a specific review assignment explained in a clear manner? *The overall strategy is clearly explained: the details of implementing the strategy is a key area for comment in this review.*
10. Is information at different levels in the safety assessment consistent and logically subdivided (e.g. main SR-Site report, main supporting references and other references)? *The derivation of solubility distributions refers out to key SKB reports which describe the underlying methodologies and data.*
11. Is information at different levels in the safety assessment consistent and logically subdivided (e.g. main SR-Site report, main supporting references and other references)? *At the level of a preliminary review it was possible to follow the trail of reports referring to solubilities at a high level.*

3. Main Review Findings

The main review findings are listed below.

1. The derivation of groundwater geochemical data, which are then used to provide the background chemistry for solubility calculations, has been described in detail with consideration of key uncertainties and sensitivities. Some additional studies by SKB could close out comments raised in the review of the SR-Can assessment. Uncertainties in redox chemistry, such as the presence of sulphide in groundwaters and oxygen penetration could be addressed in further work.
2. Spot checks on the transfer of $\log_{10}$ K values for a few species in the additional chemical elements considered in SR-Site showed that in these cases data were transferred correctly from original source information. SKB themselves highlighted that there was an issue with some of the plutonium thermodynamic data that were carried forward from SR-Can, which should be addressed.
3. Overall, the Simple Functions tool adequately simulates the key features of elemental solubility given background chemical conditions. Some side calculations using speciation codes capable of calculating solubilities at higher ionic strengths could be undertaken to explore the adequacy of the Simple Functions spreadsheet calculations during upconing of groundwater.
4. While the effect that bentonite generated colloids have in transporting radionuclides from the near field has been considered, SKB has not addressed the issue of intrinsic or eigencolloids as discussed in the review of SR-Can.
5. Radium/barium co-precipitation has been considered for the first time numerically in a Swedish safety case in SR-Site, with a resultant 1000 fold reduction in radium solubility in the central corrosion case. Consideration of the solubility of barium sulphate should be consistent with the chemistry of the near field discussed elsewhere in SR-Site, particularly given that sulphide attack on canisters has been considered. The absence/presence of microbes in the near field, that could result in sulphate reduction, should be carefully assessed based upon experimental or field evidence rather than reasoning.
6. The description of how solubility distributions were generated using Simple Functions coupled to @risk was very limited: both in terms of detail in what was undertaken and the chemical implications of the outcome. To make matters more confusing, the Fuel and Canister Report [24] appears to describe the process used to generate solubilities for SR-Can and not SR-Site.
7. The generation of a single solubility distribution per radioelement covering all of the changes in ambient chemistry over 8 glacial cycles in 1 million years needs to be substantially and robustly justified, particularly as the Simple Functions tool can be used to generate chemistry specific solubilities. This limitation arises from the inability of the SKB COMP23 tool to consider time dependent solubilities.

4. Recommendations to SSM

The details of the findings from this review can be found in Appendix 2 and Appendix 3. In summary the recommendations to SSM are as follows:

- As the use of co-precipitation in a Swedish safety case is a precedent, the derivation of the $RaSO_4$ reduction factor of 1000 as a consequence of co-precipitation should be reviewed in detail to ensure that due consideration has been given to alternative conceptual models and uncertainties, and that the derivation is supported by site specific field and experimental data.
- Only spot checks were undertaken to check that stability constants for the derivation of the thermodynamic data for Lead were correctly transferred from underlying reports. A review should be undertaken to check that the database for Lead was derived with due consideration to all sources of available data and represents an appropriate set of data given the safety case context. As SKB has itself stated that Pu solubility data have technical issues, a review of the data derivation for this radioelement should also be considered.
- It should be requested that SKB considers additional scoping calculations, perhaps utilising appropriate speciation tools, to demonstrate that the effect of high ionic strength from upconing deeper groundwaters does not lead to solubilities that are substantially different to those considered in assessment calculations using the Simple Functions spreadsheet.
- The SKB description of the methodology used to calculate solubility distributions is terse and insufficient to allow clear understanding of exactly how the calculations were undertaken (the process of calculation included sampling from the ranges of compositions given solute analysis uncertainties perhaps? What about conceptual uncertainties as well as numerical chemical analysis uncertainties?). SSM could ask SKB to update the description with sufficient detail to enable a more detailed review to be undertaken.
- As the SKB description of the way in which solubility distributions were calculated did not explain the chemical processes occurring during the calculations (for instance we would expect different solid phases to control solubility as groundwater chemistry changes) it is recommended that SSM ask SKB to update the description of the results from solubility distribution analysis to explain the chemical basis of the resulting distributions, which can then be reviewed.
- SSM could ask SKB to describe in more detail the way in which a single overall solubility distribution was calculated for each radioelement for all chemical conditions over the 1 million year assessment timescale. If groundwater redox and pH change with time then use of a single distribution needs to be much more robustly justified than is the case at the present time.

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APPENDIX 1

Coverage of SKB reports

The following SKB reports were assessed for this Interim Review.

Table 3. SKB reports reviewed during this study.

Reviewed report	Reviewed sections	Comments
SKB (2011). Main report of the SR-Site project. SKB TR-11-01	Sections 13.5, 13.6, 13.7.	Description of the results from alternative calculation scenarios.
SKB (2010). Data report for the safety assessment SR-Site. SKB TR-10-52.	Section 3.4	The audit trail for thermodynamic data underlying the calculation of solubilities.
Salas J, Gimeno M J, Auqué L, Molinero J, Gómez J, Juárez I. (2010). SR-Site – hydrogeochemical evolution of the Forsmark site. SKB TR-10-58.	All (read for information rather than reviewed)	The conceptual basis for the selection of groundwater chemistry used in solubility calculations.
SKB (2006). Main report of the SR-Can project. SKB TR-06-09.	Table 6.8 p178	Approach to calculating solubilities in SR-Can.
Grivé M, Domènech C, Montoya V, García D, and Duro L. (2010). Simple Functions Spreadsheet tool presentation. SKB TR-10-61.	All	The key tool used in solubility calculations.
Grivé M., Domènech C., Montoya V., Garcia D., and Duro L. (2010). Determination and assessment of the concentration limits to be used in SR-Can Supplement to TR-06-32. SKB report R-10-50	All	The derivation of new thermodynamic data for use in SR-Site.
SKB (2010). Radionuclide transport report for the safety assessment SR-Site. SKB TR-10-50	Appendix F: Solubility calculations	Describes the solubility distributions used in the assessment.
Grivé M, Domènech C, Montoya V, Garcia D, Duro L. (2010). Determination and assessment of the concentration limits to be used in SR-Can. TR-06-32.	All	Data derivation, verification and validation of SR-Can (and SR-Site) solubility calculations.
Grandia F, Merino J, Bruno J,	Read but not reviewed	Supports radium co-

2008. Assessment of the radium-barium co-precipitation and its potential influence on the solubility of Ra in the near-field. SKB TR-08-07		precipitation.
Bosbach D, Böttle M, Volker M (2010). Experimental study of Ra^{2+} uptake by barite ($BaSO_4$). Kinetics of solid solution formation via BaSO4 dissolution and $Ra_xBa_{1-x}SO_4$ (re) precipitation. SKB TR-10-43	Read but not reviewed	Supports radium co-precipitation.
Crawford J. (2010). Bedrock Kd data and uncertainty assessment for application in SR-Site geosphere transport calculations. SKB R-10-48	Appendix A.	Description of radium /barium / calcium chemistry in groundwaters.
SKB (2010). Fuel and canister process report for the safety assessment SR-Site. SKB TR-10-46.	Section 2.5.7	Different methodology for the calculation of solubilities to that described in the Radionuclide Transport Report

APPENDIX 2

Suggested needs for complementary information from SKB

As part of this initial review, some requests for complementary information have already been made. Both requests already made and additional requests are listed below:

1. SKB should make available details of the ANDRA report which contained the justification for inclusion of key Lead species in the SKB thermodynamic database, as outlined in SKB report R-10-50 (Grivé et al. 2010). *This request was made and SKB provided the reference.*
2. Some of the issues arising from the SR-Can review, such as the formation of eigencolloids, may have been addressed by SKB but SR-Can documentation could be updated to show where these issues have been addressed.
3. SKB should provide details of how the @risk macro was utilised with the Simple Functions spreadsheet tool to derive solubility distributions. *This request was made and SKB provided some information, although more detail would be helpful of the actual data ranges and water compositions considered.*
4. SKB could be requested to provide details and better justify the use of the @risk/Simple Functions tool for calculating the final radioelement distributions using “25% of groundwater compositions representing the temperate climate, 25% representing the permafrost climate, 25% representing glacial climate and 25% representing submerged climate” as described in the Appendix of the Radionuclide Transport Report [19].

APPENDIX 3

Suggested review topics for SSM

During the main review phase of SR-Site it is suggested that the following topics require more substantial review than was undertaken in this initial review:

1. In this interim review only spot checks concerning the transfer of thermodynamic data and the plausibility of selected species were undertaken. As SKB has itself identified an issue associated with Plutonium solubility, it is recommended that the thermodynamic data used to calculate the solubility of Plutonium and also the newly included radioelement Lead should be reviewed to verify that a plausible and self consistent dataset has been utilised in assessment calculations.
2. SR-Site has for the first time considered the numerical effect of co-precipitation in a Swedish context. The basis of the factor of 1000 adjustment to the solubility of $RaSO_4$ should be carefully reviewed to ensure that the value has been transparently and defensibly derived.
3. As discussed in Appendix 2, the @risk/ Simple Functions derivation of the solubility distributions requires a much more detailed and robust description of what was undertaken, the chemistry giving rise to the distributions and how fractions of alternative groundwaters were combined to develop solubility calculations over the whole assessment timescales. Assuming this information is available, to gain confidence that a plausible and defendable approach has been adopted, a detailed review should be undertaken of the methodology and results produced by these calculations. This should be an in-depth assessment, reviewing details to as low a level as verifying modelling input files and the output of the results.

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

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