Radionuclide Solubility Calculations (Phase 1)

NWMO-TR-2021-02

February 2021

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Amphos 21



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ABSTRACT

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Abstract

The project "NWMO Radionuclides Solubility Calculation (Phase 1)" aims at calculating the solubility limits for some elements in a crystalline Canadian reference groundwater (CR-10). The work is performed to support the preparation of safety assessments for a deep geological repository in Canada. The elements of interest are (in alphabetical order): Am, Ag, Bi, C, Ca, Cd, Cs, Cu, Fe, Hg, Mo, Nb, Np, Pa, Pb, Pd, Pu, Ra, Rn, Ru, S, Sb, Se, Sn, Sr, Tc, Th, U and Zr.

Most of the elements of interest are already included in the thermodynamic database ThermoChimie. However, ThermoChimie does not include thermodynamic data for Bi, Cu, Hg, Rn and Ru. For these specific elements, a review of the available thermodynamic information in the scientific literature is first carried out and a consistent set of thermodynamic data is selected.

Secondly, the effect of the near field on the groundwater composition is assessed, considering three different scenarios:

- Scenario 1. Groundwater directly enters the canister without interacting with the bentonite buffer or the canister materials.
- Scenario 2. Groundwater interacts with the carbon-steel container prior to contacting the used nuclear fuel waste inside the container.
- Scenario 3. Groundwater interacts with both bentonite buffer and the C-steel container prior to contacting the used nuclear fuel waste inside the container.

Finally, the radionuclide solubility limits under the three different scenarios are evaluated. Four different temperatures (15°C, 25°C, 50°C and 80°C) are considered in each scenario. The radionuclide solubility limits and the corresponding speciation are calculated. A semiquantitative description of the main associated uncertainties in solubility and speciation calculations are provided.



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1. INTRODUCTION

The objective of the NWMO Radionuclides Solubility Calculation (Phase 1) project is to calculate the solubility limits for some radionuclides in a crystalline Canadian reference groundwater (CR-10) in support to the preparation of safety assessments for a deep geological repository in Canada. The elements of interest are (in alphabetical order): Am, Ag, Bi, C, Ca, Cd, Cs, Cu, Fe, Hg, Mo, Nb, Np, Pa, Pb, Pd, Pu, Ra, Rn, Ru, S, Sb, Se, Sn, Sr, Tc, Th, U and Zr.

Table 1 describes the compositions of the reference crystalline groundwater CR-10.

The composition of the groundwater can be affected by its interaction with the components of the repository near field. The following three different scenarios are studied in this work:

- Scenario 1: Groundwater enters the canister without interacting with the bentonite buffer or the canister materials. In this scenario the CR-10 water composition has been re-equilibrated with the host-rock mineralogy at different studied temperatures.
- Scenario 2: Groundwater interacts with the carbon-steel container prior to contacting the used nuclear fuel waste inside the container. The main component of C-steel, Fe(0), will anoxically corrode by the reduction of water, and this corrosion process will have an influence in the groundwater composition.
- **Scenario 3:** Groundwater interacts with both bentonite buffer and the C-steel container prior to contacting the used nuclear fuel waste inside the container.

In all three scenarios, four different temperatures (15°C, 25°C, 50°C and 80°C) are considered for the calculation of (a) the effect of near field component on groundwater composition and (b) the element solubility and speciation.

The present document contains:

- A description of the thermodynamic database used in the calculations, including the additional data selection Bi, Cu, Hg, Rn and Ru (section 2).
- The groundwaters used in each one of the Scenarios evaluated, including details on the calculations leading to their composition (section 3).
- The calculated solubility and associated speciation for each element, at 15, 25, 50 and 80°C at each Scenario, including the associated discussion and a semi-quantitative analysis of the uncertainties affecting solubility calculations (section 4).
- Section 5 summarizes the main results, including element solubilities and the main uncertainties associated to the solubility calculations.

	CR-10
Nominal pH	7.0
Redox state	Reducing
Nominal Eh (mV)	-200
TDS (mg⋅L⁻¹)	11300
Water type	Ca-Na-Cl
Solutes (mg⋅L ⁻¹)	
Na	1900
К	15
Са	2130
Mg	60
HCO ₃	70
SO4	1000
CI	6100
Br	-
Sr	25
Li	-
F	2
I	-
В	-
Si	5
Fe	1
ΝΟ3	<1

Table 1: CR-10 Reference Groundwater Composition

2. THERMODYNAMIC DATABASE

PhreeqC/PhreeqCl Interactive version 3.6.2 (released on January 28, 2020) (Parkhurst and Appelo 2013) has been used to calculate the groundwater composition and the radionuclide solubility and speciation in the different scenarios and different temperatures.

The database used in the calculations is a modified version of the ThermoChimie database version 10a, decoupling sulphate/sulphide and C(+4)/methane reactions and with some modifications that are detailed in the sections below.

2.1 THERMODYNAMIC DATABASE: THERMOCHIMIE

The thermodynamic database (TDB) used in this work is ThermoChimie (developed by Andra/RWM/Ondraf, *www.thermochimie-tdb.com*, Giffaut et al. 2014; Grivé et al. 2015). ThermoChimie is, to date, the most complete and updated TDB for the purpose of modelling needs in performance assessments of high, low and intermediate level radioactive nuclear waste repositories (e.g. Duro et al. 2012; Hakanen et al. 2014; Ochs et al. 2014; Bruno et al. 2018; Trinchero et al. 2018; Idiart et al. 2019).

Most of the elements of interest for this study are included in ThermoChimie (see elements highlighted in green, white letters in Figure 1). However, ThermoChimie does not include thermodynamic data for Bi, Cu, Hg, Rn and Ru (elements highlighted in grey in Figure 1). In these cases, a review of the available thermodynamic data in the scientific literature has been carried out in order to select a set of internal consistent thermodynamic data which allows solubility and speciation calculations for these elements (section 2.2).



Figure 1: Periodic Table Showing Elements of Interest. Green: Elements Included in ThermoChimie Version 10a. Dark Green, White Letters: Elements in ThermoChimie vs10a of Interest for the Present Work. Grey, Black Letters: Elements not Included in ThermoChimie 10a of Interest for the Present Work. White, Grey Letters: Elements not Included in ThermoChimie and not Studied in the Present Work The solubility calculations will be performed for the temperature range 15°C to 80°C. The enthalpy data is required to perform calculations at temperatures different from 25°C. The Van't Hoff equation (Equation 1) is used to perform temperature corrections. In this approach, the temperature dependence of the equilibrium constant $log_{10}K^{\circ}(T)$ is written as a function of the enthalpy of reaction, $\Delta_r H^{\circ}_m$. The use of more complex approaches requires information of parameters such as heat capacity, information which is nearly inexistent for most of the elements of interest.

$$log_{10}K^{\circ}(T) = \frac{\Delta_r H^{\circ}{}_m(T_0)}{R\ln(10)} \left(\frac{1}{T_0} - \frac{1}{T}\right)$$
 Equation 1

The SIT approach (Specific Interaction Theory, Equation 2) is used to perform ionic strength corrections. The SIT equation calculates the activity coefficient γ_i of an ion of charge z_i in a solution of ionic strength I (as $I = 1/2\Sigma_i m_i z_i^2$), where m_i is the molality of ion *i* present in solution and A and B are empirical constants at a given temperature. The parameter a_i is the effective ion diameter, z_i is the charge and $\varepsilon(i,k,l_m)$ is the ionic interaction coefficient (kg·mol⁻¹).

$$log(\gamma_i) = -z_i^2 \left(\frac{A\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}} \right) + \sum_k \varepsilon(i, k, I_m) m_k \quad \text{Equation 2}$$

The thermodynamic data in ThermoChimie include associated uncertainties (when possible). The uncertainty covers the range within which the corresponding data can be reproduced with a probability of 95%.

2.2 THERMODYNAMIC DATA SELECTION FOR ELEMENTS NOT INCLUDED IN THERMOCHIMIE

As described above, ThermoChimie does not include thermodynamic data for Bi, Cu, Hg, Rn and Ru (elements highlighted in grey in Figure 1). Thus, a specific thermodynamic data selection has been made for those elements. The thermodynamic data is selected from a wide range of sources, including previous thermodynamic data compilations and the open scientific literature. In those cases where significant data gaps exist, estimations are used.

The data selection is focused on ligands included in the studied groundwater composition (Table 1). Thus, complexes with those elements with phosphate or organics, for which concentrations in groundwater are not provided, have not been included in the data selection.

The thermodynamic data selection follows those general guidelines:

Basic data for the basic component (primary master species) are first selected. The basic component is usually a free cation of the element of interest (e.g., Bi³⁺ for bismuth). These basic components (together with electrons and protons) are used as building blocks for the formation of all the remaining aqueous species and solid phases. Data selected for the primary master species is usually Δ_fG_m° (standard molar Gibbs energy of formation) and then the Δ_fH_m° (standard molar enthalpy of formation) or S_m° (standard molar entropy). Wherever possible, CODATA recommendations (Cox et al. 1989) are followed when selecting thermodynamic data for the primary master species.

- 2. S_m° for the reference phase is selected. In the reference phase (for example Bi(cr)), $\Delta_f G_m^\circ$ and $\Delta_f H_m^\circ$ are zero. Wherever possible, CODATA recommendations (Cox et al. 1989) are followed when selecting thermodynamic data for the reference phase.
- Aqueous stability constants and solubility equilibria are selected. Preference is given to values obtained directly from solubility experiments. Redox reactions may be an exception to this general rule, due to the experimental handicaps usually faced in solubility experiments where redox reactions are involved.
- 4. Afterwards, enthalpies or entropies are selected. If available, experimental data obtained by calorimetric measurements are preferred. When reliable data are not available, these values may be estimated. Estimations can be made by different forms (analogies with other elements and complexes, correlations by considering the charge (z) and the ionic radii (r) of different elements, empirical algorithms, etc).
- 5. When values have been selected for two of these three variables (Gibbs energy, enthalpy or entropy), the rest of the data are internally calculated using Equation 3 and Equation 4:

$$\Delta_f G_m^0 = \Delta_f H_m^0 - T \left(S_m^0 + \left(\frac{z}{2}\right) \cdot S_{m,H2(g)}^0 - \sum_i \frac{\nu_i}{\nu_{i,ref}} S_{m,i}^0 \right)$$
 Equation 3
$$\Delta_r G_m^0 = \Delta_r H_m^0 - T \Delta_r S_m^0$$
 Equation 4

- 6. ThermoChimie primarily uses SIT (Specific ion Interaction Theory) for activity corrections of the stability constants to the standard state. Ion interaction coefficients $\varepsilon(i, Na^+, I_m)$ or $\varepsilon(i, Ct, I_m)$ for aqueous species are also selected when available.
- 7. When possible, associated uncertainties are also selected. The procedure for assigning uncertainty varies between data sources and takes into account the availability of information. In some cases, reliable and traceable uncertainty was reported in the original data sources. In other cases, uncertainty has been calculated in order to cover all the reliable data available. For some specific data it is not possible to assign a realistic uncertainty value.

A more detailed description of data selection per each element is provided below.

Notice that $log_{10}K^{\circ}$ and $\varepsilon(i, j)$ values are provided with two decimal places and $\Delta_r H_m^{\circ}$ or S_m° values are provided with three decimal places in the tables below, regardless of the level of accuracy provided in the source data.

2.2.1 Bismuth

Data selection for bismuth is similar to the one performed in Duro et al. (2010) and updated to include enthalpy or entropy data relevant to the evaluation of the temperature effects.

The data sources reviewed for Bi include but are not limited to:

- Baes and Mesmer (1976);
- The Thermoddem database vs1.10_06Jun2017 (*https://thermoddem.brgm.fr/*, Blanc et al. 2012); and
- The data selection reported in Lothenbach et al. (1999).

Bi is not included in CODATA, so values for the master species Bi³⁺ and the reference state Bi(cr) have been selected from the sources summarized in Table 2.

A consistent Bi thermodynamic dataset was reported in the data selection for JAEA (Japan Atomic Energy Agency) performed by Lothenbach et al. (1999). This has been the basis of the data selection in Table 3 and Table 4. Selected data include the stability constants of Bi(III) aqueous species and solids with hydroxide and chloride, the main ligands for bismuth.

Lothenbach et al. (1999) also selected data for polymeric bismuth species. However, these species are not expected to form under the conditions of interest due to the low bismuth concentrations that will be present in solution and have not been included in the selection.

Lothenbach et al. (1999) used the SIT approach to correct the thermodynamic data to I = 0; nevertheless, only the SIT coefficients for ε (cation, CIO₄⁻) were reported. As perchlorate is not expected to be present in the groundwaters of this work, those coefficients are not relevant for the solubility calculations to be carried out in the frame of this work.

No experimental temperature-dependent data for bismuth has been identified, but estimations for entropy of the Bi aqueous hydroxides can be calculated using the Shock et al. (1997) approach (see Table 3). The approach is based on a correlation between standard molal entropies S^o_m of an aqueous hydroxide complex and the standard molal entropy of the corresponding cation, and can be applied to trivalent elements such as Bi(III). The same approach was used in the thermodynamic database Thermoddem (*https://thermoddem.brgm.fr/*, Blanc et al. 2012).

	Species	∆ _f G _m ° (kJ⋅mol⁻¹)	S _m ° (J⋅mol ⁻¹ ⋅K ⁻¹)	Reference
Reference State	Bi(cr)	a)	56.735	Wagman et al. (1965)
Master species	Bi ³⁺	95.550	-188.280	G _f form Lothenbach et al. (1999), S _f from Thermoddem

^aThis value of the reference state is 0 by convention.

Name	Reaction	log₁₀K°	Reference	∆rH _m ° (kJ⋅mol⁻¹)	Reference
Bi(OH) ²⁺	$Bi^{3+} + H_2O = Bi(OH)^{2+} + H^+$	-0.92±0.48 b)		16.206	Internal calculation ^{a)}
Bi(OH)₂⁺	$Bi^{3+} + 2 H_2O = Bi(OH)_2^+ + 2 H^+$	-2.56±1.16 ^{b)}	Lothenbach et al. (1999)	73.719	Internal calculation ^{a)}
Bi(OH)₃	$Bi^{3+} + 3 H_2O = Bi(OH)_3 + 3 H^+$	-5.31±3.59 ^{b)}		112.845	Internal calculation ^{a)}
Bi(OH)₄ ⁻	$Bi^{3+} + 4 H_2O = Bi(OH)_4^- + 4 H^+$	-18.71±3.09 ^{b)}		177.482	Internal calculation ^{a)}
BiCl ²⁺	$Bi^{3+} + CI^{-} = BiCI^{2+}$	3.65		-	-
BiCl ₂ +	$Bi^{3+} + 2 Cl^{-} = BiCl_{2}^{+}$	5.85		-	-
BiCl₃	$Bi^{3+} + 3 Cl^{-} = BiCl_{3}$	7.62	Lothenbach et al. (1999)	-	-
BiCl4 ⁻	$Bi^{3+} + 4 CI^{-} = BiCI_{4}^{-}$	9.06		-	-
BiCl ₅ ²⁻	$Bi^{3+} + 5 Cl^{-} = BiCl_5^{2-}$	8.33		-	-
BiCl63-	$Bi^{3+} + 6 Cl^{-} = BiCl_{6}^{3-}$	7.64		-	-

Table 3: Data Selection for Bi Aqueous Species

^a Internal calculation: S_m° from Shock et al. (1997).

^b High uncertainty to cover available data in previous compilations (Baes and Mesmer 1976; Smith and Martell 1976; Wagman and Evans 1982).

Table 4: Data Selection for Bi Solids

Name	Reaction	log₁₀K°	Reference	∆rHm° (kJ·mol⁻¹)	Reference
Bi ₂ O ₃ (s)	2 Bi ³⁺ + 3 H ₂ O = Bi ₂ O ₃ + 6 H ⁺	-0.76±6.18 ^{a)}	Lothenbach et al. (1999)	-	-

^a The high uncertainty is related to the high uncertainty in Bi hydrolysis species.

2.2.2 Copper

Data selection for Copper is similar to the one performed in Duro et al. (2010), updated with data from Palmer (2011) for Cu(I) hydrolysis. Enthalpy and entropy data relevant to the evaluation of temperature effects have been also incorporated when possible.

Different compilations of thermodynamic data for copper are available in the literature. The data sources reviewed for Cu include but are not limited to:

- Plyasunova et al (1997);
- Puigdomènech and Taxén (2000), Beverskog and Puigdomènech (1997) and the default database included in the SPANA program version 2020-Feb-05 (Puigdomènech 2020); and
- Powell et al. (2007).

Data selection for the primary master species Cu²⁺ and the reference state Cu(cr) follow CODATA recommendations (Cox et al. 1989) and are reported in Table 5.

Common oxidation states of copper include Cu(I) and Cu(II). Under anoxic and reducing conditions, Cu(I) prevails, whereas Cu(II) dominates the copper speciation under oxidizing conditions (Figure 2).

Puigdomènech and Taxén (2000) made one of the most extensive and accurate data compilations, including chlorides, carbonates, phosphates, sulphates, sulphides and redox aqueous species. This compilation was used as the main source of information (see Table 5, Table 6 and Table 7). In most cases, the data reported in Puigdomènech and Taxén (2000) are in agreement with the data in Plyasunova et al. (1997) and Powell et al. (2007); some exceptions are discussed below.

Thermodynamic data for Cu(II) hydrolysis species (stability constants and entropy data) have been obtained from Puigdomènech and Taxén (2000). Selected stability constants are in agreement with the data in Plyasunova et al. (1997) and Powell et al. (2007).

Puigdomènech and Taxén (2000) and Beverskog and Puigdomènech (1997) also provide thermodynamic data for the species Cu(OH)(aq) and $Cu(OH)_2^-$. Beverskog and Puigdomènech (1997) calculated thermodynamic data for these species by fitting the temperature dependence of the aqueous solubility of Cu_2O/Cu mixtures determined by Var'yash (1989) over the temperature range 150-350°C. Nevertheless, Beverskog and Puigdomènech (1997) discuss that "the solubilities reported by Var'yash (1989) do not agree completely with the data obtained in other studies", that "the reason for this discrepancy is not clear" and that "it is therefore desirable to check how the values compare with other sources of information". Notice that the stability constant reported in Puigdomènech and Taxén (2000) for $Cu(OH)_2^-$ was also considered to be overestimated in Duro et al. (2010), and those species were not included in the calculations. In the present work, the more traceable and recent data reported by Palmer (2011) (see Table 6 and Table 7) were used, who experimentally determined the thermodynamic data for $Cu_2O(cr)$ using flow-through reactors and a conventional batch autoclave at temperatures from 20°C to 400°C.

No polynuclear species have been selected in this work as they form at copper concentrations above 1 M (mol/L) (Puigdomènech and Taxén 2000).

Chloride ions may influence copper chemistry by the formation of aqueous complexes and solid phases and can be important under the conditions of the studied groundwaters (Figure 2). Thermodynamic data from Puigdomènech and Taxén (2000) have been selected. Data selection includes some consistent values for SIT coefficients and entropy data to account for temperature dependence.



Figure 2: Eh vs pH Predominance Diagram at 25°C for Copper Aqueous Species in Water, Calculated Using the Data Selection in the Present Work. $[CI]_T=[Na]_T=1.7\cdot10^{-2}$ M; $[Cu]_T=10^{-8}$ M; Solids Are not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for CR-10 Groundwater. Green Dotted Lines Stand for the Water Stability Field

Other ligands such as carbonate, sulphate or sulphide are also included in the selection; data are shown in Table 6 and Table 7.

	Species	∆ _f H _m ° (kJ⋅mol⁻¹)	S _m ° (J⋅mol ⁻¹ ⋅K ⁻¹)	Reference
Reference State	Cu(cr)	a)	33.150	Cox et al. (1989)
Master species	Cu ²⁺	64.900	-98.000	H _f and S _f from Cox et al. (1989)

Table 5: Data Selection for Cu Primary Species and Reference State

^a This value of the reference state is 0 by convention.

Name	Reaction	log ₁₀ K ^{c)}	Reference	∆rH _m ° (kJ⋅mol⁻¹)	Reference
Cu⁺	$Cu^{2+} + e^{-} = Cu^{+}$	2.83		5.689	Internal calculation ^{a)}
CuOH⁺	$Cu^{2+} + H_2O = CuOH^+ + H^+$	-7.97±0.30	Duindens ìn each	35.669	
Cu(OH)₂	$Cu^{2+} + 2 H_2O = Cu(OH)_2$ + 2 H ⁺	-16.24±0.50	and Taxén	87.957	
Cu(OH)₃ ⁻	Cu ²⁺ + 3 H ₂ O = Cu(OH) ₃ ⁻ + 3 H ⁺	-26.70±0.40	(2000)	114.882	
Cu(OH)4 ²⁻	$Cu^{2+} + 4 H_2O = Cu(OH)_4^{2-}$ + 4 H ⁺	-39.6±0.16		119.657	
Cu(OH)	$Cu^+ + H_2O = Cu(OH) + H^+$	-7.68	Delse en (0011)	-	-
Cu(OH)2 ⁻	Cu ⁺ + 2 H ₂ O = Cu(OH) ₂ ⁻ + 2 H ⁺	-18.20	Paimer (2011)	57.657	Internal calculation ^{b)}
CuCl⁺	$Cu^{2+} + Cl^{-} = CuCl^{+}$	0.64		7.721	Internal calculation ^{a)}
CuCl ₂	$Cu^{2+} + 2 Cl^{-} = CuCl_2$	0.24		15.982	
CuCl ₃ -	$Cu^{2+} + 3 Cl^{-} = CuCl_{3}^{-}$	-1.28	Puigdomènech	22.154	
CuCl ₄ ²⁻	$Cu^{2+} + 4 Cl^{-} = CuCl_4^{2-}$	-3.98	and Taxén	27.935	
CuCl	$Cu^+ + Cl^- = CuCl$	3.30	(2000)	3.763	
CuCl ₂ -	$Cu^{+} + 2 Cl^{-} = CuCl_{2}^{-}$	5.62		-17.708	
CuCl ₃ ²⁻	$Cu^{+} + 3 Cl^{-} = CuCl_{3}^{2-}$	4.68		-24.746	
CuCO₃	$Cu^{2+} + CO_3^{2-} = CuCO_3$	6.77		-0.182	Internal calculation ^{a)}
CuHCO₃⁺	$Cu^{2+} + 2 CO_3^{2-} + H^+ = CuHCO_3^+$	12.13	Puigdomènech and Taxén (2000)	-	-
Cu(CO ₃)2 ²⁻	$Cu^{2+} + 2 CO_3^{2-} = Cu(CO_3)_2^{2-}$	10.20	(2000)	37.186	Internal calculation ^{a)}
CuSO₄	$Cu^{2+} + SO_4^{2-} = CuSO_4$	2.31	Puigdomènech and Taxén (2000)	5.106	Internal calculation ^{a)}
CuHS	Cu⁺ + HS⁻ = CuHS	13.00	Puigdomènech and Taxén	-44.866	Internal calculation ^{a)}
Cu(HS)2 ⁻	$Cu^{+} + 2 HS^{-} = Cu(HS)_{2}^{-}$	17.18	(2000)	-78.863	

Table 6: Data Selection for Cu Aqueous Species

^a Internal calculation: S_m° from Puigdomènech and Taxén (2000).
 ^b Internal calculation: S_m° from Palmer (2011).
 ^c Uncertainties assigned considering the data in Plyasunova et al (1997).

Name	Reaction	log ₁₀ K ^{c)}	Reference	∆rHm° (kJ∙mol⁻¹)	Reference
Cu(OH)₂(s)	$Cu^{2+} + 2 H_2O =$ $Cu(OH)_2 + 2H^+$	-8.64	Puigdomènech	62.764	Internal
CuO(s)	$Cu^{2+} + H_2O = CuO + 2 H^+$	-7.68	(2000)	64.902	calculation ^{a)}
Cu₂O(cr)	$2 Cu^+ + H_2O = Cu_2O$ + 2 H ⁺	0.62	Palmer (2011)	-18.446	Internal calculation ^{b)}
CuCO₃(s)	$Cu^{2+} + CO_3^{2-} = CuCO_3$	11.50	Puigdomènech and Taxén (2000)	4.691	Internal calculation ^{a)}
CuS(cr)	Cu ²⁺ + HS ⁻ = CuS + H ⁺	22.06	Puigdomènech	-97.475	Internal calculation ^{a)}
Cu ₂ S(cr)	$2 \text{ Cu}^+ + \text{HS}^- = \text{Cu}_2\text{S}$ + H ⁺	34.02	and Taxén (2000)	-	-
CuSO₄(cr)	$Cu^{2+} + SO_4^{2-} = CuSO_4$	-2.94		73.042	Internal
CuSO₄:5H₂O(cr)	$Cu^{2+} + SO_4^{2-} + 5$ H ₂ O = CuSO ₄ :5H ₂ O	301.20	Duindens ìn each	-1799.030	calculation ^{a)}
Cu₄SO₄(OH)₀(s)	$4 Cu^{2+} + SO_4^{2-} + 6$ H ₂ O = Cu ₄ SO ₄ (OH) ₆ + 6 H ⁺	-15.54	and Taxén (2000)	-	-
CuO:CuSO₄(s)	2 Cu ²⁺ + SO4 ²⁻ + H ₂ O = CuO:CuSO4 + 2 H ⁺	-10.31		-	-
CuCl(s)	$Cu^+ + Cl^- = CuCl$	6.80 ± 0.40		-41.856	
CuCl ₂ (cr)	Cu ²⁺ +2 Cu ⁺ + 2 Cl ⁻ + H ₂ O = CuCl ₂ + 2 H ⁺	-3.73	Puigdomènech and Taxén (2000)	51.553	Internal calculation ^a
CuCl₂:3Cu(OH)₂(s)	4 Cu ²⁺ + 2 Cl ⁻ + 6 H ₂ O = CuCl ₂ :3Cu(OH) ₂ + 6 H ⁺	-14.92	(2000)	-	-

Table 7: Data Sel	ection for	Cu	Solids
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^a Internal calculation: S_m° from Puigdomènech and Taxén (2000).
 ^b Internal calculation: S_m° from Palmer (2011).
 ^c Uncertainties assigned considering the data in Plyasunova et al (1997).

2.2.3 Mercury

The data sources reviewed for Hg include but are not limited to:

- Powell et al. (2005);
- Benoit et al (1999); and
- Bard et al. (1985).

Data selection for the primary master species Hg²⁺ and the reference state Hg(I) follow CODATA recommendations (Cox et al. 1989) and are reported in Table 8.

Mercury has two redox states in aqueous solution, Hg(II) as Hg^{2+} (formed under oxidizing conditions) and Hg(I) as Hg_2^{2+} , formed under reducing conditions. Redox data for Hg^{2+}/Hg_2^{2+} reaction have been selected from Bard et al. (1985) (Table 9).

Data selection for Hg(II) chemistry (Table 9 and Table 10) is mainly based on the work by Powell et al. (2005), who made a critical evaluation of the equilibrium constants and reaction enthalpies for the complex formation reactions between aqueous Hg(II) and common environmental inorganic ligands as OH^- , CI^- , CO_3^{2-} or SO_4^{2-} . For each metal–ligand combination, the review identified the most reliable publications available and identified (and rejected) unreliable stability constants. In most cases, the reaction enthalpy has also been included in the selection, which allows to perform temperature corrections using the Van't Hoff equation.

Results of the data selection at 25°C in the Hg-Cl system are represented in the predominance diagram in Figure 3.



Figure 3: Eh vs pH Predominance Diagram at 25°C for Mercury Aqueous Species in Water, Calculated Using the Data Selection in the Present Work. $[CI]_T=[Na]_T=1.7\cdot10^{-2}$ M; $[Hg]_T=10^{-8}$ M; Solids Are not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for CR-10 Groundwater. Green Dotted Lines Stand for the Water Stability Field

Sulphide was not included among the ligands reviewed by Powell et al. (2005). Data selected for this system has been obtained mainly from the work by Benoit et al. (1999) and is summarized in Table 9.

Table 8: Data Selection	for Hg Primary	Species and	Reference State
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	Species	∆ _f H _m (kJ⋅mol⁻¹)	S _m ° (J⋅mol ⁻¹ ⋅K ⁻¹)	Reference
Reference State	Hg(l)	a)	75.900	Cox et al. (1989)
Master species	Hg ²⁺	170.210	-36.190	Cox et al. (1989)

^a This value of the reference state is 0 by convention.

Name	Reaction	log₁₀K°	Reference	∆ _r H _m ° (kJ·mol⁻¹)	Reference
Hg ₂ ²⁺	$Hg^{2+} + 2 e^{-} = Hg_2^{2+}$	30.80	Bard et al. (1995)	-173.500	Bard et al. (1995)
HgOH⁺	Hg ²⁺ + H ₂ O = HgOH ⁺ + H ⁺	-3.40±0.08		20.810	Martell (2004) ^{a)}
Hg(OH) ₂	$Hg^{2+} + 2 H_2O =$ $Hg(OH)_2 + 2 H^+$	-5.98±0.06	Powell et al. (2005)	51.500	Powell et al. (2005)
Hg(OH)₃ ⁻	$Hg^{2+} + 3 H_2O =$ $Hg(OH)_{3^-} + 3 H^+$	-21.10±0.30		-	-
Hg₂(OH)⁺	Hg ₂ ^{z+} + H ₂ O = Hg ₂ (OH) ⁺ + H ⁺	-5.00±0.30		-	-
Hg₂(OH)³+	$2 Hg^{2+} + H_2O = Hg_2(OH)^{3+} + H^+$	-3.33±0.03	Baes and Mesmer (1976)	12.803	Baes and Mesmer (1976)
Hg₃(OH)₃³+	3 Hg ²⁺ + 3 H ₂ O = Hg ₃ (OH) ₃ ³⁺ + 3 H ⁺	-6.42±0.15		-	-
Hg(OH)CO₃ ⁻	$Hg^{2+} + CO_3^{2-} + H_2O = Hg(OH)CO_3^{-} + H^+$	5.33	Powell et al. (2005)	-	-
HgCO₃	$Hg^{2+} + CO_3^{2-} = HgCO_3$	11.47	Powell et al. (2005)	-	-
HgHCO₃⁺	Hg ²⁺ + CO ₃ ²⁻ + H ⁺ = HgHCO ₃ ⁺	15.80	Powell et al. (2005)	-	-
Hg(CO ₃) ₂ ²⁻	$Hg^{2+} + 2 CO_3^{2-} = Hg(CO_3)_2^{2-}$	15.70	Smith and Martell (2004) ^{a)}	-	-
HgSO₄	$Hg^{2+} + SO_4^{2-} = HgSO_4$	2.57	Smith and	-	-
Hg(SO ₄) ₂ ²⁻	Hg ²⁺ + 2 SO ₄ ²⁻ = Hg(SO ₄) ₂ ²⁻	3.63	Martell (2004) ^{a)}	-	-
Hg(HS)⁺	$Hg^{2+} + HS^{-} = Hg(HS)^{+}$	30.50	Benoit et al. (1999)	-	-
Hg(HS)₂	Hg ²⁺ + 2 HS ⁻ = Hg(HS) ₂	37.50	Benoit et al. (1999)	-	-
Hg(HS)₃⁻	Hg ²⁺ + 3 HS⁻ = Hg(HS)₃⁻	42.28	Spycher and Reed (1989)	-	-
HgS	Hg ²⁺ + HS ⁻ = HgS + H ⁺	26.50	Benoit et al. (1999)	-	-
HgS(HS) ⁻	Hg ²⁺ + 2 HS ⁻ = HgS(HS) ⁻ + H ⁺	32.00	Benoit et al. (1999)	-	-
HgS(H ₂ S) ₂	Hg ²⁺ + 3 HS ⁻ + H ⁺ = HgS(H ₂ S) ₂	48.53	Spycher and Reed (1989)	-	-
HgS ₂ ²⁻	Hg ²⁺ + 2 HS ⁻ = HgS ₂ ²⁻ + 2 H ⁺	23.50	Benoit et al. (1999)	-	-
HgCl⁺	$Hg^{2+} + CI^{-} = HgCI^{+}$	7.31±0.04		-21.300	Powell et al. (2005)
HgCl₂	$Hg^{2+} + 2 CI^{-} = HgCI_2$	14.00±0.07	Powell et al. (2005)	-49.100	. ,
HgCl ₃ -	$Hg^{2+} + 3 Cl^{-} = HgCl_{3}^{-}$	14.93±0.11		-48.600	
HgCl4 ²⁻	$Hg^{2+} + 4 Cl^{-} = HgCl_4^{2-}$	15.54±0.16		-59.100	
HgOHCI	Hg ^{∠+} + Cl ⁻ + H₂O = HgOHCl + H⁺	4.27±0.35		-	-

Table 9: Data Selection for Hg Aqueous Species

^a As reported in the SPANA database.
Name	Reaction	log₁₀K°	Reference	∆ _r H _m ° (kJ⋅mol⁻¹)	Reference
Hg(g)	$Hg^{2+} + 2 e^{-} = Hg$	23.27±0.05	Internal calculation ^{a)}	-108.830	Internal calculation ^{a)}
HgO(cr)	$Hg^{2+} + H_2O = HgO + 2 H^+$	-2.44±0.06	Internal calculation ^{a)}	24.830	Internal calculation ^{a)}
HgCl₂(s)	$Hg^{2+} + 2 CI^{-} = HgCl_2$	14.57	Anderson et al. (1974) ^{b)}	-	-
Hg ₂ Cl ₂ (cr)	$Hg_2^{2+} + 2 CI^- = Hg_2CI_2$	17.84	Internal calculation ^{a)}	-98.130	Internal calculation ^{a)}
HgS(s)	$Hg^{2+} + HS^{-} = HgS + H^{+}$	38.72	Smith and Martell (2004) ^{a)}	-214.000	Smith and Martell (2004) ^{a)}

Table 10: Data Selection for Hg Solids

^a Internal calculation: From $\Delta_{f}H_{m}^{\circ}$ and S_{m}° in Cox et al. (1989).

^b As reported in the SPANA database.

2.2.4 Ruthenium

The data sources reviewed for Ru include but are not limited to:

- Sassani and Shock (1998) and the Thermoddem database vs1.10_06Jun2017 (*https://thermoddem.brgm.fr/*, Blanc et al. 2012); and
- Rard (1985, 1987).

Ru is not included in CODATA. Thermodynamic data for the master species RuO_4^{2-} and the reference state Ru(s) have been selected from Rard (1985) and summarized in Table 11.

Ru can form compounds with valence states up to VIII. Data selection for the master species of the different redox states (Ru²⁺, Ru³⁺, Ru(OH)₂²⁺, RuO₄⁻ and RuO₄(aq), besides the primary master species RuO₄²⁻) are shown in Table 12.

Sassani and Shock (1998) discussed thermodynamic data for platinum group elements, including lower Ru oxidation states (Ru(II) and Ru(III)). Some estimated enthalpy values were also reported in the publication. For aqueous hydroxides and chloride and sulphate species are summarized in Table 12. Thermodynamic data for the solid compounds are shown in Table 13.

Thermodynamic data for higher oxidation states have been obtained from the selection in Rard (1985, 1987). Data selected for aqueous Ru(IV) hydroxides include $Ru(OH)_2^{2+}$, $Ru(OH)_4(aq)$ and the polymeric species $Ru_4(OH)_{12}^{4+}$, in agreement with the discussion in Rard (1987) (Table 12). Besides hydroxide complexes, some sulphate and chloride complexes have also been included in the selection (Table 12). Thermodynamic data for solid Ru(IV) oxides are shown in Table 13. No reliable enthalpy data for Ru(IV) species have been identified.

	Species	∆ _f G _m ° (kJ·mol⁻¹)	∆ _f H _m (kJ⋅mol⁻¹)	S _m ° (kJ⋅mol ⁻¹ ⋅K ⁻¹)	Reference
Reference State	Ru(s)	a)	a)	28.610	Rard (1985)
Master species	Ru ²⁺	-306.60	-457.000	Int. Calc.*	Rard (1985)

Table 11: Data Selection	for Ru Primary S	Species and Reference Sta	te
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^a These values of the reference state are 0 by convention. * Internal calculation

Name	Reaction	log₁₀K°	Reference	∆ _r H _m ° (kJ⋅mol⁻¹)	Reference
Ru ²⁺	RuO ₄ ²⁻ + 8 H ⁺ + 4 e ⁻ = Ru ²⁺ + 4 H ₂ O	86.15	Sassani and Shock (1998)	-538.850	Internal calculation ^{a)}
Ru ³⁺	RuO4 ²⁻ + 8 H ⁺ + 3 e ⁻ = Ru ³⁺ + 4 H ₂ O	82.09	Rard (1985)		
Ru(OH)2 ²⁺	RuO_4^{2-} + 6 H ⁺ + 2 e ⁻ = $Ru(OH)_2^{2+}$ + 2 H ₂ O	68.24	b)	-	-
RuO₄	$RuO_4^{2-} = RuO_4 + 2 e^{-1}$	-26.73	Rard (1985)	219.000	Rard (1985)
RuO₄ ⁻	$RuO_4^{2-} = RuO_4^{-} + e^{-}$	-9.90	Rard (1985)	125.000	Rard (1985)
RuOH⁺	$Ru^{2+} + H_2O = RuOH^+ + H^+$	-7.57	Sassani and Shock (1998)	42.313	Internal calculation ^{a)}
Ru(OH)₂	Ru ²⁺ + 2 H ₂ O = Ru(OH) ₂ + 2 H ⁺	-15.40	· · · ·	78.649	
RuOH ²⁺	$Ru^{3+} + H_2O = RuOH^{2+} + H^+$	-2.23	Sassani and Shock (1998)	-	-
Ru(OH)₂⁺	$Ru^{3+} + 2H_2O = Ru(OH)_2^+ + 2H^+$	-3.51		-	-
Ru₄(OH) ₁₂ 4+	$4 \operatorname{Ru}(OH)_2^{2+} + 4 \operatorname{H}_2O = \operatorname{Ru}_4(OH)_{12}^{4+} + 4 \operatorname{H}^+$	7.23	Rard (1985)	-	-
RuO₄OH ⁻	$RuO_4 + H_2O = RuO_4OH^- + H^+$	-11.52	Rard (1985)		
RuCl⁺	$Ru^{2+} + CI^{-} = RuCI^{+}$	-0.51	Sassani and Shock (1998)	5.746	Internal calculation ^{a)}
RuCl ₂	$Ru^{2+} + 2 Cl^{-} = RuCl_2$	-1.32		0.979	
RuCl₃ ⁻	$Ru^{2+} + 3 Cl^{-} = RuCl_{3}^{-}$	-2.83		-13.640	
RuCl₄²-	$Ru^{2+} + 4 Cl^{-} = RuCl_{4}^{2-}$	-4.19	_	-47.078	
RuCl ²⁺	$Ru^{3+} + CI^{-} = RuCI^{2+}$	2.17	Sassani and Shock (1998)	-	-
RuCl₂⁺	$Ru^{3+} + 2 Cl^{-} = RuCl_{2}^{+}$	3.75		-	-
RuCl₃	Ru^{3+} + 3 Cl^- = $RuCl_3$	4.30		-	-
RuCl₄ ⁻	$Ru^{3+} + 4 Cl^{-} = RuCl_{4}^{-}$	4.41		-	-
RuCl₅²-	$Ru^{3+} + 5 Cl^{-} = RuCl_{5}^{2-}$	3.85		-	-
RuCl ₆ ³⁻	$Ru^{3+} + 6 Cl^{-} = RuCl_{6}^{3-}$	3.42		-	-
Ru(OH)₂Cl	$Ru(OH)_2^{2+} + CI^{-} = Ru(OH)_2CI^{+}$	1.40	Rard (1985)	-	-
Ru(OH) ₂ Cl ₂	$Ru(OH)_{2}^{2+} + 2 CI^{2} = Ru(OH)_{2}CI_{2}$	1.83		-	-
Ru(OH) ₂ Cl ₃ -	$Ru(OH)_{2}^{2+} + 3 CI^{-} = Ru(OH)_{2}CI_{3}^{-}$	1.66		-	-
Ru(OH) ₂ Cl ₄ ²⁻	$Ru(OH)_{2^{2^{+}}} + 4 CI^{2^{-}} = Ru(OH)_{2}CI_{4^{2^{-}}}$	2.76	Saccani and	-	- Intornal
RuSO₄	$Ru^{2+} + SO_4^{2-} = RuSO_4$	2.32	Shock (1998)	5.816	calculation ^{a)}
Ru(SO ₄)2 ²⁻	$Ru^{2+} + 2 SO_4^{2-} = Ru(SO_4)_2^{2-}$	3.99		15.468	
Ru(SO ₄) ₃ 4-	$Ru^{2+} + 3 SO_4^{2-} = Ru(SO_4)_3^{4-}$	5.07	o · · ·	28.487	
RuSO₄⁺	$Ru^{3+} + SO_4^{2-} = RuSO_4^+$	1.99	Sassani and Shock (1998)	-	-
Ru(SO₄)₂⁻	Ru ³⁺ + 2 SO ₄ ²⁻ = Ru(SO ₄) ₂ ⁻	2.55		-	-
Ru(SO ₄) ₃ -	Ru ³⁺ + 3 SO ₄ ²⁻ = Ru(SO ₄) ₃ ³⁻	2.09		-	-
Ru(OH)₂SO₄	$Ru(OH)_2^{2+} + SO_4^{2-} = Ru(OH)_2SO_4$	1.80	Rard (1985)	10.200	Rard (1985)

Table 12: Data Selection for Ru Aqueous Species

^a Internal calculation: S_m° from Sassani and Shock (1998). ^b Rard (1987) as reported in LLNL database.

Name	Reaction	log₁₀K°	Reference	∆rHm° (kJ∙mol⁻¹)	Reference
Ru(OH)₃:H₂O(am)	Ru ³⁺ + 4 H ₂ O = Ru(OH) ₃ :H ₂ O + 3 H ⁺	-1.61	Rard (1985)	-	-
RuO ₂ (cr)	$Ru(OH)_2^{2+} = RuO_2 + 2 H^+$	5.48		-	-
RuO ₂ :2H ₂ O(am)	$Ru(OH)_2^{2+} + 2 H_2O =$ $RuO_2:2H_2O + 2 H^+$	-0.89	Rard (1985)	-	-
RuO₄(s)	$RuO_4 = RuO_4(s)$	0.96	Rard (1985)	-	-
Laurite	$Ru^{2+} + 2 HS^{-} = RuS_2 + 2 H^{+}$ + 2 e ⁻	63.54	a)	-	-

Table 13: Data Selection for Ru Solids

^a Rard (1987) as reported in LLNL database.

2.2.5 Radon

Radon is a naturally occurring member of the uranium, thorium and actinium series. Most of the uranium series elements are solids; however, radon is a gas. Thus, its solubility cannot be determined in the same way as for the other elements of interest.

The most usual way of quantifying the radon concentration dissolved in liquid media is using the partitioning coefficient of radon gas between air and water, $K_{w/air}$.

The temperature dependence of $K_{w/air}$ is well reported in the literature. Weigel (1978) introduced an empirical equation for quantifying the temperature influence on radon partitioning between pure water and air (Equation 5) which agreed with the available experimental data at the time. This equation calculates the partition coefficient of ²²²Rn between pure water and air by assuming a constant salinity value of 0‰; T is the temperature in Celsius.

$$K_{w/air} = \frac{C_w}{C_{air}} = f(T) = 0.105 + 0.405e^{-0.0502T[^{\circ}C]}$$
 Equation 5

There are very limited data available for $K_{w/air}$ dependence with salinity. It is nevertheless possible to apply the Equation 6 derived by Weiss (Weiss et al 1970, 1971; Weiss and Kyser 1978) for other noble gases (He, Ne, Ar and Kr) to radon, as described in section 4.1.19.

$$ln\beta = a_1 + a_2 \left(\frac{100}{T}\right) + a_3 ln \left(\frac{T}{100}\right) + S \left\{b_1 + b_2 \left(\frac{T}{100}\right) + b_3 \left(\frac{T}{100}\right)^2\right\}$$
 Equation 6

3. EFFECT OF THE NEAR FIELD ON CR-10 GROUNDWATER COMPOSITION

The composition of the groundwater (Table 1) can be affected by its interaction with the components of the repository near field. Three different scenarios are studied in this work:

- Scenario 1 (SC1): Groundwater enters the canister without interacting with the bentonite buffer or the canister materials. In this scenario the CR-10 water composition has been re-equilibrated with host-rock mineralogy by using the modified ThermoChimie database to avoid undesired re-equilibration effects in the subsequent calculations in Scenario 2 and Scenario 3.
- Scenario 2 (SC2): Groundwater interacts with the carbon-steel container prior to contacting the used nuclear fuel waste inside the container. The main component of C-steel is Fe(0). In the absence of other oxidants, Fe(0) will anoxically corrode by the reduction of water, and this corrosion process will have an influence in the groundwater composition.
- Scenario 3 (SC3): Groundwater interacts with both bentonite buffer and the C-steel container prior to contacting the used nuclear fuel waste inside the container.

In all scenarios, four different temperatures (15°C, 25°C, 50°C and 80°C) are considered.

In calculations it is assumed that sulphate to sulphide reduction does not occur whereas any sulphide present in solution can be easily oxidized to sulphate if thermodynamically favoured. The reduction of carbonate to methane and the reduction of nitrate to ammonium or $N_2(g)$ are also neglected. The reason for these assumptions is that all these processes (sulphate reduction, methanogenesis and denitrification) are normally microbiologically mediated (Pedersen 2000) and the microbial activity has not been considered in this study. The absence of bacterial activity in the clay buffer is supported by the small pore space of the compacted bentonite, which makes the growth of microorganisms very difficult (SKB 2004b).

3.1 SCENARIO 1

In Scenario 1, groundwater (CR-10) enters the canister without interacting with the bentonite buffer or the canister materials.

In this scenario the initial CR-10 water composition (Table 1) has been recalculated to avoid undesired effects due to initial groundwater re-equilibration in Scenario 2 and Scenario 3. The minerals taken into account in the calculations are gypsum (at temperatures below 40°C), anhydrite (dehydrated calcium sulphate, at temperatures above 40°C), calcite, quartz, magnetite, goethite and fluorite. Most of these minerals (specifically gypsum, calcite, quartz, magnetite and fluorite) have been observed in fractures of the Canadian Shield (Blyth et al. 2009; Gascoyne and Kamineni 1992; Gascoyne 1996).

Hematite and goethite (α -FeOOH) are crystalline solid phases usually formed by recristallization or aging of the amorphous Fe(III) oxy-hydroxide ferrihydrite. The mineralogical characterisation of the fractures reports the presence of hematite (α -Fe₂O₃) (Bluth et al. 2009). The solubility of hematite is very low¹, and it is unlikely controlling the concentrations of iron in solution. Goethite and magnetite have been included in the equilibration as they provide more accurate results when comparing the original CR-10 groundwater Eh (pe) values with the re-equilibrated composition (see Table 14).

Gypsum (hydrated calcium sulphate) transforms into anhydrite (dehydrated calcium sulphate) at temperatures above 40°C-60°C (Corti and Fernandez-Prini 1984; Gailhanaou et al. 2017). Therefore, the calculations were conducted by allowing the precipitation of gypsum at T 15°C and 25°C, while assuming that anhydrite is the calcium sulphate phase forming for temperature over 40°C.

In order to overcome the uncertainties related to those assumptions, the effect of calculated sulphate and iron concentrations on the solubility of elements with a special sensitivity towards those ligands is also evaluated (see the examples of radium and selenium in sections 4.18 and 4.23).

Calculations are summarized in Figure 4.



Figure 4: Summary of the Cases Evaluated for SCENARIO 1

The resulting groundwater composition at the different temperatures of interest is shown in Table 14. The temperature increase results in a pH decrease (and a pe increase) consistent with the change of water properties with temperature (pK_w of water varies from 14 at 25°C to 12.6 at 80°C). No significant gaps on thermodynamic data for temperature correction have been identified in this calculation.

¹ Including hematite in the calculations results in pH and Eh deviations from the original CR-10 composition at 25°C.

		SCEN	ARIO 1		Unaltered CR-10
Temperature	15°C	25°C	50°C	80°C	25°C
рН	7.23	7.03	6.68	6.40	7.00
ре	-3.40	-3.26	-3.03	-2.89	-3.39
Solutes (m)					
Na	8.36·10 ⁻²	8.36·10 ⁻²	8.36·10 ⁻²	8.36·10 ⁻²	8.36·10 ⁻²
K	3.88 ∙ 10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴
Ca	5.47·10 ⁻²	5.52·10 ⁻²	5.48·10 ⁻²	5.11·10 ⁻²	5.38·10 ⁻²
Mg	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³
HCO ₃	8.00·10 ⁻⁴	9.07·10 ⁻⁴	1.05·10 ⁻³	1.06⋅10 ⁻³	1.16·10 ⁻³
SO ₄	1.19·10 ⁻²	1.23·10 ⁻²	1.17⋅10 ⁻²	7.93·10 ⁻³	1.05·10 ⁻²
CI	1.74·10⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹
F	5.84·10 ⁻⁵	6.96·10 ⁻⁵	1.06·10 ⁻⁴	1.73·10 ⁻⁴	1.06.10-4
Si	1.34·10 ⁻⁴	1.81·10 ⁻⁴	3.50·10 ⁻⁴	6.84·10 ⁻⁴	1.80·10 ⁻⁴
Fe	2.38·10 ⁻⁴	1.65·10 ⁻⁴	5.07·10 ⁻⁵	1.03·10 ⁻⁵	1.81·10 ⁻⁵

Table 14: SCENARIO 1: Groundwater Composition at the Different Temperatures of Interest After Equilibration with Main Major Host-Rock Minerals. Unaltered CR-10 is Also Included for Comparison

3.2 SCENARIO 2

In Scenario 2, groundwater interacts with the carbon-steel container prior to contacting the used nuclear fuel waste inside the container.

The main component of C-steel is Fe(0). In the absence of other oxidants, Fe(0) will anoxically corrode to $Fe(OH)_2(s)$ and with time towards Fe_3O_4 (magnetite), according to the Schikorr reaction (Duro et al. 2010; Duro et al. 2014). The global redox reaction of transformation of iron into magnetite under anoxic conditions is shown in Reaction 1.

3 Fe (s) + 4 H₂O \leftrightarrow Fe₃O₄ (s) + 4 H₂(g) Reaction 1

C-steel corrosion (and therefore, Fe(0) corrosion) is considered to be kinetically controlled. Corrosion rates can be affected by different parameters, such as temperature, or the hydrodynamics of the system. In order to evaluate the uncertainty associated with those parameters, the corrosion rates presented below have been used in the calculations based on literature research:

- The aerobic corrosion rate in all calculations is selected as 2 μm·y⁻¹ reported by King (2007) (NWMO TR-2007-01).
- The anaerobic corrosion rate has considered three different values to evaluate if it has a significant influence in the results of the calculations:
 - A mean value of 1 μm·y⁻¹, which is the mean corrosion rate for Base Case simulations in King and Kolar (2012) (NWMO TR-2012-07).

- $\circ~$ A high corrosion rate of 5 $\mu m \cdot y^{-1},$ as reported in King and Kolar (2012) (NWMO TR-2012-07).
- A low corrosion rate of 0.005 μ m y⁻¹, from Smart and Hochs (2006). This value is the one used in Duro et al. (2010).

The corrosion rate is expected to increase with temperature according to an Arrhenius relationship (Smart and Hoch 2010). To include the effect of temperature on the corrosion rates, the corrosion rate values described above have been scaled by the factors reported in Table 15 (Smart and Hoch 2010).

T (°C)	Factor Aerobic Conditions	Factor Anaerobic Conditions
15	0.87	0.31
25	1.14	0.69
50	2.06	3.96
80	3.76	23.23

Table 15: Scaling Factors of Steel Corrosion Rates with Temperature, Calculated from the Equations Reported in Smart and Hoch (2010)

Due to the input characteristics of the geochemical code PHREEQC/PHREEQCI (Parkhurst and Appelo 2013) which will be used for the solubility/speciation calculations in this work, the C-steel corrosion rate in μ m·y⁻¹ must be converted to mol(Fe)·m⁻²·s⁻¹. A C-steel density of 7,860 kg·m⁻³ with a composition of 98% Fe (from Sriram and Tromans 1985, as reported in Duro et al. 2010) is used for the conversion.

A steel reactive surface area of 21.2 m² (including a steel vessel inner surface area of 3.6 m² and a total steel surface area of used fuel container basket of 17.6 m²) is used in the calculations (see Appendix A). By considering the porosity of the bentonite (38.2%) and a total amount of bentonite in the buffer box of 2.3085 m³ (see Appendix A), the ratio of the steel surface area to the water volume is calculated as 0.02 m² of reactive surface area per dm³ of water.

The initial amount of steel in the media is assumed to be sufficiently large not to be exhausted in any case.

The generation of hydrogen shown in Reaction 1 is important to be considered in the calculation; the final composition of the groundwater retained for the solubility calculation is set to achieve a maximum hydrogen pressure. Two different limiting hydrogen pressures have been used in the calculations (see Appendix A):

- 6.4 MPa, corresponding to the nominal swelling pressure of Highly Compacted Bentonite (HCB) at saturation within the Buffer Box; and
- 3.8 MPa, corresponding to the nominal swelling pressure of HCB for Placement Room and tunnel seals.

As a result of the different conditions described above, different sensitivity cases have been considered in the calculations; the parameters used for each case are summarized in Table 16 and Figure 5.

	1	2	3	4	5	6
Temperature(°C)	15, 25, 50,	15, 25, 50,	15, 25, 50,	15, 25, 50,	15, 25, 50,	15, 25, 50,
	80	80	80	80	80	80
Aerobic	2 µm₊y⁻¹	2 µm⋅y⁻¹	2 µm⋅y⁻¹	2 µm⋅y⁻¹	2 µm∙y⁻¹	2 µm∙y⁻¹
corrosion rate a)	(x T factor)					
Anaerobic	1 µm₊y⁻¹	1 µm⋅y⁻¹	5 µm∙y⁻¹	5 µm∙y⁻¹	0.005	0.005
corrosion rate a)	(x T factor)	(x T factor)	(x T factor)	(x T factor)	µm₊y⁻¹	µm∙y⁻¹
					(x T factor)	(x T factor)
Steel surface	0.02 m ^{2.} dm ⁻³					
area exposed						
to corrosion						
Maximum H ₂ (g)	6.4 MPa	3.8 MPa	6.4 MPa	3.8 MPa	6.4 MPa	3.8 MPa
pressure						

Table 16: Parameters Used for the Different Cases in SCENARIO 2

^a Must be converted to mol(Fe)·m⁻²·s⁻¹ for PHREEQCI calculations.



Figure 5: Summary of the Different Cases Evaluated for SCENARIO 2. Cases with the Same Colour Provide Exactly the Same Groundwater Compositions

The results for all the simulated cases are given in Appendix B. A detailed analysis of the results *at a given temperature* indicates that calculated groundwater compositions are very similar for all cases (cases with the same colour in Figure 5 provide exactly the same results). The only parameter having a very small influence on the simulated groundwater composition is the maximum hydrogen pressure that the system is allowed to develop due to the steel corrosion. The changes in maximum hydrogen pressure result in differences in pH or Eh of less than 0.1 log units (at a given temperature).

The parameters for Scenario 2 – Case 1 (labeled as "SC2 - base case" in Figure 5) have been used to obtain the calculated groundwater compositions at 15°C, 25°C, 50°C and 80°C summarized in Table 17. These groundwater compositions are used in the solubility calculations for Scenario 2 conditions in section 4.

		SCEN	ARIO 2	
Temperature	15°C	25°C	50°C	80°C
pH .	8.73	8.46	7.81	7.17
pe	-9.63	-9.36	-8.71	-8.07
Solutes (m)				
Na	8.38·10 ⁻²	8.37·10 ⁻²	8.37·10 ⁻²	8.37·10 ⁻²
K	3.89·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴
Ca	5.44·10 ⁻²	5.47·10 ⁻²	5.42·10 ⁻²	5.06·10 ⁻²
Mg	2.51·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10⁻³
HCO ₃	4.09·10 ⁻⁵	4.53·10 ⁻⁵	7.61·10 ⁻⁵	1.58·10 ⁻⁴
SO ₄	1.19·10 ⁻²	1.23·10 ⁻²	1.17·10 ⁻²	7.94·10 ⁻³
CI	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹
F	5.85·10 ⁻⁵	6.97·10⁻⁵	1.06.10-4	1.73·10 ⁻⁴
Si	1.34·10 ⁻⁴	1.81·10 ⁻⁴	3.50·10 ⁻⁴	6.84·10 ⁻⁴
Fe	3.10·10 ⁻⁴	3.06·10 ⁻⁴	2.93·10 ⁻⁴	2.67·10⁻⁴

Table 17: SCENARIO 2: Groundwater Composition at the Different Temperatures of Interest After Interaction with C-steel Container

The comparison of Scenario 1 and Scenario 2 calculated results indicates that, independently of the system temperature, the interaction of groundwater with C-steel and its corresponding corrosion products increases the alkalinity and the reducing character of the groundwater.

3.3 SCENARIO 3

In Scenario 3, groundwater interacts with both bentonite buffer and the C-steel container prior to contact the used nuclear fuel waste inside the container.

Different mineralogical compositions for bentonite have been reported in the literature. The composition of the MX-80 bentonite used in Duro et al. (2010) (from SKB 2004a) has been used in the calculations in the present work and is reported in Table 18.

	Mineral (wt%)
Montmorillonite	87±3 ^{a)}
Quartz	3.0±0.5
Cristobalite	2.0±0.5
Mica	4±1
Albite	3±1
Anortoclasse	0±1
Calcite+siderite	0±1

Table 18: Mineralogical Composition of the Clay Fraction of Bentonite MX-80, from SKB(2004a)

0.07±0.05 0.7±0.2

Details on how bentonite mineralogical composition has been handled in the calculations are provided below and summarized in Table 19.

Pyrite

Gypsum

The main component of bentonite is montmorillonite. However, its dissolution rate is very slow under near neutral pH (Cama et al. 2000) so that montmorillonite dissolution is a minor process that will hardly affect the geochemical evolution of the system. The illitization of montmorillonite is also believed to have minor influences on the pore water chemistry in the repository environment (Karnland 1995). Therefore, both montmorillonite dissolution and montmorillonite illitization have not been explicitly included in the calculations.

Cristobalite and quartz have not been distinguished in the calculations. Groundwater compositions are equilibrated with 5 wt% of SiO₂ (quartz), considering this amount as the sum of initial quartz and cristobalite content in MX-80 bentonite (3 wt% and 2 wt%, respectively).

Even if the nominal value of carbonates is 0 in SKB (2004a), 0.7 wt% of calcite and 0.7 wt% of siderite have been considered in the calculations. The inclusion of those carbonates is to account for the buffering capacity as well as in the radionuclide complexation capacity of carbonates.

Precipitation / dissolution of calcium sulphate may control the calcium availability in the system, directly affecting those reactions where calcium or sulphate are involved. Therefore, precipitation (or dissolution) of CaSO₄·2H₂O (gypsum) has been considered in the calculations at 15°C and 25°C. In the case of higher temperatures (50°C and 80°C) precipitation (or dissolution) of dehydrated calcium sulphate (CaSO₄(s), anhydrite) has been considered in calculations.

Pyrite dissolution is shown in Reaction 2. Pyrite is considered to dissolve according to the kinetic rate law described by Williamson and Rimstidt (1994) (Equation 7).

$$FeS_{2}(s) + 3.75O_{2}(g) + 3.5H_{2}O \leftrightarrow Fe(OH)_{3}(s) + 2SO_{4}^{2-} + 4H^{+}$$
Reaction 2

^a The montmorillonite content of 87% agrees with the reference value of >80 wt% suggested in NWMO-TR-2019-07 (Dixon 2019).

$$R_{py}(mol \cdot m^{-2} \cdot s^{-1}) = 10^{-8.19(\pm 0.10)} \frac{[O_2(aq)]^{0.50(\pm 0.04)}}{[H^+]^{0.11(\pm 0.01)}}$$
 Equation 7

To obtain the moles of mineral per dm³ shown in Table 19 two different cases have been considered (see Appendix A):

- Scenario 3 Case A corresponds to porosity of 38.2% and density of 1700 kg·m⁻³; and
- Scenario 3 Case B corresponds to porosity of 41.8% and density of 1600 kg m⁻³.

Besides the minerals described above, additional secondary iron minerals (goethite, magnetite) have been allowed to precipitate if oversaturated.

Table 19: Composition of Bentonite Used in SCENARIO 3 Calculations, in moles of Mineral per dm⁻³ of Water. Case A Corresponds to Porosity of 0.382 and Density of 1700 kg·m⁻³; Case B Corresponds to Porosity of 0.418 and Density of 1600 kg·m⁻³

		Mineral (mol∙dm⁻³)
		Case A	Case B
Montmorillonite	Not reactive		
Quartz + cristobalite	Equilibrium	3.70	3.19
Mica	Not reactive		
Albite	Not reactive		
Calcite	Equilibrium	0.31	0.27
Siderite	Equilibrium	0.27	0.23
Pyrite	Kinetics	0.026	0.022
Gypsum	Equilibrium	0.181	0.156

Another process that could have a significant role in the geochemical evolution of the system is the surface protonation of montmorillonite. The protonation of the surface edge of montmorillonite contributes to pH buffering according to Reaction 3 and Reaction 4, where ">sOH" stands for the surface groups of the solid.

>sOH + H⁺ ↔ >sOH₂⁺	Reaction 3
>sOH ↔ >sO⁻ + H⁺	Reaction 4

Bradbury and Baeyens (2002) considered two different types of weak protonation-deprotonation surface sites, $S_{w1}OH$ and $S_{w2}OH$, for MX-80 montmorillonite. They obtained the log *K* for the protonation-deprotonation reactions and the capacities of each site from the analyses of batch titration experiments on dispersed systems. The log *K* values and site capacities used in this report are those of Bradbury and Baeyens (2002), listed in Table 20. The surface area of MX-80 montmorillonite used in the calculations is $31.3 \text{ m}^2 \cdot \text{g}^{-1}$ (Bradbury and Baeyens 2002). To obtain the moles of sites per dm³, Scenario 3 – case A and Scenario 3 - case B porosity and density data described above have been used.

The effect of temperature on the surface chemistry of Na-montmorillonite and K-montmorillonite was studied by Tertre et al. (2006), Duc et al. (2008) and Rozalén et al. (2009). In all these

publications, temperature is reported to have a very small effect on the acid-base properties of montmorillonite, at least in comparison with the effect of temperature on the pK_w of water. Thus, the log *K* values reported in Table 20 have been used at all the studied temperatures.

Table 20: Properties of Montmorillonite Surface Sites Used in SCENARIO 3 Calculations. Log K of Protonation and Deprotonation Reactions Have Been Obtained from Bradbury and Baeyens (2002). Case A Corresponds to Porosity of 0.382 and Density of 1700 kg·m⁻³; Case B Corresponds to Porosity of 0.418 and Density of 1600 kg·m⁻³

Surface	Log K	Site capacities			
		Cas	Case A		se B
		mol-kg ⁻²	mol∙dm⁻³	mol∙kg⁻²	mol∙dm⁻³
s _{w1} OH		4.00·10 ⁻²	0.15	4.00·10 ⁻²	0.13
$>$ S _{W1} OH + H ⁺ \leftrightarrow $>$ S _{W1} OH ₂ ⁺	4.5				
$>$ s w ₁ OH \leftrightarrow $>$ s w ₁ O ⁻ + H ⁺	-7.9				
s _{w2} OH		4.00·10 ⁻²	0.15	4.00·10 ⁻²	0.13
$>$ S _{W2} OH + H ⁺ \leftrightarrow $>$ S _{W2} OH ₂ ⁺	6.0				
$>$ s w ₂ OH \leftrightarrow $>$ s w ₂ O ⁻ + H ⁺	-10.5				

The cation exchange capacity of the MX-80 bentonite used in Duro et al. (2010) (from SKB 2004a) has been used in the calculations in the present work and is reported in Table 21. The values are in agreement with the values suggested in NWMO-TR-2019-07 (Dixon 2019); those values are also provided in the table for comparison. To obtain the moles of sites per dm⁻³, Scenario 3 – case A and Scenario 3 - case B porosity and density data described above have been used.

Table 21: Initial Exchange Composition of MX-80 Bentonite (meq/100g) Used in the Calculations. Values in moles per dm⁻³ of Water Have Been Calculated for Repository Conditions; Case A Corresponds to Porosity of 0.382 and Density of 1700 kg·m⁻³; Case B Corresponds to Porosity of 0.418 and Density of 1600 kg·m⁻³. Reference Values from Dixon (2019) Are Also Provided for Comparison

	Dixon (2019) ^{a)}	SKB (2004a)		
CEC (meq·100g ⁻¹)	>75	75±2		
NaX KX	<i>meq</i> • 100g ⁻¹ >50	<i>meq∙100g</i> ⁻¹ 54 1.5	Case A mol·dm ⁻³ 2.09 0.058	Case B mol∙dm ⁻³ 1.80 0.050
MgX₂ CaX₂	<6 <15	6 13.5	0.116	0.100
FeX ₂		0	0	0

^a Provided for comparison purposes only.

Selectivity exchange coefficients for cation exchange reactions (Reaction 5, Reaction 6 and Reaction 7) have been also selected from Bradbury and Baeyens (2002). Partial substitution of interlayer major cations by Fe²⁺ in montmorillonite would also be expected, according to Reaction 8. An average value of 0.4 (Charlet and Tournassat 2005) was used in the calculations.

The temperature influence on the exchange constants has been considered negligible, and the same constants have been used for all temperatures.

$2 \text{ NaX} + \text{Ca}^{2+} \leftrightarrow \text{CaX}_2 + 2\text{Na}^+$	Log $K = 0.41$	Reaction 5
$2 \text{ NaX} + \text{Mg}^{2+} \leftrightarrow \text{MgX}_2 + 2\text{Na}^+$	Log K = 0.34	Reaction 6
NaX + K⁺ ↔ KX + Na⁺	Log K = 0.60	Reaction 7
$2 \text{ NaX} + \text{Fe}^{2+} \leftrightarrow \text{FeX}_2 + 2\text{Na}^+$	Log K = 0.40	Reaction 8

C-steel corrosion processes (see section 3.2) have also been included in the calculations; the parameters are summarized in Table 22.

Table 22: C-steel Corrosion Parameters Used for the Cases in SCENARIO 3. Case A Corresponds to Porosity of 0.382 and Density of 1700 kg·m⁻³; Case B Corresponds to Porosity of 0.418 and Density of 1600 kg·m⁻³

	Case A	Case B
Temperature (°C)	15, 25, 50, 80	15, 25, 50, 80
Aerobic corrosion rate ^{a)}	2 µm⋅y⁻¹ (x T factor)	2 µm⋅y⁻¹ (x T factor)
Anaerobic corrosion rate ^{a)}	`1 μm⋅y⁻¹´ (x T factor)	`1 μm⋅y⁻1´ (x T factor)
Steel surface area exposed to corrosion	0.02 m ² ·dm ⁻³	0.02 m ² ·dm ⁻³
Maximum H₂(g) pressure	6.4 MPa	3.8 MPa

^a Must be converted to $mol(Fe) \cdot m^{-2} \cdot s^{-1}$ for PHREEQC calculations.

As a result of the different conditions and parameters described above, the different cases summarized in Figure 6 have been calculated; the corresponding groundwater compositions are summarized in Table 23.

The differences in bentonite porosity and density (Case A corresponds to porosity 38.2% and density 1700 kg·m⁻³ and Case B corresponds to porosity 41.8% and density 1600 kg m⁻³) result in small differences in the calculated groundwater compositions at a given temperature. Results for Scenario 3 – Case A (green squares in Figure 6) at 15°C, 25°C, 50°C and 80°C are used in the solubility calculations under Scenario 3 conditions reported in Section 4. The results obtained in Scenario 3 - Case B are used to perform sensitivity analysis calculations.



Figure 6: Summary of the Different Cases Evaluated for SCENARIO 3

Table 23: SCENARIO 3: Groundwater Composition at the Different Temperatures of Interest After Interaction with Bentonite and C-steel Container. Case A Corresponds to Porosity of 0.382 and Density of 1700 kg·m⁻³; Case B Corresponds to Porosity of 0.418 and Density of 1600 kg·m⁻³

				SCEN	ARIO 3			
		Cas	se A			Cas	se B	
	(E	Base Case fo	or Scenario	3)	(Sensi	tivity Analy	sis for Scen	ario 3)
Temp.	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C
рН	9.03	8.77	8.16	7.54	8.75	8.54	8.10	7.51
ре	-9.93	-9.67	-9.06	-8.44	-9.54	-9.32	-8.89	-8.29
Solutes (m)								
Na	2.48·10 ⁻¹	2.43·10 ⁻¹	2.27·10 ⁻¹	2.10·10 ⁻¹	2.26·10 ⁻¹	2.24·10 ⁻¹	2.18·10 ⁻¹	2.03·10 ⁻¹
K	1.83∙10 ⁻³	1.79∙10 ⁻³	1.66∙10 ⁻³	1.53⋅10 ⁻³	1.67∙10 ⁻³	1.65 ⋅ 10 ⁻³	1.60∙10 ⁻³	1.48·10 ⁻³
Ca	1.45·10 ⁻²	1.39·10 ⁻²	1.17·10 ⁻²	9.18·10 ⁻³	1.23·10 ⁻²	1.20·10 ⁻²	1.11·10 ⁻²	8.91·10 ⁻³
Mg	6.02·10 ⁻³	5.79·10 ⁻³	5.02·10 ⁻³	4.10·10 ⁻³	5.11·10 ⁻³	5.01·10 ⁻³	4.69·10 ⁻³	3.91·10 ⁻³
HCO ₃	6.91·10 ⁻⁵	8.16·10⁻⁵	1.59·10 ⁻⁴	3.66·10 ⁻⁴	1.19·10 ⁻⁴	1.36·10 ⁻⁴	1.82·10 ⁻⁴	3.99·10 ⁻⁴
SO ₄	1.19·10 ⁻²	1.23·10 ⁻²	1.17·10 ⁻²	7.93·10 ⁻³	1.19·10 ⁻²	1.23·10 ⁻²	1.17·10 ⁻²	7.93·10 ⁻³
CI	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹					
F	5.84·10 ⁻⁵	6.96·10 ⁻⁵	1.06·10 ⁻⁴	1.73·10 ⁻⁴	5.84·10 ⁻⁵	6.96·10 ⁻⁵	1.06·10 ⁻⁴	1.73·10 ⁻⁴
Si	1.54·10 ⁻⁴	2.03·10 ⁻⁴	3.75·10 ⁻⁴	7.12·10 ⁻⁴	1.44·10 ⁻⁴	1.93·10 ⁻⁴	3.72·10 ⁻⁴	7.10·10 ⁻⁴
Fe	9.32·10 ⁻⁵	8.56·10 ⁻⁵	6.90·10 ⁻⁵	5.35·10 ⁻⁵	7.79·10 ⁻⁵	7.33·10 ⁻⁵	6.54·10 ⁻⁵	5.18·10 ⁻⁵

The groundwater results obtained in Scenario 3 (influence by both bentonite and C-Steel corrosion) are similar to those obtained in Scenario 2 (influence by steel corrosion only). Bentonite effect results in a slight pH increase (and a slight pe decrease) in comparison with the results in Scenario 2. The groundwater composition of the exchangeable cations (and related elements) are also affected by bentonite properties.

4. RADIONUCLIDE SOLUBILITY CALCULATIONS

The approach for assessing the radionuclide solubility limits under the three defined scenarios of interest is as follows:

- Selection of the solid phase most likely to precipitate in the studied system at each Scenario. In general, this selection is mainly based on the expert judgement considering that a) solids with complex chemical composition are unlikely to form by precipitation and b) the less crystalline phases are kinetically favoured and consequently they constitute the initial solubility limiting solid phases (Ostwald's rule). In several cases, the solubility of different solids likely to form are reported.
- Calculation of the solubility of the solid phase most likely to precipitate and the corresponding aqueous speciation. The studied element is assumed to be in equilibrium with the selected solid phase in the porewater composition at each temperature of interest.

Phosphate and organics compounds, whose concentrations in CR-10 are not available, have not been included in the calculations. Nitrate has neither been included (as shown in Table 1 only an upper-limit value is available in CR-10). However, if the presence of those ligands affects the solubility or speciation of any of the studied elements, this has been semiquantitatively discussed, when possible.

In the calculations it is assumed that sulphate to sulphide reduction does not occur and the reduction of carbonate to methane is also neglected. The uncertainty due to sulphide presence has been semi-quantitatively assessed for elements sensitive to this ligand (see section 5).

As mentioned in section 2.1, the Van't Hoff equation (Equation 1) is used to perform calculations at temperatures different than 25°C. In this approach, the temperature dependence of the equilibrium constant $log_{10}K^{\circ}(T)$ is written as a function of the enthalpy of reaction, $\Delta_r H^{\circ}_m$. Whenever possible, experimental data are selected in the database to obtain this parameter. Nevertheless, aqueous and solid chemistry and geochemistry of radionuclides has been mostly studied at room temperature, mainly because performing experiments at temperatures different than 25°C is not straightforward and requires dedicated efforts and specific equipment. Therefore, besides experimental data, estimated enthalphy and entropy values are also included in the thermodynamic database to fill in the data gaps.

For aqueous species, most of the available methods uses correlations between entropies of analogous complexes and parameters such as crystallographic radii, molar volumes and mass, electrical charge, etc. Three methods are commonly used in ThermoChimie (and in the data selection for Bi, Cu, Hg and Ru in section 2.2) in order to fill in data gaps:

- Langmuir (1978) and related references: based on the correlation among entropies of aqueous complexes and the charge (z) of the complexes.
- Shock et al. (1997) and related references: based on the correlation among experimental standard molal entropies of an aqueous hydroxide complex and the standard molal entropy of the corresponding cation.
- Sverjensky et al. (1997) and related references: based on the correlation between entropy of reaction and standard molal entropies of the cation and the ligand.

On the contrary, methods to estimate the enthalpy or entropy data of solid compounds are limited. One of the most used methods was described in Latimer (1951, 1952), in which the entropy of a solid salt is based on adding ionic contributions of the negative and positive ions. Nevertheless, there is a lack of knowledge on the applicability of these estimation procedures for amorphous solid compounds. This limits its use when building the thermodynamic database.

Temperature dependent parameters (either experimental or estimated) are available for most major ions (e.g. C) and some toxic elements (e.g. Ag, Pb). Even though, there are still data gaps that cannot be covered with estimations. In the case of radionuclides, enthalpy data are lacking for some carbonate and silicate aqueous species and some non-crystalline solids (e.g. Th).

Three different situations have been identified (Table 24):

- Those systems for which reaction enthalpies are available for both the solid compound and the main aqueous species.
- Those systems for which reaction enthalpies are not available for the solid compound or the main aqueous species.
- Those systems for which reaction enthalpies are not available for the solid compound neither for the main aqueous species.

For those systems with no reaction enthalpy parameters, qualitative analysis on the influence of temperature on the solubility has been done, using analogies and similitudes among elements or qualitative observations from experiments at temperatures other than 25°C.

Table 24: Qualitative Analysis of Available Enthalpy Data for the Elements of Interest in
the Present Work

Δ _r H° _m available for both solid and main aqueous species	Δ _r H° _m not available for the solid or for the main aqueous species	Δ _r H° _m not available for the solid neither the main aqueous species
Ag, C, Ca, Cd, Cu, Fe, Mo, Nb, Pb, Pd, Ra, S, Sb, Se, Sr	Am, Bi, Hg, Np, Pu, Sn, Tc, U	Pa, Ru, Th, Zr

The SIT approach (Equation 2) is used in order to perform ionic strength corrections. The first part of the expression is the Debye-Hückel term, that accounts for the long-range electrostatic interactions and is of special relevance in dilute solutions. At higher ionic strengths, the ϵ term accounts for short-range, non-electrostatic interactions.

If reliable individual interaction coefficients are available, it is possible to calculate $log_{10}K^0$ values accordingly. Whenever correction using the SIT approach is impossible, due to lack of data, the Debye-Hückel term will dominate the correction.

For the SIT approach (Equation 2), two main parameters will play a key role in the activity calculations:

- The ionic strength (I) of the solution. In diluted solutions the Debye-Hückel term will dominate the correction.
- The charge (z) of the dominant aqueous species. If the aqueous speciation of an element is dominated by highly charged species, the influence of the SIT correction will be higher than if the aqueous speciation is dominated by a neutral species.

ThermoChimie includes the following SIT interaction coefficients ϵ (anion, Na⁺), ϵ (cation, Cl⁻), ϵ (cation, ClO₄⁻) and ϵ (cation, NO₃⁻). For systems including the appropriate SIT interaction coefficients, the database also includes the consistent complexation constants if required. Interactions with sodium and chloride, major ions in CR-10 groundwater, are the most relevant ones in CR-10 conditions and in the altered groundwaters after CR-10 interaction with the near field of the repository. Interactions with other relevant ligands such as calcium, sulphate and carbonate are handled in the database by the inclusion of the appropriate complexation constants.

Solubility calculation results are provided in the following sub-sections. For each element, the following information is included:

- Information about the element that can be relevant for the solubility assessment, including the main oxidation states, the ligands mostly affecting its chemistry, and the availability of enthalpy data for solids and aqueous species relevant under the studied conditions.
- The calculated solubility (m, moles of solute per kg solvent) and associated speciation for each temperature at each Scenario, in the form of tables, and the associated discussion.
- A semi-quantitative analysis of the uncertainties affecting solubility calculations (e.g., sulphate to sulphide reduction or coprecipitation).

4.1 Ag

Silver is a metallic element. Under the conditions studied in the present work, it will only be in the oxidation state +I. Its aqueous chemistry will be mainly driven by complexation against soft ligands such as chlorine, carbonate or sulfate, depending on the groundwater composition.

The enthalpy data are available for all relevant solid and aqueous species in the calculations.

4.1.1 Ag Solubility in Scenario 1

In Scenario 1 conditions, AgCl(s) is expected to be the solubility limiting phase for all the studied temperatures. Calculated aqueous concentrations range from 10^{-6} m at 15° C to 10^{-4} m at 80° C (Table 25), as the solubility increases with temperature. The aqueous chemistry of silver will be governed by chlorine complexation, with AgCl₂⁻ species being the predominant one at all studied temperatures (Table 26).

The effect of chloride concentration in the solubility is shown in Figure 7; an increase of chloride concentration from 10^{-2} M to 10^{-1} M (where M is mols of solute per liter of solvent) increases AgCl(s) solubility one order of magnitude.



Figure 7: AgCl(s) Solubility (Solid Black Line) and Underlying Aqueous Ag Speciation (Dashed Lines) as a Function of Chloride Concentration at 25° C, [Na]_T=1·10⁻² M, pH=7. Vertical Dotted Line Indicates [CI]_T=1.7·10⁻¹ M, as Expected Under Scenario 1 Conditions

Table 25: Silver Solubility-Controlling Phase and Concentrations Under SCENARIO 1
Conditions

	SCENARIO 1				
		Concentr	ation (m)		
Solid phase	15°C	25°C	50°C	80°C	
AgCl(s)	6.28·10 ⁻⁶	1.08·10⁻⁵	3.62·10 ⁻⁵	1.26·10 ⁻⁴	

			SCEN	ARIO 1	
Solid phase	Speciation	15°C	25°C	50°C	80°C
-	AgCl ₂	56%	55%	52%	48%
AgCl(s)	AgCl₄ ³⁻	21%	22%	25%	29%
•••		20%	20%	19%	18%

Table 26: Silver	Speciation	Under SCENARIO 1	Conditions
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4.1.2 Ag Solubility in Scenario 2

Scenario 2 results (Table 27 and Table 28) are almost identical to that of Scenario 1, as the effect of pH/pe variations and Fe concentration among both scenarios does not affect silver solubility nor speciation.

	SCENARIO 2				
	Concentration (m)				
Solid phase	15°C	25°C	50°C	80°C	
AgCI(s)	6.28·10 ⁻⁶	1.08·10 ⁻⁵	3.61·10 ⁻⁵	1.26·10 ⁻⁴	

Table 27: Silver Solubility-Controlling Phase and Concentrations Under SCENARIO 2
Conditions

Table 28: Silver Speciation Under SCENARIO 2 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	AgCl ₂ ⁻	56%	55%	52%	48%	
AgCl(s)	AgCl₄ ³⁻	21%	22%	25%	28%	
	AgCl ₃ ²⁻	20%	20%	19%	18%	

4.1.3 Ag Solubility in Scenario 3

As for Scenario 1 and Scenario 2, AgCl(s) is expected to exert silver solubility control in Scenario 3, AgCl₂⁻ species being the predominant species at all studied temperatures (Table 29 and Table 30).

Table 29: Silver Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

	SCENARIO 3					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
AgCl(s)	6.35·10 ⁻⁶	1.09·10 ⁻⁵	3.61·10 ⁻⁵	1.24·10 ⁻⁴		

		SCENARIO 3				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
-	AgCl ₂	55%	54%	52%	48%	
AgCl(s)	AgCl ₄ ³⁻	22%	23%	25%	28%	
	AgCl ₃ ²⁻	20%	20%	19%	18%	

Table 30: Silver Speciation Under SCENARIO 3 Conditions

4.1.4 Uncertainties

The Ag solubility limits is directly related to the chloride concentration in the system; an increase in chloride groundwater concentrations results in an increase in Ag solubility (see Figure 7).

An additional uncertainty for silver is the content of sulphide in groundwater and the possible formation of Ag-sulphide solid phases. The formation of such phases will decrease drastically the aqueous concentration of Ag in the system compare to the solubility control exerted by AgCl(s) (see discussion in section 5 and Table 207).

4.2 Am

The only relevant redox state for americium under the studied conditions is Am(+III).

The Am chemistry is mainly affected by the pH of the system and the porewater carbonate concentration. Silicates have also been identified to form strong aqueous complexes with americium (Guillamount et al. 2003).

Depending on the groundwater conditions, several solid phases, either carbonates $(Am(CO_3)(OH)(cr), Am(CO_3)(OH)(am), Am(CO_3)(OH) \cdot 0.5H_2O(cr), Am_2(CO_3)_3(s)$ and $Am(CO_3)_2Na \cdot 5H_2O(s))$, or hydroxides $(Am(OH)_3(am))$, may exert a solubility control of Am (see Figure 8). All of them have been evaluated in each scenario.



Figure 8: Carbonate vs pH Predominance Diagram at 25°C for Americium. [Am]_T= $9 \cdot 10^{-5}$ M; [CI]_T=[Na]_T= $8 \cdot 10^{-2}$ M; [Si]_T= $1.8 \cdot 10^{-4}$ M. Red Dot Indicates pH/Carbonate Conditions for Scenario 1 Groundwater at 25°C

The available enthalpy for these solids and for the relevant Am(III) aqueous species is summarised in Table 31.

Solid phase	Available enthalpy data
Am(CO₃)(OH)(cr)	\checkmark
Am(CO ₃)(OH)(am)	×
$Am(CO_3)(OH) \cdot 0.5H_2O(cr)$	\checkmark
$Am_{2}(CO_{3})_{3}(s)$	×
Am(CO ₃) ₂ Na·5H ₂ O(s)	×
Am(OH)₃(am)	×
Aqueous phase	Available enthalpy data
Aqueous phase AmOSi(OH) ₃ ²⁺	Available enthalpy data ×
Aqueous phase AmOSi(OH) ₃ ²⁺ Am(CO ₃) ⁺	Available enthalpy data × √
Aqueous phase AmOSi(OH) ₃ ²⁺ Am(CO ₃) ⁺ Am ³⁺	Available enthalpy data ✓ ✓
Aqueous phase AmOSi(OH) ₃ ²⁺ Am(CO ₃) ⁺ Am ³⁺ Am(SO ₄) ⁺	Available enthalpy data ✓ ✓ ✓
Aqueous phase AmOSi(OH) ₃ ²⁺ Am(CO ₃) ⁺ Am ³⁺ Am(SO ₄) ⁺ Am(OH) ²⁺	Available enthalpy data ✓ ✓ ✓ ✓ ✓

4.2.1 Am Solubility in Scenario 1

Some authors have studied the relation between the americium carbonate and hydroxidecarbonate phases in terms of carbonate concentration. Runde et al. (1992) concluded that the limiting pressure between the carbonate and hydroxide-carbonate americium phases was 0.01 atm; Vitorge (1992) found out that at $pCO_2 > 0.1$ atm the solid precipitated was $Am_2(CO_3)_3(s)$ while at $pCO_2 < 10^{-13}$ atm it was $Am(OH)_3(s)$. Between both pressures the solid precipitating was $AmCO_3OH(s)$. Felmy et al. (1990) determined that between pH 5.5 and 13.1, $AmCO_3OH(s)$ was the thermodynamically stable solid phase when the total carbonate concentration was lower than 0.1 M. $Am(CO_3)_2Na\cdot5H_2O(s)$ may play a decisive role at high carbonate and sodium concentrations.

Under the studied conditions of Scenario 1, different phases may exert the solubility control of americium. The amorphous hydroxycarbonate phase $Am(CO_3)(OH)(am)$, or the $Am_2(CO_3)_3(s)$ solid are the most likely phase controlling Am solubilities at low temperature ranges, while a more crystalline phase, as $Am(CO_3)(OH)(cr)$, may become the phase controlling Am solubilities at higher temperatures (Table 32).

Table 32: Americium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions. Values in Bold Correspond to the Most Likely Ones at Each Temperature

	SCENARIO 1						
	Concentration (m)						
Solid phase	15°C	25°C	50°Ć	80°C			
Am(CO₃)(OH)(cr)	6.89·10 ⁻¹¹	1.12·10 ⁻¹⁰	4.54-10 ⁻⁹	5.72-10 ⁻⁷			
Am(CO₃)(OH)(am)	9.65 -10 ⁻⁵	2.27 · 10 ⁻⁵					
$Am(CO_3)(OH) \cdot 0.5H_2O(cr)$	1.06·10 ⁻⁷	1.45·10 ⁻⁷	3.97·10 ⁻⁶	3.36.10-4			
$Am_2(CO_3)_3(s)$	9.89-10 ⁻⁶	1.59 -10 ⁻⁵					
$Am(CO_3)_2Na \cdot 5H_2O(s)$	1.59·10 ⁻⁵	2.76·10⁻⁵					
Am(OH)₃(cr)	6.04·10 ⁻⁴	2.65·10 ⁻³					

 $AmOSi(OH)_3^{2+}$, $Am(CO_3)^+$ and Am^{3+} are the main aqueous Am species in solution at 25°C (Table 33). The influence of Si in $Am_2(CO_3)_3(cr)$ solubility is shown in Figure 9; an increase in Si concentration in the system will result in a slight increase in the Am solubility.



Figure 9: $Am_2(CO_3)_3(cr)$ Solubility (Solid Black Line) and Underlying Aqueous Am Speciation (Dashed Lines) as a Function of Si Concentration at 25°C, $[CI]_T=1.7\cdot10^{-1}$ M, $[Na]_T=8.4\cdot10^{-2}$ M, $[C]_T=9\cdot10^{-4}$ M, $[Ca]_T=5.5\cdot10^{-3}$ M, $[Mg]_T=2.5\cdot10^{-3}$ M, $[K]_T=3.9\cdot10^{-4}$ M, pH=7. Quartz or SiO₂(am) Are not Allowed to Precipitate in this Calculation. Vertical Dotted Line Indicates $[Si]_T=1.8\cdot10^{-4}$ M, as Expected Under Scenario 1 Conditions

Significant differences in solubility (Table 32) and speciation (Table 33) are observed when the temperature increases. The results show that $AmOSi(OH)_3^{2+}$ is the main species at low temperatures, but $Am(CO_3)^+$ becomes the predominant species at 50°C and 80°C (see Figure 10). The lack of enthalpy data for the silicate species $AmOSi(OH)_3^{2+}$ (see Table 33) makes it difficult to verify the accuracy of those calculations at T≠25°C.

		SCENARIO 1				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	AmOSi(OH) ₃ ²⁺	58%	39%	1%	0%	
	Am(CO ₃) ⁺	4%	27%	97%	100%	
	Am ³⁺	25%	20%	1%	0%	
	Am(SO₄)⁺	7%	7%	0%	0%	
	AmOSi(OH)₃ ²⁺	57%	38%			
Am ₂ (CO ₃) ₃ (s)	Am(CO₃)⁺	4%	27%			
	Am ³⁺	25%	20%			
	Am(SO₄)⁺	8%	7%			



Figure 10: Americium Speciation Under SCENARIO 1 Conditions in Equilibrium with $Am(CO_3)(OH)(cr)$

4.2.2 Am Solubility in Scenario 2

The pH of groundwater in Scenario 2 is higher than in Scenario 1. The amorphous hydroxycarbonate phase, $Am(CO_3)(OH)(am)$, or the hydroxide solid phase $Am(OH)_3(cr)$ are the most likely phase controlling Am solubilities at low temperature ranges under Scenario 2 conditions; while a more crystalline phase, as $Am(CO_3)(OH)(cr)$ or $Am(CO_3)(OH) \cdot 0.5H_2O(cr)$, may become the phase controlling Am solubilities at higher temperatures (Table 34).

As a result of changes of pH and carbonate concentrations of groundwater in Scenario 2 (in comparison with Scenario 1), $\text{AmOSi}(\text{OH})_3^{2+}$ species predominance is higher in Scenario 2 (Table 35) than in scenario 1. The lack of enthalpy data for $\text{AmOSi}(\text{OH})_3^{2+}$ makes it difficult to evaluate the accuracy of the calculations at T \neq 25°C.

Table 34: Americium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions. Values in Bold Correspond to the Most Likely Ones at Each Temperature

	SCENARIO 2						
	Concentration (m)						
Solid phase	15°C 25°C 50°Ć 80°C						
Am(CO₃)(OH)(cr)	4.01·10 ⁻¹¹	5.09·10 ⁻¹¹	4.60-10 ⁻¹⁰	9.80-10 ⁻⁸			
Am(CO₃)(OH)(am)	5.55-10 ⁻⁶	1.01 ∙ 10 ⁻⁵					
$Am(CO_3)(OH) \cdot 0.5H_2O(cr)$	6.17·10 ⁻⁸	6.57·10 ⁻⁸	4.03-10 ⁻⁷	5.80-10 ⁻⁵			
$Am_2(CO_3)_3(s)$	9.22·10 ⁻⁵	1.36·10 ⁻⁴					
$Am(CO_3)_2Na\cdot5H_2O(s)$	1.19·10 ⁻⁴	2.34·10 ⁻⁴					
Am(OH)₃(cr)	6.91·10 ⁻⁷	3.72 · 10 ⁻⁶	3.72·10 ⁻⁴				

		SCENARIO 2					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
-	AmOSi(OH) ₃ ²⁺	91%	80%	11%	0%		
	Am(CO₃)⁺	0%	2%	71%	99%		
Am(CO₃)(OH)(cr)	Am ³⁺	1%	2%	1%	0%		
	Am(OH) ²⁺	3%	6%	5%	0%		
	Am(OH)₂⁺	4%	9%	12%	1%		
	AmOSi(OH)₃²+	91%	80%	25%			
	Am(CO₃)⁺	0%	2%	19%			
Am(OH)₃(cr)	Am ³⁺	1%	2%	2%			
	Am(OH) ²⁺	3%	6%	16%			
	Am(OH)₂⁺	4%	9%	37%			

Table 35: Americium Speciation Under SCENARIO 2 Conditions

4.2.3 Am Solubility in Scenario 3

Calculated Am solubility and the associated speciation under Scenario 3 conditions are shown in Table 36 and Table 37. The amorphous hydroxycarbonate phase, $Am(CO_3)(OH)(am)$, or the hydroxide solid $Am(OH)_3(cr)$ are the most likely phase controlling Am solubilities at low temperature ranges, while a more crystalline phase, as $Am(CO_3)(OH)(cr)$ or $Am(CO_3)(OH)\cdot 0.5H_2O(cr)$, may become the phase controlling Am solubilities at higher temperatures. The differences between Scenario 3 and Scenario 2 are due to the difference of groundwater pH and carbonate concentration.

	SCENARIO 3				
	Concentration (m)				
Solid phase	15°C	25°C	50°Ć	80°C	
Am(CO₃)(OH)(cr)	1.15·10 ⁻¹¹	1.45·10 ⁻¹¹	1.88-10 ⁻¹⁰	4.17-10 ⁻⁸	
Am(CO ₃)(OH)(am)	1.63-10 ⁻⁶	2.93-10 ⁻⁶	9.73·10 ⁻⁵		
$Am(CO_3)(OH) \cdot 0.5H_2O(cr)$	1.77·10 ⁻⁸	1.87·10 ⁻⁸	1.64-10 ⁻⁷	2.46-10 ⁻⁵	
$Am_2(CO_3)_3(s)$	4.23·10 ⁻⁵	5.02·10 ⁻⁵			
$Am(CO_3)_2Na\cdot5H_2O(s)$	1.39·10 ⁻⁵	1.60·10 ⁻⁵			
Am(OH) ₃ (cr)	1.98-10 ⁻⁷	1.07-10 ⁻⁶	2.11·10 ⁻⁴		

 Table 36: Americium Solubility-Controlling Phase and Concentrations Under SCENARIO

 3 Conditions. Values in Bold Correspond to the Most Likely Ones at Each Temperature

		SCENARIO 3				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
•	AmOSi(OH) ₃ ²⁺	89%	74%	6%	0%	
	Am(CO ₃) ⁺	0%	4%	78%	99%	
Am(CO₃)(OH)(cr)	Am ³⁺	1%	1%	0%	0%	
	Am(OH) ²⁺	3%	5%	3%	0%	
	Am(OH)₂⁺	6%	16%	13%	1%	
	AmOSi(OH)₃²+	89%	74%	12%		
	Am(CO ₃) ⁺	0%	4%	52%		
Am(OH)₃(cr)	Am ³⁺	1%	1%	0%		
	Am(OH) ²⁺	3%	5%	6%		
	Am(OH)₂⁺	6%	16%	29%		

Table 37: Americium Speciation Under SCENARIO 3 Conditions

4.2.4 Uncertainties

Some uncertainties have been identified to estimate the behaviour of americium solubility and speciation under the studied conditions.

One of the main uncertainties affecting the americium solubility and speciation is the effect of the groundwater phosphate concentration. In the selected groundwaters for the three scenarios, phosphate is not considered. However, the concentration of phosphate in groundwater is likely to be controlled by equilibrium with hydroxyapatite (Bruno et al. 2001, 2002). Under these conditions, the resulting phosphate concentration in groundwater could lead to Am phosphate solid phases (AmPO₄·xH₂O(am)) to exert the solubility control and promote a decrease of Am aqueous concentration comparing with the results showed above without phosphate (see discussion in section 5 and Table 208).

Another uncertainty is associated with the possible formation of a solid-solution of Am with calcite. This would limit the solubility of Am, giving lower aqueous Am concentration than that in equilibrium with americium carbonate or hydroxide solids. This process is expected to occur in the light of very high partition coefficient of Am with calcite (Curti 1999).

Finally, an important uncertainty when estimating the evolution of the Am solubility with temperature is the lack of enthalpy data for the Am silicate aqueous species and most of the solid phases expected to exert the solubility control for Am (see Table 31).

4.3 Bi

The most stable oxidation state of bismuth under the conditions of this study is Bi(+III). Bi(+V) is a strong oxidant being able to oxidize water, and thus, it is not be relevant for this study.

The available enthalpy data for the most relevant Bi solids and aqueous species is summarised in Table 38.

Solid phase	Available enthalpy data
Bi ₂ O ₃ (s)	×
Aqueous phase	Available enthalpy data
Bi(OH)₃(aq)	\checkmark

 Table 38: Available Enthalpy Data for Correcting Temperature Effects on Bi Behaviour

4.3.1 Bi Solubility in Scenario 1

Under Scenario 1 conditions, $Bi_2O_3(s)$ has been selected as the solid phase controlling Bi solubility. The main Bi aqueous species in equilibrium with this solid phase is the neutral Bi hydroxide species (Bi(OH)₃(aq)) at all studied temperatures (Table 40).

The Bi solubility increases when temperature increases (Table 39). At 80°C, the calculation results in Bi concentration higher than $1 \cdot 10^{-2}$ m in equilibrium with Bi₂O₃(s). The high concentration indicates that Bi is not solubility limited by the solid phase Bi₂O₃(s) under the Scenario 1 conditions at 80°C. Besides, no other solid phases are identified to decrease Bi concentration in groundwater. However, the lack of enthalpy data for the Bi₂O₃(s) (see Table 38) makes difficult to verify the accuracy of the calculations at T≠25°C.

Table 39: Bismuth Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Bi ₂ O ₃ (s)	2.40·10 ⁻⁶	1.17·10⁻⁵	3.95.10-4	n.s.l.*		

*n.s.l. – Not solubility limited.

Table 40: Bismuth Speciation Under SCENARIO 1 Conditions

		SCENARIO 1			
Solid phase	Speciation	15°C	25°C	50°C	80°C
Bi ₂ O ₃ (s)	Bi(OH)₃(aq)	100%	100%	100%	100%

4.3.2 Bi Solubility in Scenario 2

Given that the bismuth chemistry is not affected by variations in groundwater composition caused by steel canister corrosion, the Bi solubility limiting phase and the Bi speciation of Scenario 2 (Table 41 and Table 42) are almost identical to that of Scenario 1. $Bi_2O_3(s)$ has been selected as Bi solubility limiting phase and $Bi(OH)_3(aq)$ is the main Bi aqueous species in equilibrium with this solid phase under Scenario 2 conditions.

Table 41: Bismuth Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Bi ₂ O ₃ (s)	2.40·10 ⁻⁶	1.16·10 ⁻⁵	3.94·10 ⁻⁴	n.s.l.*		

*n.s.l. – Not solubility limited.

Table 42: Bismuth Speciation Under SCENARIO 2 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
Bi ₂ O ₃ (s)	Bi(OH)₃(aq)	100%	100%	100%	100%	

4.3.3 Bi Solubility in Scenario 3

The results of Bi solubility limiting phase and speciation for Scenario 3 (Table 43 and Table 44) are almost identical to the results of Scenario 1 and Scenario 2. The interaction of groundwater with bentonite buffer has no impact on the Bi solubility and speciation behaviour. $Bi_2O_3(s)$ has been selected as Bi solubility limiting phase and $Bi(OH)_3(aq)$ is the main Bi aqueous species in equilibrium with this solid phase for such scenario.

Table 43: Bismuth Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

	SCENARIO 3					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Bi ₂ O ₃ (s)	2.39·10 ⁻⁶	1.16·10 ⁻⁵	3.93·10 ⁻⁴	n.s.l.*		

*n.s.l. – Not solubility limited.

		SCENARIO 3				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
Bi ₂ O ₃ (s)	Bi(OH)₃(aq)	100%	100%	100%	100%	

Table 44: Bismuth Speciation Under SCENARIO 3 Conditions

4.3.4 Uncertainties

The main uncertainty affecting Bi solubility and speciation behaviour with temperature is the lack of enthalpy data for the solid phase controlling the solubility of Bi (see Table 38). Note that the main Bi aqueous species ($Bi(OH)_3(aq)$) has enthalpy data, and it is for that reason that its concentration in equilibrium with the solid phase at different temperatures can be estimated. No additional literature data that can help to reduce this uncertainty has been identified.

In addition, bismuth can also form strong complexes with sulphide. However, it is difficult to predict the effect of the potential presence of sulphide in the system as very few thermodynamic data are available in the literature for bismuth sulphides. In this study, it was assumed that sulphate to sulphide reduction does not occur as microbial activity is not taken into account.

4.4 C

The carbon aqueous speciation for the groundwaters studied in the present work depends mainly on the pH and to a minor extent on the Ca and Fe concentrations in the groundwater solution. Detailed explanations on the calculation of the compositions of the groundwaters in the different Scenarios (and thus on carbon concentration calculations) are provided in section 3.

Enthalpy data are available for the most relevant solid and aqueous species in the calculations.

4.4.1 C Solubility in Scenario 1

C concentration under the chemical conditions of interest (Table 45) will be mainly determined by calcite solubility. Carbon aqueous speciation is dominated by HCO_3^- species with minor contributions of Ca(HCO_3)⁺ (Table 46).

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C 25°C 50°C 80°C					
CaCO ₃ (s) (Calcite) ^{a)}	8.00·10 ⁻⁴	9.07·10 ⁻⁴	1.05·10 ⁻³	1.06·10 ⁻³		

Table 45: Carbon Concentrations Under SCENARIO 1 Conditions

^a Further details provided in section 3.

		SCENARIO 1				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	HCO ₃ -	73%	73%	71%	68%	
	Ca(HCO₃)⁺	15%	13%	9%	6%	
	CO₂(aq)	8%	11%	18%	24%	
	Na(HCO ₃)	2%	2%	1%	1%	
CaCO ₃ (s) (Calcite) ^{a)}	Fe(CO ₃)	1%	0%	0%	0%	
	CaCO₃(aq)	1%	1%	1%	1%	
	CO3 ²⁻	0%	0%	0%	0%	
	Na(CO₃) ⁻	0%	0%	0%	0%	
	Mg(CO₃)(aq)	0%	0%	0%	0%	

^a Further details provided in section 3.

4.4.2 C Solubility in Scenario 2

Under Scenario 2 conditions, C concentrations (Table 47) will also be mainly driven by calcite solubility. Due to the presence of iron in groundwater produced by the steel canister corrosion, C aqueous speciation is dominated by HCO_3^- species and Fe(II)-carbonate species (Table 48).

Table 47: Carbon Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2				
	Concentration (m)				
Solid phase	15°C	25°C	50°C	80°C	
CaCO ₃ (s) (Calcite) ^{a)}	4.09·10 ⁻⁵	4.53·10 ⁻⁵	7.61·10 ⁻⁵	1.58·10 ⁻⁴	

^{*a*)} Further details provided in section 3.

Table 48: Carbon Speciation Under SCENARIO 2 Conditions

			SCEN	ARIO 2	
Solid phase	Speciation	15°C	25°C	50°C	80°C
	HCO ₃	45%	55%	71%	79%
	Ca(HCO₃)⁺	9%	9%	9%	6%
	CO ₂ (aq)	0%	0%	1%	5%
	Na(HCO₃)	1%	1%	1%	1%
(Calcite) ^{a)}	Fe(CO ₃)	24%	17%	6%	2%
	CaCO₃(aq)	13%	12%	8%	5%
	CO3 ²⁻	3%	2%	1%	0%
	Na(CO₃) ⁻	1%	1%	1%	2%
	Mg(CO₃)(aq)	0%	0%	0%	0%

^a Further details provided in section 3.

4.4.3 C Solubility in Scenario 3

In Scenario 3, C concentration (Table 49) and speciation (Table 50) is affected by the presence of bentonite, due to the groundwater pH changes caused by bentonite (in comparison with Scenario 2) and the effect of the bentonite exchanger on the calcium aqueous concentration.

A sensitivity analysis that takes into account the two slightly different groundwater compositions reported in section 3.3 has been made. Case A (base case for Scenario 3) corresponds to bentonite porosity of 0.382 and density of 1700 kg·m⁻³; case B (used for the sensitivity analysis) corresponds to bentonite porosity of 0.418 and density of 1600 kg·m⁻³. Calculated results for both cases are reported in Table 49 and Table 50. In Scenario 3, for both cases, calcite is the solid exerting the solubility control on carbon. HCO₃⁻ has been found to be the predominant C species independently of the studied cases and the system temperatures.

Table 49: Carbon Concentrations Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

	SCENARIO 3									
	Concentration (m)									
		Cas	e A		Case B					
	(Base case for Scenario 3)				(Sensitivity analysis for Scenario 3)					
Solid phase	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C		
CaCO₃(s) (Calcite) ^{a)}	6.91·10 ⁻⁵	8.16·10 ⁻⁵	1.59·10 ⁻⁴	3.66·10 ⁻⁴	1.19·10 ⁻⁴	1.36.10-4	1.82·10 ⁻⁴	3.99.10-4		

^a Further details provided in section 3.

Table 50: Carbon Speciation Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

					SCE	NARIO 3	3			
			Case A				Case B			
		(Base	(Base case for Scenario 3) (S				(Sensitivity analysis for Scenario			
Solid phase	Speciation	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C	
	HCO₃ ⁻	54%	62%	75%	80%	69%	73%	77%	81%	
	Ca(HCO₃)⁺	3%	3%	2%	1%	3%	3%	2%	1%	
	CO₂(aq)	0%	0%	1%	2%	0%	0%	1%	2%	
	Na(HCO₃)	5%	4%	3%	2%	5%	5%	3%	2%	
(Calcita)a)	Fe(CO₃)	14%	9%	3%	1%	8%	6%	2%	1%	
(Calcile)-	CaCO₃(aq)	7%	7%	4%	2%	4%	4%	3%	2%	
	CO ₃ ²⁻	6%	5%	2%	1%	4%	3%	2%	1%	
	Na(CO₃)⁻	4%	6%	8%	9%	3%	4%	7%	9%	
	Mg(CO₃)(aq)	2%	2%	1%	0%	1%	1%	1%	0%	

^a Further details provided in section 3.

4.4.4 Uncertainties

The formation of the most reduced form of carbon C(-IV), represented by methane (CH₄) is the main uncertainty found for this element. The reduction of carbonate to methane would be thermodynamically plausible under the studied conditions although it is kinetically hindered. The presence or absence of bacterial activity which is able to reduce carbonate to methane will affect this process (microbial activity has not been considered in the present work).

4.5 Ca

Calcium is an alkaline earth element. The Ca concentration in groundwater influences (directly or indirectly) the aqueous speciation of most radionuclides and therefore their solubilities. Detailed explanations on the calculation of the compositions of the groundwaters in three different Scenarios (and thus on Ca concentration calculations) are provided in section 3.

Enthalpy data are available for all relevant solid and aqueous species in the calculations.

4.5.1 Ca Solubility in Scenario 1

Calcium concentration in Scenario 1 (Table 51) is mainly determined by calcite solubility and also influenced by the dissolution of minerals such as gypsum. Its aqueous speciation is dominated by the free cation, Ca^{2+} , and the sulphate complex $Ca(SO_4)(aq)$ (Table 52).

Table 51: Calcium Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
CaCO ₃ (s) (Calcite) ^{a)}	5.47·10 ⁻²	5.52·10 ⁻²	5.48·10 ⁻²	5.11·10 ⁻²			

^{a)} Mainly determined by calcite solubility and also influenced by the dissolution of calcium sulphate minerals. Further details provided in section 3.

Table 52: Calcium Speciation Under SCENARIO 1 Conditions

		SCENARIO 1					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
$C_{2}C_{2}(c)$ (Calcita) ^{a)}	Ca ²⁺	91%	91%	91%	94%		
	Ca(SO₄)(aq)	9%	9%	9%	6%		

^a Mainly determined by calcite solubility and also influenced by the dissolution of calcium sulphate minerals. Further details provided in section 3.

4.5.2 Ca Solubility in Scenario 2

Calcium is a non-redox sensitive element, so its concentration in Scenario 2 (Table 53) will not be influenced by Eh changes in groundwater produced by the steel canister corrosion. However, it will be affected by changes in pH and carbonate concentration of the groundwater.

Its aqueous speciation in Scenario 2 is mainly determined by calcite solubility and influenced by calcium sulphate minerals, similar to the one in Scenario 1. Ca speciation is mainly driven by the free aqueous cation Ca^{2+} (Table 54).

Table 53: Calcium Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
CaCO ₃ (s) (Calcite) ^{a)}	5.44·10 ⁻²	5.47·10 ⁻²	5.42·10 ⁻²	5.06·10 ⁻²			

^a Mainly determined by calcite solubility and also influenced by the dissolution of calcium sulphate minerals. Further details provided in section 3.

Table 54: Calcium Speciation Under SCENARIO 2 Conditions

		SCENARIO 2						
Solid phase	Speciation	15°C	25°C	50°C	80°C			
	Ca ²⁺	91%	91%	91%	94%			
	Ca(SO₄)(aq)	9%	9%	9%	6%			

^a Mainly determined by calcite solubility and also influenced by the dissolution of calcium sulphate minerals. Further details provided in section 3.

4.5.3 Ca Solubility in Scenario 3

In Scenario 3, calcium concentration (Table 55) and speciation (Table 56) is affected by both: a) the pH, carbonate and sulphate concentration of the system, and b) the interaction with bentonite and the associated ion-exchange reactions.

A sensitivity analysis taking into account the two slightly different groundwater compositions reported in section 3.3 has been made. Case A (base case for Scenario 3) corresponds to bentonite porosity of 0.382 and density of 1700 kg·m⁻³; case B (used for the sensitivity analysis) corresponds to bentonite porosity of 0.418 and density of 1600 kg·m⁻³. The calculated results for both cases are reported in Table 55 and Table 56. Independently of the study cases, Ca aqueous concentrations are very similar at all studied temperatures, Ca²⁺ being the predominance species.

	SCENARIO 3									
	Concentration (m)									
		Cas	e A		Case B					
	(Base case for Scenario 3)				(Sensitivity analysis for Scenario 3)					
Solid phase	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C		
CaCO₃(s) (Calcite) ^{a)}	1.45·10 ⁻²	1.39·10 ⁻²	1.17·10 ⁻²	9.18·10 ⁻³	1.23·10 ⁻²	1.20·10 ⁻²	1.11·10 ⁻²	8.91·10 ⁻³		

Table 55: Calcium Concentrations Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

^a Mainly determined by calcite solubility and also influenced by the dissolution of calcium sulphate minerals. Further details provided in section 3.

Table 56: Calcium Speciation Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

			SCENARIO 3							
			Cas	se A		Case B				
		(Base	(Base case for Scenario 3)				(Sensitivity analysis for Scenario 3)			
Solid phase	Speciation	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C	
CaCO₃(s)	Ca ²⁺	89%	88%	88%	91%	88%	87%	88%	91%	
(Calcite) ^{a)}	Ca(SO₄)(aq)	11%	12%	12%	9%	12%	12%	12%	9%	

^a Mainly determined by calcite solubility and also influenced by the dissolution of calcium sulphate minerals. Further details provided in section 3.

4.5.4 Uncertainties

The calcium solubility and speciation behaviour in groundwaters will be affected by the pH of the system and by the concentration of ligands produced from dissolution processes of main minerals, such as carbonate or sulphate. Thus, variations in those parameters will significantly affect the calculated concentration and speciation of Ca.

4.6 Cs

Caesium is a non-redox sensitive alkaline earth element. Overall, caesium aqueous chemistry is weakly affected by the groundwater changes as its reactivity is relatively limited.

Enthalpy data are available for all relevant aqueous species in the calculations.
4.6.1 Cs Solubility in Scenario 1

In Scenario 1 conditions, Cs is not solubility limited. No Cs solid is likely to be formed under the studied conditions (Table 57). The aqueous chemistry of caesium, calculated assuming a concentration of 10^{-8} m, will be governed by the free cation, Cs⁺ (Table 58).

Table 57: Caesium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1						
		Concent					
Solid phase	15°C	25°C	50°C	80°C			
None	n.s.l.*	n.s.l.*	n.s.l.*	n.s.l.*			

*n.s.l. – Not solubility limited.

Table 58: Caesium Speciation Under SCENARIO 1 Conditions Calculated With $[Cs]_T=10^{-8} m$

	SCENARIO 1						
Speciation	15°C	25°C	50°C	80°C			
Cs⁺	94%	93%	92%	90%			
CsCl(aq)	6%	7%	8%	10%			

4.6.2 Cs Solubility in Scenario 2

As mentioned above for Scenario 1, caesium is not expected to be solubility limited under Scenario 2 conditions (see Table 59). The free cation (Cs^+) is the main species in solution (Table 60).

Table 59: Caesium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2							
	Concentration (m)							
Solid phase	15°C	25°C	50°C	80°C				
None	n.s.l.*	n.s.l.*	n.s.l.*	n.s.l.*				

*n.s.l. – Not solubility limited.

	SCENARIO 2						
Speciation	15°C	25°C	50°C	80°C			
Cs⁺	94%	93%	92%	90%			
CsCl(aq)	6%	7%	8%	10%			

Table 60: Caesium Speciation Under SCENARIO 2 Conditions Calculated With $[Cs]_T=10^{-8} m$

4.6.3 Cs Solubility in Scenario 3

Table 61 and Table 62 presents the results obtained for caesium solubility and speciation under Scenario 3 conditions. Similar to Scenario 1 and Scenario 2, it is expected that Cs will not be solubility limited in Scenario 3 conditions, Cs⁺ being the predominance aqueous species in solution.

Table 61: Caesium Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

	SCENARIO 3						
		Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C			
None	n.s.l.*	n.s.l.*	n.s.l.*	n.s.l.*			

*n.s.l. – Not solubility limited.

Table 62: Caesium Speciation Under SCENARIO 3 Conditions Calculated With $[Cs]_T=10^{-8} m$

	SCENARIO 3						
Speciation	15°C	25°C	50°C	80°C			
Cs⁺	94%	93%	92%	90%			
CsCl(aq)	6%	7%	8%	10%			

*n.s.l. – Not solubility limited

4.6.4 Uncertainties

Although caesium is not expected to be solubility limited, its mobility in the groundwater is linked to the sorption and/or cationic exchange processes. Thus, the ionic strength of the solution, as well as variations in the concentrations of the competing mono- and di-valent cations in the system, such as Na⁺, K⁺, Ca²⁺ or Mg²⁺, may affect Cs retention processes.

4.7 Cd

Cd(+II) will prevail under environmental conditions. The concentration of soft ligands such as chlorine will control the chemical behaviour of this element.

Enthalpy data are available for all relevant solid and aqueous species in the calculations.

4.7.1 Cd Solubility in Scenario 1

 $Cd(CO_3)(s)$ is the solid phase expected to be the solubility limiting phase for cadmium under the studied temperature range (Table 63). Solubility slightly increases from $8 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ m when temperature rises from $15^{\circ}C$ to $80^{\circ}C$. The main reason behind this behaviour is the decrease of pH with increasing temperature and the effect of this modification on carbonate speciation.

As shown in Table 64, the aqueous chemistry of cadmium is governed by chlorine complexation. The effect of chloride concentration in $Cd(CO_3)(s)$ solubility is shown in Figure 11. An increase of chloride concentration from 10^{-2} M to 10^{-1} M increases Cd solubility one order of magnitude.



Figure 11: CdCO₃(s) Solubility (Solid Black Line) and Underlying Aqueous Cd Speciation (Dashed Lines) as a Function of Chloride Concentration at 25°C, [Na]_T= $1 \cdot 10^{-2}$ M, pH=7. Vertical Dotted Line Indicates [Cl]_T= $1.7 \cdot 10^{-1}$ M, as Expected Under Scenario 1 Conditions

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Cd(CO ₃)(s)	8.54·10 ⁻⁵	8.92·10 ⁻⁵	9.79·10⁻⁵	1.08·10 ⁻⁴		

Table 63: Cadmium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

Table 64: Cadmium Speciation Under SCENARIO 1 Conditions

		SCENARIO 1						
Solid phase	Speciation	15°C	25°C	50°C	80°C			
	CdCl⁺	57%	59%	61%	61%			
Cd(CO ₃)(s)	CdCl ₂ (aq)	26%	23%	18%	13%			
	Cd ²⁺	12%	13%	17%	23%			

4.7.2 Cd Solubility in Scenario 2

Table 65 and Table 66 present the solubility of Cd in equilibrium with $Cd(CO_3)(s)$ and its corresponding aqueous speciation under Scenario 2 conditions. No differences are observed between the Scenario 1 and Scenario 2 results, indicating that the steel canister corrosion process is not affecting the behaviour of Cd in a significant way.

Table 65: Cadmium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Cd(CO ₃)(s)	8.50·10 ⁻⁵	8.87·10 ⁻⁵	9.94·10 ⁻⁵	1.07·10 ⁻⁴		

Table 66: Cadmium Speciation Under SCENARIO 2 Conditions

		SCENARIO 2					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
	CdCl ⁺	57%	59%	61%	61%		
Cd(CO₃)(s)	CdCl₂(aq)	26%	23%	18%	13%		
	Cd ²⁺	12%	13%	17%	23%		

4.7.3 Cd Solubility in Scenario 3

Under Scenario 3 conditions (see results in Table 67 and Table 68), $Cd(CO_3)(s)$ is also expected to exert Cd solubility control. Cd aqueous speciation in equilibrium with this solid phase is similar to those estimated in Scenario 1 and Scenario 2.

In Scenario 3, a sensitivity analysis taking into account the two slightly different groundwater compositions reported in section 3.3 has been make. Case A (base case for Scenario 3) corresponds to bentonite porosity of 0.382 and density of 1700 kg·m⁻³; case B (used for the sensitivity analysis) corresponds to bentonite porosity of 0.418 and density of 1600 kg·m⁻³. The slight differences in magnesium concentrations in both groundwaters result in small differences in calculated solubilities (Table 67). No differences in calculated aqueous speciation are noticed (Table 68).

Table 67: Cadmium Solubility-Controlling Phase and Concentrations Under SCENARIO 3Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Correspondsto a Sensitivity Analysis

	SCENARIO 3										
	Concentration (m)										
	Case A				Case B						
	(B	ase case fo	or Scenario	3)	(Sensitivity analysis for Scenario 3)						
Solid phase	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C			
Cd(CO ₃)(s)	2.16 · 10⁻⁵	2.15 · 10 ⁻⁵	2.05·10 ⁻⁵	1.95·10 ⁻⁵	1.85·10 ⁻⁵	1.87 . 10 ⁻⁵	1.99·10 ⁻⁵	1.88•10 ⁻⁵			

Table 68: Cadmium Speciation Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

			SCENARIO 3						
			Case A				Ca	ase B	
		(Base	e case fo	or Scena	ario 3)	(Sensiti	vity analy	sis for So	cenario 3)
Solid phase	Speciation	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C
	CdCl⁺	57%	58%	60%	60%	57%	58%	60%	60%
Cd(CO₃)(s)	CdCl₂(aq)	25%	23%	18%	13%	26%	23%	18%	13%
	Cd ²⁺	12%	14%	17%	22%	12%	13%	17%	22%

4.7.4 Uncertainties

In this study, it was assumed that sulphate to sulphide reduction does not occur as microbial activity is not taken into account. However, in the presence of sulphide, cadmium sulphide species may form, and Cd may precipitate as CdS(s), which will promote lower Cd solubilities than the ones obtained for $CdCO_3(s)$ in this study (see Table 207).

4.8 Cu

Copper is a metallic redox sensitive element that in nature can be found in two oxidation states (+I and +II). In anoxic and reducing environments, Cu(+I) species are predominant (see Figure 2).

Enthalpy data are available for all relevant solid and aqueous species in the calculations.

4.8.1 Cu Solubility in Scenario 1

Aqueous copper concentrations under reducing conditions are expected to be controlled by the precipitation of Cu(I) oxide or the formation of Cu(s). Under the reducing conditions of the selected groundwater, Cu(s) has been selected as a possible solubility limiting phase at all the studied temperatures (Table 69). Both the increase of the temperature and the change of groundwater redox conditions by varying the temperatures lead to an increase of the Cu solubility from $5.27 \cdot 10^{-9}$ to $1.01 \cdot 10^{-6}$ m with temperature from 15° C to 80° C.

As seen in Figure 12, the copper solubility is driven by chloride concentration. An increase in Cl concentration from 10^{-2} M to 10^{-1} M increases the Cu(cr) solubility several orders of magnitude. CuCl₂⁻ is the main species in all temperature range of interest (Table 70).



Figure 12: Cu(cr) Solubility (Solid Black Line) and Underlying Aqueous Cu Speciation (Dashed Lines) as a Function of Chloride Concentration at 25°C, $[Na]_T=1\cdot10^{-2}$ M, pH=7. Vertical Dotted Line Indicates $[CI]_T=1.7\cdot10^{-1}$ M, as Expected Under Scenario 1 Conditions

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Cu(cr)	5.27·10 ⁻⁹	1.52·10 ⁻⁸	1.35·10 ⁻⁷	1.01·10 ⁻⁶		

Table 69: Copper Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

Table 70: Copper Speciation Under SCENARIO 1 Conditions

		SCENARIO 1					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
	CuCl ₂ -	94%	94%	92%	88%		
Cu(cr)	CuCl ₃ ²	4%	4%	3%	2%		
	CuCl(aq)	2%	3%	5%	9%		

4.8.2 Cu Solubility in Scenario 2

The Cu solubility, assuming Cu(cr) as solubility limiting phase, under Scenario 2 conditions is reported in Table 71. The corresponding aqueous speciation in equilibrium with this solid is summarized in Table 72.

Copper is a redox sensitive element, so its solubility is affected by the change of the pe of the system. The decrease of pe of groundwater (from pe=-3.26 in Scenario 1 to pe=-9.36 in Scenario 2 at 25° C) due to canister corrosion leads to a significant decrease of the solubility of copper in Scenario 2 (from 10^{-8} to 10^{-14} m at 25° C), in comparison with Scenario 1.

The solubility behaviour of copper with temperature is in agreement with the pe evolution (from pe=-9.63 at 15°C to pe=-8.07 at 80°C in Scenario 2).

Table 71: Copper Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
Cu(cr)	3.11·10 ⁻¹⁵	1.21·10 ⁻¹⁴	2.82·10 ⁻¹³	6.68·10 ⁻¹²			

		SCENARIO 2					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
-	CuCl ₂	94%	94%	92%	88%		
Cu(cr)	CuCl ₃ ²	4%	4%	3%	2%		
	CuCl(aq)	2%	3%	5%	9%		

Table 72: Copper Speciation Under SCENARIO 2 Conditions

4.8.3 Cu Solubility in Scenario 3

As observed in Scenario 2, the concentration of copper in equilibrium with Cu(cr) is significantly lower under the reducing conditions of Scenario 3 (Table 73) than that in Scenario 1. Copper chlorine complexation is the process controlling the aqueous speciation of this element in the whole range of temperatures of interest (Table 74).

Table 73: Copper Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

	SCENARIO 3					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Cu(cr)	1.54·10 ⁻¹⁵	5.88·10 ⁻¹⁵	1.25·10 ⁻¹³	2.84·10 ⁻¹²		

		SCENARIO 3					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
-	CuCl ₂	94%	94%	92%	88%		
Cu(cr)	CuCl ₃ ²	4%	4%	3%	2%		
	CuCl(aq)	2%	3%	5%	9%		

4.8.4 Uncertainties

In this study, it was assumed that sulphate to sulphide reduction does not occur as microbial activity is not taken into account. However, in the presence of sulphide, sulphide solid phases could be formed, modifying Cu solubility (see the discussion in section 5 and Table 207).

4.9 Fe

Iron is a redox sensitive element that will be found as Fe(+II) under the mildly reducing to strongly reducing conditions of the studied groundwaters (Figure 13). Detailed explanations on the calculations leading to Fe groundwater concentrations are provided in section 3.

Enthalpy data are available for all solid and aqueous species in the calculations.



Figure 13: Eh vs pH Predominance Diagram at 25°C for Iron Aqueous Species in Water. [Fe]_T=10⁻⁵ M. Solids Are not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for Scenario 1 Groundwater at 25°C. Green Dotted Lines Stand for the Water Stability Field

4.9.1 Fe Solubility in Scenario 1

Goethite and magnetite have been included in the calculations in order to estimate Fe concentrations in groundwater under Scenario 1 conditions as reported in Table 75 (further details are provided in section 3.1). The main iron species in solution is Fe²⁺ with minor contributions of sulphate, carbonate and chloride species (Table 76).

	SCENARIO 1						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
α-FeOOH (Goethite) ^{a)} Fe₃O₄ (Magnetite) ^{a)}	2.38·10 ⁻⁴	1.65·10 ⁻⁴	5.07·10 ⁻⁵	1.03·10 ⁻⁵			

Table 75: Iron Concentrations Under SCENARIO 1 Conditions

^a Further details provided in section 3.

Table 76: Iron Speciation Under SCENARIO 1 Conditions

Solid phase	Speciation	15°C	25°C	50°C	80°C
	Fe ²⁺	85%	84%	84%	85%
	Fe(SO₄)(aq)	5%	6%	8%	7%
α -reoon (Goethite) ^a	FeCl⁺	6%	5%	5%	5%
Fe ₃ O ₄ (wagnetite) ²⁷	Fe(CO₃)(aq)	3%	3%	2%	1%
	Fe(OH)⁺	0%	0%	0%	1%

^a Further details provided in section 3.

4.9.2 Fe Solubility in Scenario 2

In Scenario 2, groundwater interacts with the carbon-steel container prior to contacting the used nuclear fuel waste inside the container. The main component of C-steel is Fe(0). In the absence of other oxidants, Fe(0) will anoxically corrode to Fe(OH)₂(s) and with time towards Fe₃O₄ (magnetite). C-steel corrosion (and therefore, iron corrosion) has been considered to be kinetically controlled in order to get the iron concentration in the groundwater at the different temperatures as reported in Table 77.

Iron speciation under Scenario 2 conditions (Table 78) is similar to the one reported in Scenario 1.

Table 77: Iron Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Fe ₃ O ₄ (Magnetite) ^{a)}	3.10·10 ⁻⁴	3.06·10 ⁻⁴	2.93·10 ⁻⁴	2.67·10 ⁻⁴		

^a Kinetically controlled by C-steel corrosion process. Details provided in section 3.

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	Fe ²⁺	83%	82%	82%	82%	
	Fe(SO₄)(aq)	5%	6%	8%	7%	
Fe ₃ O ₄ (Magnetite) ^{a)}	FeCl⁺	5%	5%	5%	5%	
	Fe(CO₃)(aq)	3%	3%	2%	1%	
	Fe(OH)⁺	2%	3%	3%	4%	

Table 78: Iron Speciation Under SCENARIO 2 Conditions

^a Kinetically controlled by C-steel corrosion process. Details provided in section 3.

4.9.3 Fe Solubility in Scenario 3

In Scenario 3, Fe concentration (Table 79) and speciation (Table 80) is affected by the presence of bentonite, due to pH changes by groundwater interaction with bentonite (in comparison with Scenario 2) and the effect of the bentonite exchanger on iron aqueous concentration.

A sensitivity analysis taking into account two slightly different groundwater compositions reported in section 3.3 has been made. Case A (base case for Scenario 3) corresponds to bentonite porosity of 0.382 and density of 1700 kg·m⁻³; case B (used for the sensitivity analysis) corresponds to bentonite porosity of 0.418 and density of 1600 kg·m⁻³. The results of the two cases are reported in Table 79 and Table 80. Very small changes in the estimated solubilities are observed for the two cases. Fe aqueous speciation is the same for both cases; Fe²⁺ being the predominance species at all temperatures.

Table 79: Iron Concentrations Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

	SCENARIO 3							
	Concentration (m)							
	Case A			Case B				
	(Base case for Scenario 3)			(Sensitivity analysis for Scenario 3)				
Solid phase	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C
Fe ₃ O ₄ (Magnetite) ^{a)}	9.32·10 ⁻⁵	8.56·10 ⁻⁵	6.90·10 ⁻⁵	5.35·10 ⁻⁵	7.79·10 ⁻⁵	7.33·10 ⁻⁵	6.54·10 ⁻⁵	5.18·10 ⁻⁵

^a Kinetically controlled by C-steel corrosion process and influenced by ion-exchange processes in bentonite. Details provided in section 3.

		SCENARIO 3							
		Case A				Ca	ase B		
		(Base case for Scenario 3)			(Sensiti	vity analy	sis for So	cenario 3)	
Solid phase	Speciation	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C
	Fe ²⁺	71%	72%	72%	73%	72%	73%	72%	73%
Ea.O.	Fe(SO₄)(aq)	6%	7%	10%	9%	6%	8%	10%	9%
(Magnotito)a)	FeCI+	5%	5%	4%	4%	5%	5%	4%	4%
(waynetite)»	Fe(CO₃)(aq)	11%	9%	6%	5%	13%	11%	7%	5%
	Fe(OH)+	4%	5%	6%	8%	2%	3%	6%	8%

Table 80: Iron Speciation Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

^a Kinetically controlled by C-steel corrosion process and influenced by ion-exchange processes in bentonite. Details provided in section 3.

4.9.4 Uncertainties

In this study, it was assumed that sulphate to sulphide reduction does not occur as microbial activity is not taken into account. However, in the presence of sulphide, solid phases such as pyrite may form, leading to lower Fe solubilities (see Table 207).

4.10 Hg

Hg is a chemical element with properties between a metal and a metalloid. This element can be found in nature under different oxidation states ranging from 0 to +II, although in the conditions of interest for this study Hg will be mainly as Hg(+I) (Figure 3). In the environment mercury has a strong tendency to form complexes with chlorine but also organo-metallic complexes such as the methylmercury, dimethylmercury, etc.

Enthalpy data is not available for the main aqueous species Hg₂(OH)⁺ (Table 81).

Table 81: Available Enthalpy Data for Correcting Temperature Effects on Hg Behaviour

Aqueous	Available
phase	enthalpy data
Hg₂(OH)⁺	×
Hg_{2}^{2+}	\checkmark
HgCl₂(aq)	\checkmark
HgCl ₃	\checkmark
HgCl ₄ ²⁻	\checkmark

4.10.1 Hg solubility in Scenario 1

Under Scenario 1 conditions Hg is not solubility limited; no solid Hg is likely to be formed under the studied conditions (Table 82). The aqueous chemistry of mercury, calculated assuming a very low concentration (10^{-10} m) , will be governed by Hg₂(OH)⁺ (Table 83).

The lack of enthalpy data for the main aqueous species (see Table 81) makes it difficult to verify the accuracy of the calculated speciation at $T \neq 25^{\circ}$ C.

Table 82: Mercury Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
None	n.s.l.* n.s.l.* n.s.l.* n.s.l.*						

*n.s.l. – Not solubility limited.

Table 83: Mercury Speciation Under SCENARIO 1 Conditions Calculated with $[Hg]_T=10^{-10} m$

		SCEN	ARIO 1	
Speciation	15°C	25°C	50°C	80°C
Hg₂(OH)⁺	98%	97%	88%	63%
Hg_2^{2+}	2%	2%	5%	8%
HgCl₂(aq)	0%	0%	2%	8%
HgCl₃⁻	0%	0%	2%	12%
HgCl₄ ²⁻	0%	0%	2%	9%

4.10.2 Hg Solubility in Scenario 2

Under Scenario 2 conditions, Hg is not solubility limited (Table 84). Due to the strongly reducing conditions of the groundwater in Scenario 2, Hg(+I) dominates the aqueous chemistry (Table 85).

Table 84: Mercury Solubility-Controlling Phase and Concentrations Under SCENARIO 2
Conditions

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
None	n.s.l.*	n.s.l.*	n.s.l.*	n.s.l.*		

*n.s.l. – Not solubility limited.

Table 85: Mercury Speciation Under SCENARIO 2 Conditions Calculated with $[Hg]_{T}=10^{-10}\,m$

		SCEN	ARIO 2	
Speciation	15°C	25°C	50°C	80°C
Hg₂(OH)⁺	100%	100%	100%	98%
Hg ₂ ²⁺	0%	0%	0%	2%

4.10.3 Hg Solubility in Scenario 3

The Hg solubility and speciation behavior under Scenario 3 conditions is similar to that observed under Scenario 2 conditions (Table 86); Hg₂(OH)⁺ being its aqueous predominant species (Table 87).

Table 86: Mercury Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

	SCENARIO 3						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
None	n.s.l.*	n.s.l.*	n.s.l.*	n.s.l.*			

*n.s.l. – Not solubility limited.

Table 87: Mercury Speciation Under SCENARIO 3 Conditions Calculated with $[Hg]_T=10^{-10} m$

	SCENARIO 2					
Speciation	15°C	25°C	50°C	80°C		
Hg₂(OH)⁺	100%	100%	100%	99%		
Hg_2^{2+}	0%	0%	0%	1%		

4.10.4 Uncertainties

Hg has a complex chemistry and the scarcity of thermodynamic data under reducing conditions results in some uncertainties in the solubility and speciation for this element.

Hg has been assumed to be not solubility limited. If liquid elemental mercury (Hg(I)) is assumed to control mercury concentrations in groundwater, this would result in very low Hg concentrations in solution, of about 10⁻²⁰ m or 10⁻²⁵ m, under the targeted groundwaters studied in this work. These mercury concentrations are very low comparing with some values measured in the environment (Wang et al. 2018) and thus assuming that Hg(I) could exert a solubility control may not be realistic.

Hg is also well known to form strong complexes with organics (for example methyl-mercury species), although there is a general lack of thermodynamic data for Hg organic complexes. Furthermore, it can also form compounds and complexes with sulphide (Benoit et al. 1999), which may modify its solubility (Table 207).

Finally, the lack of enthalpy data for the main aqueous species expected makes it difficult to verify the accuracy of the calculated speciation at $T \neq 25^{\circ}$ C.

4.11 Mo

Molybdenum is a redox sensitive element. Mo(+IV) and Mo(+VI) are the most common oxidation states in nature. The main parameters affecting the chemistry of this element are the pH and Eh of the system, although the calcium concentration of groundwater may also play a significant role.

Enthalpy data are available for all relevant solid and aqueous species in the calculations.

4.11.1 Mo Solubility in Scenario 1

Two different solid phases may exert the solubility control of Mo (Table 88) under Scenario 1 conditions. If CaMoO₄(s) is the phase controlling Mo solubility, the concentration of molybdenum in groundwater would be about 10^{-6} m. If the oxide solid phase (MoO₂(s)) exerts the solubility control, the concentration of Mo at 25°C is about two orders of magnitude lower, around 10^{-8} m. Small variations in both, the Eh or the pH of the system could lead to changes in the solid exerting the solubility control (see Figure 14).

Molybdate, MoO₄²⁻, is the predominant aqueous species under the whole range of temperature of interest in Scenario 1 (Table 89).

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
CaMoO₄(s)	3.24·10⁻ ⁶	3.44 ⋅ 10 ⁻⁶	4.12·10 ⁻⁶	5.61·10⁻ ⁶		
MoO ₂ (s)	6.55·10 ⁻⁹	2.04·10 ⁻⁸	3.86·10 ⁻⁷	1.10·10 ⁻⁵		

 Table 88: Molybdenum Solubility-Controlling Phase and Concentrations Under

 SCENARIO 1 Conditions

 Table 89: Molybdenum Speciation Under SCENARIO 1 Conditions

			SCENA	ARIO 1	
Solid phase	Speciation	15°C	25°C	50°C	80°C
$C_{2}M_{2}O_{1}(z)$	MoO ₄ ²⁻	100%	100%	99%	94%
	HMoO₄ ⁻	-	-	-	6%
$M_{O}O_{1}(s)$	MoO ₄ ²⁻	100%	100%	99%	94%
WOO ₂ (S)	HMoO₄ ⁻	-	-	-	6%



Figure 14: Eh vs pH Predominance Diagram at 25°C for Molybdenum Aqueous Species in Water, Calculated Using the Data Selection in the Present Work. $[Ca]_T=5.5\cdot10^{-3}$ M; $[Mo]_T=10^{-5}$ M. Red Dot Indicates pH/Eh Conditions for Scenario 1 Groundwater at 25°C. Green Dotted Lines Stand for the Water Stability Field

4.11.2 Mo Solubility in Scenario 2

 $MoO_2(s)$ becomes significantly more insoluble under the Scenario 2 conditions than under Scenario 1. Unrealistic solubility values between 10^{-15} m and 10^{-13} m are calculated in equilibrium with $MoO_2(s)$ in Scenario 2. The decrease in the solubility of $MoO_2(s)$ in Scenario 2 is related to the lack of thermodynamic data for Mo(+IV) aqueous species; as a consequence, the aqueous chemistry of molybdenum is completely governed by the Mo(+VI) anion $MoO_4^{2^-}$ (Table 91). The $MoO_2(s)$ dissolution reaction is then significantly affected by the very reducing conditions of Scenario 2, due to the redox transition between the Mo(+IV) solid and the Mo(+VI)aqueous species (see Equation 8).

$$MoO_2(s) + 2H_2O = MoO_4^{2-} + 2e^{-} + 4H^+$$
 Equation 8

On the contrary, CaMoO₄(s) (which is a Mo(+VI) solid) is not affected by this redox transition between the solid and the aqueous speciation (Equation 9). If CaMoO₄(s) is exerting the solubility control, Mo solubility and speciation results are very similar under Scenario 1 and Scenario 2 conditions (see Table 90).

 $CaMoO_4(s) + 2H_2O = Ca^{2+} + MoO_4^{2-}$ Equation 9

Table 90: Molybdenum Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
CaMoO₄(s)	3.25·10 ⁻⁶	3.46·10 ⁻⁶	4.12·10 ⁻⁶	5.35·10 ⁻⁶		
MoO ₂ (s)	2.26·10 ⁻¹⁵	6.73·10 ⁻¹⁵	5.53·10 ⁻¹⁴	5.43·10 ⁻¹³		

		SCENARIO 2						
Solid phase	Speciation	15°C	25°C	50°C	80°C			
CaMoO₄(s)	MoO ₄ ²⁻	100%	100%	100%	99%			
MoO ₂ (s)	MoO ₄ ²⁻	100%	100%	100%	99%			

4.11.3 Mo Solubility in Scenario 3

Similar to what was observed in Scenario 2, $MoO_2(s)$ is significantly less soluble under Scenario 3 conditions (Table 92), resulting to unrealistic Mo aqueous concentrations. This is related to the lack of thermodynamic data for Mo(+IV) aqueous species and the significant effect of Eh on $MoO_2(s)$ dissolution.

It is worth noting, that the concentration of calcium in Scenario 3 groundwater is lower than in Scenario 1 or in Scenario 2, which leads to an increase in the solubility of CaMoO₄(s) (Table 92) in comparison with Scenario 1 and Scenario 2. At all studied temperatures the anionic species $MoO_4^{2^2}$ is the predominant Mo aqueous species.

In Scenario 3, a sensitivity analysis taking into account the two slightly different groundwater compositions reported in section 3.3 has been made. Case A (base case for Scenario 3) corresponds to bentonite porosity of 0.382 and density of 1700 kg·m⁻³; case B (used for the sensitivity analysis) corresponds to bentonite porosity of 0.418 and density of 1600 kg·m⁻³. The slight differences in the Eh value and calcium concentration in both groundwaters result in small differences in calculated Mo solubilities (Table 92). No differences in Mo aqueous speciation are noticed (Table 93).

Table 92: Molybdenum Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

				SCEN	ARIO 3					
	Concentration (m)									
		Cas	se A			Cas	se B			
	(Base case for Scenario 3)			(Sensitivity analysis for Scenario 3)						
Solid phase	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C		
CaMoO₄(s) MoO₂(s)	1.31 • 10 ⁻⁵ 9.13 • 10 ⁻¹⁵	1.46⋅10 ⁻⁵ 2.8410 ⁻¹⁴	1.98 • 10 ⁻⁵ 2.75 • 10 ⁻¹³	2.90·10 ⁻⁵ 2.89·10 ⁻¹²	1.49∙10 ⁻⁵ 4.09∙10 ⁻¹⁵	1.63∙10 ⁻⁵ 1.62∙10 ⁻¹⁴	2.06·10 ⁻⁵ 3.43·10 ⁻¹³	2.95·10 ⁻⁵ 4.34·10 ⁻¹²		

Table 93: Molybdenum Speciation Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

			SCENARIO 3								
			Cas	se A			Ca	ase B			
		(Base	(Base case for Scenario 3)			(Sensiti	vity analy	ysis for So	cenario 3)		
Solid phase	Speciation	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C		
CaMoO ₄ (s)	MoO ₄ ²⁻	100%	100%	100%	99%	100%	100%	100%	99%		
MoO ₂ (s)	MoO ₄ ²⁻	100%	100%	100%	99%	100%	100%	100%	99%		

4.11.4 Uncertainties

The most important uncertainty concerning molybdenum solubility and speciation is the scarcity of thermodynamic data available in the literature, specially for reduced Mo aqueous species. This uncertainty has an impact on the possible solid phases ($CaMoO_4(s)$ or $MoO_2(s)$) that can control Mo solubility under reducing conditions and their solubility under different Eh conditions.

If microbial activity is taken into account, the reduction of sulphate to sulphide could also result in the formation of molybdenum sulphides, although the scarcity of thermodynamic data will also affect this system.

4.12 Nb

Niobium is mainly found in the oxidation state +V in natural waters. The main parameter affecting Nb aqueous speciation is the pH of the system.

Enthalpy data for relevant Nb species, both aqueous and solid phases, are available in the calculations.

4.12.1 Nb Solubility in Scenario 1

Niobium solubility is expected to be controlled by the solid phase Nb₂O₅(s) which derives Nb aqueous concentration in the groundwater about $\approx 10^{-7}$ m in all the studied temperature range (Table 94). Nb aqueous speciation is governed by the hydroxide complexes, Nb(OH)₆⁻ being the predominant one (Table 95).

Table 94: Niobium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1							
	Concentration (m)							
Solid phase	15°C	25°C	50°C	80°C				
Nb ₂ O ₅ (s)	1.10·10 ⁻⁷	1.00·10 ⁻⁷	1.01·10 ⁻⁷	1.24·10 ⁻⁷				

			SCEN	ARIO 1	
Solid phase	Speciation	15°C	25°C	50°C	80°C

96%

4%

95%

5%

Nb(OH)6

 $Nb(OH)_7^{2-}$

97%

2%

96%

2%

Table 95: Niobium Speciation Under SCENARIO 1 Conditions

4.12.2 Nb Solubility in Scenario 2

Nb₂O₅(s)

Under Scenario 2 conditions, the aqueous concentration of niobium is likely to be limited by the solid phase $Nb_2O_5(s)$ (Table 96). Nb solubilities in Scenario 2 are greater than in Scenario 1, mainly due to the effect of pH on Nb aqueous speciation.

The groundwater pH in Scenario 2 is higher than in Scenario 1, resulting in an increase of the presence of Nb(OH) $7^{2^{\circ}}$ species in the Nb speciation scheme (Table 96 and Figure 15).

	SCENARIO 2								
	Concentration (m)								
Solid phase	15°C	25°C	50°C	80°C					
Nb ₂ O ₅ (s)	8.61·10 ⁻⁶	5.24·10 ⁻⁶	1.75·10⁻ ⁶	7.83·10 ⁻⁷					

 Table 96: Niobium Solubility-Controlling Phase and Concentrations Under SCENARIO 2

 Conditions

Table 97: Niobium Speciation Under SCENARIO 2 Conditions

		SCENARIO 2						
Solid phase	Speciation	15°C	25°C	50°C	80°C			
Nb₂O₅(s)	Nb(OH)6	38%	49%	75%	90%			
	Nb(OH) ₇ ²⁻	62%	51%	25%	10%			



Figure 15: Nb₂O₅(s) Solubility (Solid Black Line) and Underlying Aqueous Nb Speciation (Dashed Lines) as a Function of pH at 25°C, $[Na]_T=8\cdot10^{-2}$ M, $[CI]_T=1\cdot10^{-1}$ M

4.12.3 Nb Solubility in Scenario 3

Results obtained for Scenario 3, assuming $Nb_2O_5(s)$ as the Nb solubility limiting phase, has also shown the effect of the groundwater pH on the solubility and speciation (Table 98 and Table 99).

In Scenario 3, a sensitivity analysis that takes into account the two slightly different groundwater compositions reported in section 3.3 has been made. Case A (base case for Scenario 3) corresponds to bentonite porosity of 0.382 and density of 1700 kg·m⁻³; case B (used for the sensitivity analysis) corresponds to bentonite porosity of 0.418 and density of 1600 kg·m⁻³. The slight differences in pH values in groundwaters of both cases result in small differences in the calculated Nb solubilities (Table 98) and speciation (Table 99).

Table 98: Niobium Solubility-Controlling Phase and Concentrations Under SCENARIO 3Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Correspondsto a Sensitivity Analysis

	SCENARIO 3										
	Concentration (m)										
		Cas	se A			Cas	se B				
	(B	ase case fo	or Scenario	3)	(Sens	itivity analys	sis for Scena	ario 3)			
Solid phase	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C			
Nb ₂ O ₅ (s)	2.82·10 ⁻⁵	1.66·10 ⁻⁵	5.11·10 ⁻⁶	2.06·10 ⁻⁷	9.27·10 ⁻⁶	6.83·10 ⁻⁶	4.19·10 ⁻⁶	1.89·10 ⁻⁶			

Table 99: Niobium Speciation Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

		SCENARIO 3							
			Cas	se A			Cas	se B	
		(Base	(Base case for Scenario 3)			(Sensiti	ivity analys	sis for Sce	nario 3)
Solid phase	Speciation	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C
Nb ₂ O ₅ (s)	Nb(OH)6 ⁻ Nb(OH)7 ²⁻	23% 77%	32% 68%	57% 43%	79% 21%	37% 63%	45% 55%	61% 39%	81% 19%

4.12.4 Uncertainties

There is a general lack of thermodynamic data for Nb in literature, which constitutes an important drawback when studying the solubility and speciation behaviour of this element.

Laboratory experiments (Lothenbach et al. 2000; Talerico et al. 2004) indicate that calciumniobiate phases could be formed under alkaline conditions. Although no thermodynamic data for these solids are available, Talerico et al. (2004) obtained an empirical relationship between calcium concentration, pH and niobium solubility. However, the formation of this kind of solid phases has not been studied at pH values below 9.2.

4.13 Np

Neptunium is an actinide element that presents different oxidation states depending on the redox conditions of the surrounding environment. Np(+IV) is the more relevant oxidation state under the studied conditions (Figure 16).



Figure 16: Eh vs pH Predominance Diagram for Neptunium at 25°C. $[Np]_T=10^{-6}$ M; $[CO_3^{2-}]_T=9\cdot10^{-4}$ M. Red Dot Indicates pH/Eh Conditions for Scenario 1 Groundwater at 25°C. Green Dotted Lines Stand for the Water Stability Field

The available enthalpy data for relevant Np solids and aqueous species is summarised in Table 100.

Table 100: Available Enthalpy Data for Correcting Temperature Effects on Np Behaviour

Solid phase	Available enthalpy data
NpO ₂ .2H ₂ O(am)	\checkmark
Aqueous phase	Available enthalpy data
Np(OH) ₄	\checkmark
Np(CO ₃)(OH) ₃	×

4.13.1 Np Solubility in Scenario 1

Neptunium solubility is expected to be controlled by the solid phase NpO₂·2H₂O(am) under conditions for Scenario 1 at the whole range of temperatures of interest. The calculated Np solubility is about 10^{-9} m, and no significant changes are observed at different temperatures (Table 101). The underlying Np aqueous speciation is mainly dominated by the species Np(OH)₄(aq), with minor contributions of Np(CO₃)(OH)₃⁻ (Table 102).

Table 101: Neptunium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1							
	Concentration (m)							
Solid phase	15°C	25°C	50°C	80°C				
NpO ₂ ·2H ₂ O(am)	8.74·10 ⁻¹⁰	1.08·10 ⁻⁹	1.97·10 ⁻⁹	3.70·10 ⁻⁹				

Table 102: Neptunium Speciation Under SCENARIO 1 Conditions

		SCENARIO 1				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
NpO ₂ ·2H ₂ O(am)	Np(OH)₄(aq)	86%	92%	96%	97%	
	Np(CO ₃)(OH) ₃ ⁻	11%	4%	0%	0%	

4.13.2 Np Solubility in Scenario 2

Np solubility under the Scenario 2 conditions (Table 103), assuming NpO₂·2H₂O(am) as the solubility limiting phase, is similar to that under Scenario 1 conditions. Due to higher pH value of the groundwater in Scenario 2, an unique Np aqueous species Np(OH)₄(aq) is expected (Table 104).

Table 103: Neptunium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

		SCENA	RIO 2			
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
NpO ₂ ·2H ₂ O(am)	7.57·10 ⁻¹⁰	1.00·10 ⁻⁹	1.89·10 ⁻⁹	3.60·10 ⁻⁹		

		SCENARIO 2					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
NpO ₂ -2H ₂ O(am)	Np(OH)₄(aq)	99%	100%	100%	99%		

Table 104: Neptunium Speciation Under SCENARIO 2 Conditions

4.13.3 Np Solubility in Scenario 3

Calculated solubility and speciation results for Scenario 3 are almost identical to those observed in Scenario 2. Independent of the temperature, the solid phase NpO₂·2H₂O(am) will exert the solubility control of Np. Neptunium concentration is about 10^{-9} m and its aqueous speciation will be dominated by the species Np(OH)₄(aq) (see Table 105 and Table 106).

Table 105: Neptunium Solubility-Controlling Phase and Concentrations Under SCENARIO3 Conditions

	SCENARIO 3					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
NpO ₂ ·2H ₂ O(am)	7.60·10 ⁻¹⁰	1.00·10 ⁻⁹	1.89·10 ⁻⁹	3.59·10 ⁻⁹		

Table 106: Neptunium Speciation Under SCENARIO 3 Conditions

		SCENARIO 3					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
NpO ₂ -2H ₂ O(am)	Np(OH)₄(aq)	99%	100%	100%	100%		

4.13.4 Uncertainties

No major uncertainties have been identified for this element under the studied conditions. Although no enthalpy data is available for the species $Np(CO_3)(OH)_3^-$, this does not have an important effect on the calculation results, as the aqueous speciation of neptunium under the studied conditions is highly dominated by $Np(OH)_4$ (aq) (for which enthalpy is available).

4.14 Pa

Protactinium mainly occurs in the oxidation state +IV and +V, although Pa(+IV) is very sensitive to oxidation and it is only stable under very strong acid media and very low Eh values. The most important characteristic for this element is its high tendency to hydrolyse.

The available enthalpy data for relevant Pa solids and aqueous species is summarised in Table 107.

Solid phase	Available enthalpy data
Pa ₂ O ₅ (s)	×
Aqueous phase	Available enthalpy data
PaO₂ ⁺	×
PaO₂(OH)(aq)	\checkmark
PaO ₂ (OH) ₂	×

4.14.1 Pa Solubility in Scenario 1

Protactinium solubility under Scenario 1 conditions is expected to be controlled by the solid phase $Pa_2O_5(s)$ (Table 108). Its aqueous chemistry, in equilibrium with this solid phase, is dominated by PaO_2^+ and $PaO_2(OH)(aq)$ species (Table 109).

A small increase of Pa solubility is observed when temperature increases from 15°C to 80°C. The lack of enthalpy data (see Table 107) makes it difficult to verify the accuracy of the calculations at T \neq 25°C. No additional literature information that can help to decrease this uncertainty has been identified.

Table 108: Protactinium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Pa₂O₅(s)	1.25·10 ⁻⁹	2.30·10 ⁻⁹	9.67·10 ⁻⁹	5.18·10 ⁻⁸		

Table 109: Protactinium Speciation Under SCENARIO 1 Conditions

		SCENARIO 1				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
Pa₂O₅(s)	PaO ₂ ⁺	65%	56%	31%	11%	
	PaO₂(OH)(aq)	34%	43%	69%	89%	

4.14.2 Pa Solubility in Scenario 2

Pa solubility, assuming $Pa_2O_5(s)$ as the solubility limiting phase, under Scenario 2 conditions is reported in Table 110 and its corresponding aqueous speciation in equilibrium with the selected solid is summarized in Table 111. As pH values of groundwater under Scenario 2 conditions are higher than those under Scenario 1, Pa speciation in Scenario 2 is slightly affected, $PaO_2(OH)(aq)$ being the predominance Pa species, specially in the high temperature ranges.

However, the lack of enthalpy data (see Table 107) makes it difficult to verify the accuracy of the calculations at $T \neq 25^{\circ}$ C.

Table 110: Protactinium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Pa₂O₅(s)	7.45·10 ⁻¹⁰	1.21·10 ⁻⁹	6.95·10 ⁻⁹	4.70·10 ⁻⁸		

Table 111: Protactinium Speciation Under SCENARIO 2 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
Pa₂O₅(s)	PaO ₂ (OH)(aq)	57%	83%	96%	98%	
	PaO ₂ (OH) ₂	40%	13%	1%	0%	

4.14.3 Pa Solubility in Scenario 3

Calculated solubility and speciation results for Scenario 3 (Table 112 and Table 113) are similar to those observed for Scenario 2. As in Scenario 1 and Scenario 2, solubility and speciation results at T≠25°C must be used with caution given the lack on enthalpy data for some Pa aqueous species and solid phases.

Slight differences in solubility in different scenarios are related to the pH variations of groundwaters in different scenarios (Figure 17).



Figure 17: $Pa_2O_5(s)$ Solubility (Solid Black Line) and Underlying Aqueous Pa Speciation (Dashed Lines) as a Function of pH at 25°C, Eh=-0.6 V. Vertical Dotted Line Indicates pH Values Expected Under Scenario 1 (pH ca. 7), Scenario 2 (pH ca. 8.5) and Scenario 3 (pH ca. 8.8) Conditions

Table 112: Protactinium Solubility-Controlling Phase and Concentrations Und	ler
SCENARIO 3 Conditions	

	SCENARIO 3					
	Concentration (m)					
Solid phase	15°C 25°C 50°C 80°C					
Pa ₂ O ₅ (s)	1.03·10 ⁻⁹	1.35·10 ⁻⁹	6.89·10 ⁻⁹	4.64·10 ⁻⁸		

Table 113: Protactinium Speciation Under SCENARIO 3 Conditions

		SCENARIO 3				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
Pa₂O₅(s)	PaO ₂ (OH)(aq)	41%	74%	97%	99%	
	PaO ₂ (OH) ₂ ⁻	57%	24%	1%	0%	

4.14.4 Uncertainties

The assessment of Pa solubility is limited by the lack of reliable experimental thermodynamic data, as they are very scarce and controversial. Furthermore, its specific chemical characteristics makes it difficult to direct compare with other actinides.

4.15 Pb

Lead may occur in the oxidation states +II and +IV in nature. Under the studied conditions its main state will be Pb(+II). Its chemistry will be mainly affected by the concentration of different ligands such as chloride and carbonate.

Enthalpy data are available for all relevant solid and aqueous species in the calculations.

4.15.1 Pb Solubility in Scenario 1

Under Scenario 1 conditions, the most likely solubility limiting phases for lead are cerussite, $Pb(CO_3)(s)$ and hydrocerussite, $Pb_3(CO_3)_2(OH)_2(s)$. Lead equilibrium concentration at 25°C varies between from $3.10 \cdot 10^{-6}$ to $8.27 \cdot 10^{-6}$ m, depending which solid phase is considered to exert the solubility control (Table 114). Lead aqueous chemistry is dominated by the species $PbCI^+$ and the free cation (Pb^{2+}). Species with other ligands such as carbonates and sulphates also appear in its speciation scheme in minor proportion (Table 115). High chloride concentrations ($[CI]_T > 10^{-1}$ M) can increase lead solubility due to the formation of Pb-Cl complexes (Figure 18); on the contrary, increasing carbonate aqueous concentration decreases its solubility (Figure 19).

Lead solubility increases with temperature whether cerussite or hydrocerussite exerts the Pb solubility control. The main reason behind this behaviour is the decrease of pH of groundwater when increasing temperature and the effect of carbonate aqueous chemistry.



Figure 18: Pb(CO₃)(s) (Cerussite) Solubility (Solid Black Line) and Underlying Aqueous Pb Speciation (Dashed Lines) as a Function of CI Concentration at 25°C, $[C]_T=9\cdot10^{-4}$ M, $[Na]_T=8.4\cdot10^{-2}$ M, $[Ca]_T=5.5\cdot10^{-3}$ M, $[Mg]_T=2.5\cdot10^{-3}$ M, $[K]_T=3.9\cdot10^{-4}$ M, pH=7. Calcite Is not Allowed to Precipitate in this Calculation. Vertical Dotted Line Indicates $[CI]_T=1.7\cdot10^{-1}$ M, as Expected Under Scenario 1 Conditions



Figure 19: Pb(CO₃)(s) (Cerussite) Solubility (Solid Black Line) and Underlying Aqueous Pb Speciation (Dashed Lines) as a Function of Carbonate Concentration at 25°C, $[CI]_T=1.7\cdot10^{-1}$ M, $[Na]_T=8.4\cdot10^{-2}$ M, $[Ca]_T=5.5\cdot10^{-3}$ M, $[Mg]_T=2.5\cdot10^{-3}$ M, $[K]_T=3.9\cdot10^{-4}$ M, pH=7. Calcite Is not Allowed to Precipitate in this Calculation. Vertical Dotted Line Indicates $[C]_T=9\cdot10^{-4}$ M, as Expected Under Scenario 1 Conditions

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C 25°C 50°C 80°C					
PbCO ₃ (s) (Cerussite)	1.82·10⁻ ⁶	3.10·10⁻ ⁶	1.03·10⁻⁵	3.71·10 ⁻⁵		
Pb ₃ (CO ₃) ₂ (OH) ₂ (s) (Hydrocerussite)	5.62·10 ⁻⁶	8.27 · 10⁻ ⁶	1.76·10⁻⁵	3.56 · 10⁻⁵		

Table 114: Lead Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

			SCEN	ARIO 1	
Solid phase	Speciation	15°C	25°C	50°C	80°C
-	PbCl⁺	33%	34%	35%	34%
	Pb ²⁺	26%	26%	25%	22%
PbCO₃(s)	Pb(CO₃)(aq)	20%	17%	11%	6%
(Cerussite)	PbCl ₂ (aq)	10%	11%	13%	13%
	Pb(SO ₄)(aq)	8%	8%	8%	5%
	Pb(OH)⁺	2%	3%	7%	17%
	PbCl⁺	33%	34%	35%	34%
	Pb ²⁺	26%	26%	25%	22%
Pb ₃ (CO ₃) ₂ (OH) ₂ (s)	Pb(CO₃)(aq)	20%	17%	11%	6%
(Hydrocerussite)	PbCl ₂ (aq)	10%	11%	13%	13%
	Pb(SO₄)(aq)	8%	8%	8%	5%
	Pb(OH)⁺	2%	3%	7%	17%

4.15.2 Pb Solubility in Scenario 2

Pb solubility under Scenario 2 conditions, assuming cerussite or hydrocerussite solubility control, is reported in Table 116 and its corresponding aqueous speciation in equilibrium with the solid phase is summarized in Table 117. Lead aqueous chemistry under Scenario 2 conditions is dominated by lead hydroxides (Pb(OH)⁺) with minor contribution from other species such as PbCl⁺, Pb²⁺ or Pb(CO)₃(aq).

The differences of results between Scenario 1 and Scenario 2 are mainly due to the changes of pH in the different groundwaters in different scenarios.

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
PbCO ₃ (s) (Cerussite)	3.28·10⁻ ⁶	5.91·10 ⁻⁶	2.06·10⁻⁵	7.06·10 ⁻⁵		
Pb₃(CO₃)₂(OH)₂(s) (Hydrocerussite)	1.01·10 ⁻⁶	1.74·10⁻ ⁶	6.08·10 ⁻⁶	2.07 · 10 ⁻⁵		

 Table 116: Lead Solubility-Controlling Phase and Concentrations Under SCENARIO 2

 Conditions

			ARIO 2		
Solid phase	Speciation	15°C	25°C	50°C	80°C
-	PbCl⁺	18%	18%	18%	18%
	Pb ²⁺	14%	13%	13%	12%
$FDCO_3(5)$	Pb(CO₃)(aq)	11%	9%	5%	3%
(Celussile)	PbCl₂	6%	6%	7%	7%
	Pb(OH)⁺	42%	46%	49%	54%
	PbCl⁺	18%	18%	18%	18%
	Pb ²⁺	14%	13%	13%	12%
(Hydrocerussite)	Pb(CO₃)(aq)	11%	9%	5%	3%
	PbCl ₂	6%	6%	7%	7%
	Pb(OH)⁺	42%	46%	49%	54%

4.15.3 Pb Solubility in Scenario 3

Pb solubility under Scenario 3 conditions, assuming cerussite or hydrocerussite as solubility control phase, is reported in Table 118. The aqueous chemistry of lead under scenario 3 conditions is dominated by lead hydroxides ($Pb(OH)^+$) and carbonates ($Pb(CO_3)(aq)$) (Table 119). Changes observed between Scenario 2 and Scenario 3 are mainly driven by the differences in pH and carbonate content of the studied groundwaters induced by the reaction with bentonite buffer.

Table 118: Lead Solubility-Controlling Phase and Concentrations Under SCENARIO 3
Conditions

	SCENARIO 3					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
PbCO ₃ (s) (Cerussite)	1.55·10⁻ ⁶	2.67·10⁻ ⁶	8.20·10 ⁻⁶	2.56 · 10⁻⁵		
Pb ₃ (CO ₃) ₂ (OH) ₂ (s) (Hydrocerussite)	4.78·10 ⁻⁷	7.91·10 ⁻⁷	2.42·10 ⁻⁶	7.75·10 ⁻⁶		

		SCENARIO 3				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
•	 PbCl⁺	10%	9%	9%	9%	
	Pb ²⁺	8%	7%	7%	6%	
(Corussito)	Pb(CO₃)(aq)	24%	19%	13%	9%	
(Cerussile)	Pb(OH)⁺	45%	49%	56%	62%	
	Pb(OH)₂(aq)	7%	8%	8%	8%	
	PbCl⁺	10%	9%	9%	9%	
	Pb ²⁺	8%	7%	7%	6%	
(Hydrocerussite)	Pb(CO₃)(aq)	24%	19%	13%	9%	
	Pb(OH)⁺	45%	49%	56%	62%	
	Pb(OH)₂(aq)	7%	8%	8%	8%	

Table 119: Lead Speciation Under SCENARIO 3 Conditions

4.15.4 Uncertainties

The main uncertainty affecting the assessment of lead solubility and speciation refers to the presence of microbes and the reduction of sulphate to sulphide. The presence of sulphides could lead to the formation of highly insoluble solids as galena (PbS(s)), significantly decreasing Pb solubility (Table 207).

4.16 Pd

Palladium can be found in several oxidation states in nature, being +II the most common in aqueous media. Its aqueous chemistry is dominated by $Pd(OH)_2(aq)$, and high chloride concentrations ([CI]_T>0.5 M) may affect its solubility (Figure 20).

Enthalpy data are available for all relevant solid and aqueous species in the calculations.



Figure 20: Pd(OH)₂(s) Solubility (Solid Black Line) and Underlying Aqueous Pd Speciation (Dashed Lines) as a Function of Chloride Concentration at 25°C, $[Na]_{T}$ = 1·10⁻² M, pH=7. Vertical Dotted Line Indicates $[CI]_{T}$ =1.7·10⁻¹ M, as Expected Under Scenario 1 Conditions

4.16.1 Pd Solubility in Scenario 1

 $Pd(OH)_2(s)$ is the most likely solid phase to exert the solubility control of Pd. Table 120 and Table 121 shows Pa solubility and speciation results under Scenario 1 conditions. Pd equilibrium concentrations range between $2.89 \cdot 10^{-6}$ m and $2.39 \cdot 10^{-5}$ m, depending on the studied temperature. Pd aqueous chemistry is dominated by the hydroxide species $Pd(OH)_2(aq)$ in the whole temperature range.

Table 120: Palladium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C 25°C 50°C 80°C					
Pd(OH) ₂ (s)	2.89·10 ⁻⁶	4.14·10 ⁻⁶	9.76·10⁻ ⁶	2.39·10 ⁻⁵		

		SCENARIO 1			
Solid phase	Speciation	15°C	25°C	50°C	80°C
Pd(OH) ₂ (s)	Pd(OH) ₂ (aq)	92%	96%	99%	100%
	PdCl ₄ ²⁻	6%	3%	0%	0%

Table 121: Palladium Speciation Under SCENARIO 1 Conditions

4.16.2 Pd Solubility in Scenario 2

The solubility of Pd, assuming $Pd(OH)_2(s)$ as the solubility limiting phase, and its corresponding aqueous speciation in equilibrium with the selected solid phase under Scenario 2 conditions is presented in Table 122 and Table 123. No significant differences are observed between Scenario 1 or Scenario 2 results, as Pd is not affected by the Eh changes of the system. $Pd(OH)_2(aq)$ dominates the aqueous chemistry of Pd at all the studied temperature conditions.

Table 122: Palladium Solubility-Controlling Phase and Concentrations Under SCENARIO2 Conditions

	SCENARIO 2			
	Concentration (m)			
Solid phase	15°C	25°C	50°C	80°C
Pd(OH) ₂ (s)	2.67·10 ⁻⁶	3.98·10⁻ ⁶	9.70·10 ⁻⁶	2.39 · 10⁻⁵

Table 123: Palladium Speciation Under SCENARIO 2 Conditions

		SCENARIO 2			
Solid phase	Speciation	15°C	25°C	50°C	80°C
Pd(OH) ₂ (s)	Pd(OH)₂(aq)	100%	100%	100%	100%

4.16.3 Pd Solubility in Scenario 3

Calculated solubility and speciation results under Scenario 3 conditions (Table 124 and Table 125), assuming $Pd(OH)_2(s)$ as the most likely solid phase that exerts the solubility control of palladium, are identical to the results under Scenario 2 conditions; independent of the studied temperature. The main aqueous Pd species is $Pd(OH)_2(aq)$.

	SCENARIO 3			
	Concentration (m)			
Solid phase	15°C	25°C	50°C	80°C
Pd(OH)₂(s)	2.67·10 ⁻⁶	3.98·10⁻ ⁶	9.70·10 ⁻⁶	2.39·10 ⁻⁵

Table 124: Palladium Solubility-Controlling Phase and Concentrations Under SCENARIO3 Conditions

Table 125: Palladium Speciation Under SCENARIO 3 Conditions

		SCENARIO 3			
Solid phase	Speciation	15°C	25°C	50°C	80°C
Pd(OH) ₂ (s)	Pd(OH)₂(aq)	100%	100%	100%	100%

4.16.4 Uncertainties

There are some uncertainties associated with the experimental determination of $Pd(OH)_2(s)$ solubility, related to:

- Pd measurements close to Pd detection limits,
- poor characterization of the solid phases, or
- lack of adequate filtration procedures during the experiments (see the discussion in Rai et al. 2012).

This may affect the calculated Pd solubility values, which may be slightly overestimated.

The reduction of sulphate to sulphide is an uncertainty that may affect Pd solubility. If sulphate was allowed to be reduced to sulphide, Pd-sulphide solid phases such as PdS(s) may exert the solubility control of Pd under reducing conditions. The equilibration with PdS(s) calculation will result in extremely low aqueous palladium concentration, as the thermodynamic data used for PdS(s) corresponds to that of visotskite, a very crystalline phase studied under high temperature experiments.

4.17 Pu

Plutonium is a redox sensitive element that in nature could be found as +III, +IV, +V and +VI oxidation states. This element presents strong interactions with some of the ligands present in the groundwaters of interest, i.e. carbonate, sulfate.

Enthalpy data are available for most solids and aqueous species in the calculations, except for the $Pu(OH)_3(cr)$ solid phase (see Table 126).

Solid phase	Available enthalpy data		
PuO ₂ ·2H ₂ O(s)	\checkmark		
Pu(OH)₃(cr)	×		
Aqueous phase	Available enthalpy data		
Pu(SO₄)⁺	\checkmark		
Pu ³⁺	\checkmark		
Pu(CO₃)⁺	\checkmark		
Pu(OH) ²⁺	\checkmark		
Pu(SO ₄) ₂	\checkmark		
Pu(OH) ₂ ⁺	\checkmark		
Pu(OH)₃(aq)	\checkmark		

 Table 126: Available Enthalpy Data for Correcting Temperature Effects on Pu Behaviour

4.17.1 Pu Solubility in Scenario 1

Under Scenario 1 conditions, $PuO_2 \cdot 2H_2O(s)$ is the most likely Pu solubility limiting phase. Calculated Pu solubility and speciation are presented in Table 127 and Table 128. Although in the solid phase Pu is in the oxidation state +IV, in the aqueous phase Pu(+III) species dominate the aqueous chemistry. The Pu solubility will increase if carbonate or sulphate concentrations in solution increase, as seen in Figure 21 and Figure 22.

A solubility increase with temperature is observed. This solubility increase is correlated with a change in the Pu calculated speciation. $Pu(SO_4)^+$, Pu^{3+} and $Pu(CO_3)^+$ are observed at 25°C, while $Pu(CO_3)^+$ is the main Pu species in solution at 80°C.


Figure 21: PuO₂·2H₂O(s) Solubility (Solid Black Line) and Underlying Aqueous Pu Speciation (Dashed Lines) as a Function of Carbonate Concentration at 25°C, $[CI]_T=1.7\cdot10^{-1}$ M, $[Na]_T=8.4\cdot10^{-2}$ M, $[Ca]_T=5.5\cdot10^{-2}$ M, $[Mg]_T=2.5\cdot10^{-3}$ M, $[K]_T=3.9\cdot10^{-4}$ M, $[SO_4]_T=1.2\cdot10^{-2}$ M, pH=7, Eh=-0.19 V. Calcite and Gypsum Are not Allowed to Precipitate in This Calculation. Vertical Dotted Line Indicates $[C]_T=9\cdot10^{-4}$ M, as Expected Under Scenario 1 Conditions



Figure 22: $PuO_2 \cdot 2H_2O(s)$ Solubility (Solid Black Line) and Underlying Aqueous Pu Speciation (Dashed Lines) as a Function of Sulfate Concentration at 25°C, $[CI]_T =$ $1.7 \cdot 10^{-1}$ M, $[Na]_T = 8.4 \cdot 10^{-2}$ M, $[Ca]_T = 5.5 \cdot 10^{-2}$ M, $[Mg]_T = 2.5 \cdot 10^{-3}$ M, $[K]_T = 3.9 \cdot 10^{-4}$ M, $[C]_T =$ $9 \cdot 10^{-4}$ M, pH=7, Eh=-0.19 V. Calcite and Gypsum Are not Allowed to Precipitate in This Calculation. Vertical Dotted Line Indicates $[SO_4]_T = 1.2 \cdot 10^{-2}$ M, as Expected Under Scenario 1 Conditions

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
PuO ₂ ·2H ₂ O(s)	1.19·10 ⁻⁸	1.69·10 ⁻⁸	1.90·10 ⁻⁷	5.26·10 ⁻⁶		

 Table 127: Plutonium Solubility-Controlling Phase and Concentrations Under SCENARIO

 1 Conditions

		SCENARIO 1			
Solid phase	Speciation	15°C	25°C	50°C	80°C
	Pu(SO₄)⁺	38%	32%	2%	0%
	Pu ³⁺	45%	31%	2%	0%
	Pu(CO₃)⁺	5%	23%	94%	100%
PuO₂-2H₂O(s)	Pu(OH) ²⁺	7%	9%	2%	0%
	Pu(SO ₄) ₂	5%	4%	0%	0%
	Pu(OH)₂⁺	0%	0%	0%	0%
	Pu(OH)₃(aq)	0%	0%	0%	0%

4.17.2 Pu Solubility in Scenario 2

Under scenario 2 conditions, which implies a strongly reducing and more alkaline groundwater, Pu behaves different than in Scenario 1 (Figure 23). $PuO_2 \cdot 2H_2O(s)$ or $Pu(OH)_3(cr)$ could control Pu solubility under those conditions.

Calculated Pu solubility and speciation are presented in Table 129 and Table 130. The lack of enthalpy data for $Pu(OH)_3(cr)$ makes it difficult to verify the accuracy of the calculations for this solids at T \neq 25°C.



Figure 23: Eh vs pH Predominance Diagram at 25°C for Plutonium. $[Pu]_T=10^{-6}$ M. Red Dot Indicates pH/Eh Conditions for Scenario 1 at 25°C; Blue Dot Indicates pH/Eh Conditions for Scenario 2 at 25°C. Green Dotted Lines Stand for the Water Stability Field

Table 129: Plutonium Solubility-Controlling Phase and Concentrations Under SCENARIO2 Conditions

	SCENARIO 2						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
PuO ₂ ·2H ₂ O(s)	6.64·10 ⁻⁸	1.46·10 ⁻⁷	3.56·10 ⁻⁶	1.38·10 ⁻⁴			
Pu(OH)₃(cr)	5.35·10 ⁻⁹	5.66·10 ⁻⁸	3.46·10⁻⁵	4.17⋅10 ⁻³			

			SCEN	ARIO 2	
Solid phase	Speciation	15°C	25°C	50°C	80°C
-	Pu(SO₄)⁺	12%	9%	2%	0%
	Pu ³⁺	14%	9%	1%	0%
	Pu(CO₃)⁺	1%	7%	69%	93%
PuO ₂ .2H ₂ O(s)	Pu(OH) ²⁺	66%	66%	22%	4%
	Pu(SO ₄) ₂	1%	1%	0%	0%
	Pu(OH)₂⁺	5%	8%	5%	2%
	Pu(OH)₃(aq)	0%	1%	1%	1%
	Pu(SO₄)⁺	12%	9%	2%	2%
	Pu ³⁺	14%	9%	1%	1%
	Pu(CO₃)⁺	1%	7%	63%	4%
Pu(OH)₃(cr)	Pu(OH) ²⁺	66%	66%	26%	54%
	Pu(SO ₄) ₂	1%	1%	0%	0%
	Pu(OH)₂ ⁺	5%	8%	6%	27%
	Pu(OH)₃(aq)	0%	1%	1%	12%

4.17.3 Pu Solubility in Scenario 3

Similarly to Scenario 2, under Scenario 3 conditions, $PuO_2 \cdot 2H_2O(s)$ or $Pu(OH)_3(cr)$, may exert a solubility control over Pu. Plutonium solubility and aqueous speciation calculated in equilibrium with both solid phases are presented in Table 131 and Table 132.

Additionally, a sensitivity analysis taking into account two slightly different groundwater compositions reported in section 3.3 has been made. Case A (base case for Scenario 3) corresponds to bentonite porosity of 0.382 and density of 1700 kg·m⁻³; case B (used for the sensitivity analysis) corresponds to bentonite porosity of 0.418 and density of 1600 kg·m⁻³. The differences in pH and groundwater compositions for Case A and Case B result in small differences in the calculated Pu solubilities (Table 131) and speciation (Table 132) between both cases.

Table 131: Plutonium Solubility-Controlling Phase and Concentrations Under SCENARIO3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case BCorresponds to a Sensitivity Analysis

				SCEN	ARIO 3			
	Concentration (m)							
		Cas	se A			Cas	se B	
	(Base case for Scenario 3)			(Sensitivity analysis for Scenario 3)				
Solid phase	15°C	25°C	50°C	30°C	15°C	25°C	50°C	80°C
PuO ₂ ·2H ₂ O(s)	1.71·10 ⁻⁸	3.95·10 ⁻⁸	1.40·10 ⁻⁶	1.66·10 ⁻⁴	5.53·10 ⁻⁸	9.92·10 ⁻⁸	1.62·10 ⁻⁶	1.67·10 ⁻⁴
Pu(OH)₃(cr)	1.37·10 ⁻⁹	1.53 • 10 ⁻⁸	1.56 10 ⁻⁵	1.77·10 ⁻³	5.72·10 ⁻⁹	4.94·10 ⁻⁸	2.27·10 ⁻⁵	1.89 10 ⁻³

					SCE	ENARIO 3	3		
			Case A				Ca	ase B	
		(Base	e case fo	or Scena	ario 3)	(Sensiti	vity analy	sis for So	cenario 3)
Solid phase	Speciation	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C
	Pu(SO₄)⁺	8%	5%	1%	0%	13%	8%	1%	0%
	Pu ³⁺	7%	4%	0%	0%	11%	6%	0%	0%
	Pu(CO₃)⁺	3%	12%	80%	98%	5%	21%	83%	98%
PuO ₂ -2H ₂ O(s)	Pu(OH) ²⁺	67%	60%	11%	1%	57%	53%	10%	1%
	Pu(SO ₄) ₂ -	1%	1%	0%	0%	2%	1%	0%	0%
	Pu(OH) ₂ +	10%	14%	6%	1%	5%	7%	4%	1%
	Pu(OH)₃	8%	5%	1%	0%	13%	8%	1%	0%
	Pu(SO₄)⁺	8%	5%	1%	0%	13%	8%	1%	0%
	Pu ³⁺	7%	4%	0%	0%	11%	6%	0%	0%
	Pu(CO₃)⁺	3%	12%	79%	21%	5%	21%	82%	21%
Pu(OH)₃(cr)	Pu(OH) ²⁺	67%	60%	12%	23%	57%	53%	11%	24%
	Pu(SO ₄) ₂	1%	1%	0%	0%	2%	1%	0%	0%
	Pu(OH) ₂ +	10%	14%	6%	27%	5%	7%	5%	27%
	Pu(OH)₃	1%	2%	2%	29%	0%	1%	2%	27%

Table 132: Plutonium Speciation Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

4.17.4 Uncertainties

The chemistry of Pu is very complex, leading to several different uncertainties in Pu solubility and speciation calculation.

 $Pu(OH)_3(s)$ is only stable at very reducing conditions, close to the line of water reduction. Small variations in the redox conditions could lead to aqueous plutonium concentrations exceeding the solubility of Pu(+IV) hydrous oxide, which will lead to the precipitation of Pu(+IV) solid and the dissolution of Pu(+III) solids. This leads to some uncertainties regarding Pu solubility and speciation behaviour under strongly reducing conditions. Furthermore, the lack of enthalpy data for Pu(OH)₃(cr) makes it difficult to verify the accuracy of the calculations for this solid at T \neq 25°C.

In addition, phosphates have been identified to form stable Pu(III) solid phases that lead to slightly lower Pu equilibrium concentrations than those calculated in different scenarios in this work (see Table 208).

Finally, the sensitivity of Pu(+III) chemistry to pH, carbonate and sulfate in groundwater makes the solubility analysis very sensible to small variations in groundwater compositions and complicates the analysis of the results at different temperatures.

4.18 Ra

Radium is a non-redox-sensitive alkaline-earth element. Its chemical behaviour is similar to other alkaline-earth elements such as strontium and calcium.

Enthalpy data are available for all relevant solid and aqueous species in the calculations.

4.18.1 Ra Solubility in Scenario 1

Ra(SO₄)(s) is the solubility limiting phase of radium under the Scenario 1 conditions. The main parameter expected to affect radium solubility and speciation is sulphate concentration in groundwater; Ra(SO₄)(s) solubility decreases as sulphate concentration in solution increases (see Figure 24).

The solubility of radium increases as a function of the temperature from $8.57 \cdot 10^{-8}$ m at 15° C to $3.36 \cdot 10^{-6}$ m at 80° C (Table 133). Free radium is the main aqueous species at all studied temperatures (Table 134).



Figure 24: Ra(SO₄)(s) Solubility as a Function of Sulphate Concentration at 25°C; the Effect of Other Ligands Is not Taken into Account in this Graph. Vertical Dotted Line Indicates $[SO_4^{2^2}]_T=1.2 \cdot 10^{-2}$ M, as Expected Under Scenario 1 Conditions

Table 133: Radium Solubility-Controlling Phase and Concentrations Under SCEN	ARIO 1
Conditions	

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Ra(SO₄)(s)	8.57·10 ⁻⁸	1.53·10 ⁻⁷	6.17·10 ⁻⁷	3.36·10 ⁻⁶		

		SCENARIO 1				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	Ra ²⁺	77%	76%	76%	81%	
Ra(504)(S)	Ra(SO₄)(aq)	20%	21%	21%	15%	

Table 134: Radium Speciation Under SCENARIO 1 Conditions

4.18.2 Ra Solubility in Scenario 2

Radium chemistry is not affected neither by iron nor by the pH and pe conditions of the groundwater. Thus, assuming $Ra(SO_4)(s)$ as Ra solubility limiting phase, no differences are observed on the solubility and speciation results obtained in Scenario 2 (see Table 135 and Table 136) in comparison to those obtained in Scenario 1.

Table 135: Radium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Ra(SO₄)(s)	7.05·10 ⁻⁸	1.24·10 ⁻⁷	4.77·10 ⁻⁷	2.46·10 ⁻⁶		

Table 136: Radium Speciation Under SCENARIO 2 Conditions

		SCENARIO 2			
Solid phase	Speciation	15°C	25°C	50°C	80°C
$P_{2}(SO_{1})(c)$	Ra ²⁺	73%	72%	71%	76%
Ra(50₄)(S)	Ra(SO₄)(aq)	24%	26%	27%	21%

4.18.3 Ra Solubility in Scenario 3

As in the case of Scenario 2 both, the solubility and the speciation of radium, assuming that $Ra(SO_4)(s)$ is exerting solubility control under Scenario 3 conditions (Table 137 and Table 138) are similar to those observed in Scenario 1 and Scenario 2.

		SCEN	ARIO 3			
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Ra(SO₄)(s)	8.56·10 ⁻⁸	1.52·10 ⁻⁷	6.15·10 ⁻⁷	3.35·10 ⁻⁶		

Table 137: Radium Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

Table 138: Radium Speciation Under SCENARIO 3 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
Ra(SO₄)(s)	Ra ²⁺	77%	76%	76%	81%	
	Ra(SO₄)(aq)	20%	21%	21%	15%	

4.18.4 Uncertainties

The assumption of equilibrium with a pure phase of Ra (RaSO₄(s)) as the process controlling Ra solubility may be not accurate, as Ra has been reported to incorporate into other minerals such as barite, BaSO₄(s) (Curti 1999; Bruno et al. 2007; Grandia et al. 2008; Ceccarello et al. 2004). Thus, the concentration of radium in groundwater will probably not be limited by a pure Ra(SO₄)(s) phase but by a Ra-Ba solid-solution; the formation of such phases will result in lower Ra concentration in equilibrium. Grandia et al. (2008) applied thermodynamics of aqueous-solid solution equilibria and calculated Ra concentration in solution in the order of 10^{-11} m, in the upper range of observed radium concentrations in natural environments.

4.19 Rn

As a gaseous element, thermodynamic data for radon aqueous chemistry is almost inexistent. Thus, its aqueous speciation cannot be properly described. The most usual way of quantifying the radon concentration dissolved in liquid media is using the partitioning coefficient of radon gas between water and air, $K_{w/air}$.

Some authors have estimated the water/air partition coefficient of radon by means of empirical equations (Weigel, 1978; Schubert et al. 2012). In the present work the approach by Schubert et al. (2012) has been followed. This approach allows to evaluate the water/air partition coefficient as a function of temperature and salinity. As seen in Figure 25, the $K_{w/air}$ is expected to decrease as temperature or salinity of the water increase(s).



Figure 25: Dependence of the Partitioning Coefficient of Radon Gas between Water and Air ($K_{w/air}$) with Temperature, at 0% Salinity (Blue Line) and 32% Salinity (Orange Line) (Adapted from Schubert et al. 2012)

4.19.1 Rn Solubility in Scenario 1, 2 and 3

Schubert et al. (2012) used Equation 10 derived by Weiss et al. (Weiss et al. 1970, 1971; Weiss and Kyser 1978) for other noble gases. In Equation 10, *S* is the salinity, *T* is the temperature (in Kelvin), and a_1 to b_3 refer to six adjustable parameters.

$$ln\beta = a_1 + a_2 \left(\frac{100}{T}\right) + a_3 ln \left(\frac{T}{100}\right) + S \left\{b_1 + b_2 \left(\frac{T}{100}\right) + b_3 \left(\frac{T}{100}\right)^2\right\}$$
 Equation 10

Schubert et al. (2012) performed a series of laboratory experiments to evaluate the dependence of the partition coefficient upon both water temperature and salinity. Using this information, the authors derived the values for the six adjustable parameters, a_1 to b_3 , reported in Table 139.

Table 139: Parameters a_1 to b_3 Reported in Schubert et al. (2012). The Data Set Corresponds to the Most Recommendable One Reported in Table 1 of the Original Article

Parameter	Value
a ₁	-76.14
a ₂	120.36
a ₃	31.26
b₁	-0.2631
b ₂	0.1673
b ₃	-0.0270

Besides the six adjustable parameters, salinity is also needed in order to apply Equation 10. Considering the sodium and chloride concentrations in the different Scenarios (Table 14, Table 17 and Table 23), a salinity of ≈10‰ has been used in all Scenarios.

The Bunsen coefficient in Equation 10 and $K_{w/air}$ are related via Equation 11.

$$K_{w/air} = \beta \cdot \frac{T}{273.15}$$
 Equation 11

Equation 10 and Equation 11 have been used to calculate radon $K_{w/air}$ at each temperature shown in Table 140.

Table 140: Radon K_{w/air} Under SCENARIO 1, SCENARIO 2 and SCENARIO 3 Conditions

SCENARIO 1, 2, 3						
Radon K _{w/air}						
15°C	15°C 25°C 50°C 80°C					
0.28	0.21	0.12	0.09			

Radon partition coefficient decreases when the temperature increases, indicating that radon solubility will be lower at the higher temperatures. This is in agreement with literature observations (Weigel 1978; Clever 1979; Schubert et al. 2012; Ye et al. 2019).

4.19.2 Uncertainties

Although the dependence of the water/air partition coefficient of radon with temperature is well known, its dependence on other parameters such as salinity are less studied. This leads to a lack of information for the solubility calculations for radon.

4.20 Ru

Ruthenium is a chemical element with a rather complex redox chemistry. Under the groundwater conditions studied, Ru will be found mainly in the redox states +III and +II (Figure 26). Thermodynamic data available in the literature for this element is very scarce, which limits the accuracy of the solubility analysis.



Figure 26: Eh vs pH Predominance Diagram at 25°C for Ruthenium Aqueous Species in Water, Calculated Using the Data Selection in the Present Work. $[Ru]_T=10^{-6}$ M. Solids Are not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for Scenario 1 at 25°C; Blue Dot Indicates pH/Eh Conditions for Scenario 2 at 25°C. Green Dotted Lines Stand for the Water Stability Field

The available enthalpy data for relevant Ru solids and aqueous species is summarised in Table 141.

Table 141: Available Enthalpy Data for Correcting Temperature Effects on Ru Behaviour

Solid phase	Available enthalpy data
Ru(OH) ₃ ·2H ₂ O(s)	×
Aqueous phase	Available enthalpy data
Ru(OH) ₂ +	×
Ru ²⁺	\checkmark
RuOH⁺	\checkmark
Ru(OH)₂(aq)	\checkmark
RuSO₄(aq)	\checkmark

4.20.1 Ru Solubility in Scenario 1

Under Scenario 1 condition, $Ru(OH)_3 \cdot 2H_2O(s)$ has been selected as the Ru solubility limiting phase. Ru solubility and speciation under Scenario 1 conditions are presented in Table 142 and Table 143.

The lack of enthalpy data for the main Ru(+III) aqueous species, $Ru(OH)_{2^{+}}$ (see Table 141) makes it difficult to verify the accuracy of the calculations at T \neq 25°C. These results must be considered as tentative values only.

Table 142: Ruthenium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1					
		Concentr	ation (m)			
Solid phase	15°C 25°C 50°C 80°C					
Ru(OH) ₃ ·2H ₂ O(s)	3.21·10 ⁻⁹	1.65⋅10 ⁻⁹	3.77·10 ⁻⁹	7.34·10 ⁻⁹		

		SCENARIO 1				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	Ru(OH)₂ ⁺	32%	100%	100%	100%	
	Ru ²⁺	54%	0%	0%	0%	
	RuOH⁺	5%	0%	0%	0%	
	Ru(OH)₂(aq)	1%	0%	0%	0%	
Ku(UH)3·2H2U(S)	RuSO₄(aq)	5%	0%	0%	0%	
	$Ru(SO_{4})_{2}^{2}$	1%	0%	0%	0%	
	Ru(SO ₄) ₃ ⁴⁻	1%	0%	0%	0%	
	RuĈl⁺	1%	0%	0%	0%	

Table 143: Ruthenium Speciation Under SCENARIO 1 Conditions

4.20.2 Ru Solubility in Scenario 2

As in the previous Scenario, $Ru(OH)_{3}\cdot 2H_2O(s)$ has been selected as Ru solubility limiting phase for Scenario 2. Solubility and speciation results for Scenario 2 are presented in Table 144 and Table 145. Ruthenium is a redox sensitive element and thus the changes in pH/Eh values of groundwater induced by the steel canister corrosion will strongly affect the solubility and speciation behaviour of this element (Figure 26). Ru(+II) species will dominate its aqueous chemistry in this Scenario at T=25°C. The lack of enthalpy data for the main Ru(+III) aqueous species, $Ru(OH)_2^+$ (see Table 141) makes it difficult to verify the accuracy of the calculations at T \neq 25°C; these solubility and speciation results must be considered as tentative values only.

Table 144: Ruthenium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2					
		Concent	ration (m)			
Solid phase	15°C 25°C 50°C 80°C					
Ru(OH) ₃ ·2H ₂ O(s)	1.32·10 ⁻⁶ 2.23·10 ⁻⁹ 2.80·10 ⁻¹⁰ 1.25·10 ⁻⁹					

Table 145: Ruthenium Speciation Under SCENARIO 2 Conditions

Solid phase	Speciation	15°C	25°C	50°C	80°C
-	Ru(OH)₂⁺	0%	3%	100%	100%
	Ru ²⁺	7%	8%	0%	0%
Ru(OH)₃·2H₂O(s)	RuOH⁺	21%	22%	0%	0%
	Ru(OH)₂(aq)	71%	67%	0%	0%
	RuSO₄(aq)	1%	1%	0%	0%

4.20.3 Ru Solubility in Scenario 3

Solubility and speciation results, assuming $Ru(OH)_3 \cdot 2H_2O(s)$ as the Ru solubility limiting phase, under Scenario 3 conditions are presented in Table 146 and Table 147. As in Scenario 2, under Scenario 3 conditions Ru aqueous chemistry is dominated by Ru(+II) species at T=25°C.

Ru solubility and speciation results at T \neq 25°C must be considered as tentative values only due to the lack of enthalpy data for Ru(OH)₂⁺.

Table 146: Ruthenium Solubility-Controlling Phase and Concentrations Under SCENARIO3 Conditions

	SCENARIO 3					
		Concentration (m)				
Solid phase	15°C	25°C	50°C	80°C		
Ru(OH) ₃ ·2H ₂ O(s)	1.11·10⁻ ⁶	1.82∙10 ⁻⁹	1.26⋅10 ⁻¹⁰	5.32·10 ⁻¹⁰		

		SCENARIO 2			
Solid phase	Speciation	15°C	25°C	50°C	80°C
	Ru(OH)₂⁺	0%	2%	100%	100%
	Ru ²⁺	2%	2%	0%	0%
Ru(OH)₃-2H₂O(s)	RuOH⁺	13%	13%	0%	0%
	Ru(OH)₂(aq)	85%	82%	0%	0%
	RuSO₄(aq)	0%	0%	0%	0%

Table 147: Ruthenium Speciation Under SCENARIO 3 Conditions

4.20.4 Uncertainties

The assessment of Ru solubility and speciation behaviour is limited by the lack of reliable thermodynamic data, specially for Ru(+III) aqueous species (Rard 1985, 1987).

4.21 S

Under the conditions of the present work, only S(+VI) (sulphate) species are taken into account, as the microbiologically mediated reduction of sulphate to sulphide is not considered in this work. Detailed explanations on the calculations leading to sulphate groundwater concentrations are provided in section 3.

Enthalpy data are available for all solid and aqueous species in the calculations.

4.21.1 S Solubility in Scenario 1

Sulphate concentration under Scenario 1 conditions (Table 148) are mainly controlled by calcium sulphate solids. Gypsum (hydrated calcium sulphate) transforms into anhydrite (dehydrated calcium sulphate) at temperatures above 40°C-60°C; therefore, the calculations were conducted by allowing the precipitation of gypsum at T 15°C and 25°C, while assuming that anhydrite is the calcium sulphate phase at 50°C and 80°C.

At all studied temperatures sulphate speciation is dominated by SO_4^{2-} and the calcium sulphate complex $Ca(SO_4)(aq)$ (Table 149).

	SCENARIO 1						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
CaSO₄·2H₂O (Gypsum) ^{a)}	1.19·10 ⁻²	1.23·10 ⁻²					
CaSO₄(s) (Anhydrite) ^{a)}			1.17·10 ⁻²	7.93·10 ⁻³			

Table 148: Sulphate Concentrations Under SCENARIO 1 Conditions

^a Mainly determined by gypsum solubility at T<40°C and anhydrite solubility at T>40°C. Further details provided in section 3.

Table 149: Sulphate Speciation Under SCENARIO 1 Conditions

		SCENARIO 1				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
-	SO ₄ ²⁻	57%	57%			
CaSO₄·2H₂O (Gypsum) ^{a)}	Ca(SO₄)(aq)	41%	41%			
	Mg(SO ₄)(aq)	1%	1%			
	SO4 ²⁻			57%	58%	
CaSO₄(s) (Anhydrite)ª)	Ca(SO₄)(aq)			41%	40%	
	Mg(SO₄)(aq)			2%	2%	

^a Mainly determined by gypsum solubility at T<40°C and anhydrite solubility at T>40°C. Further details provided in section 3.

4.21.2 S Solubility in Scenario 2

As sulphate to sulphide reduction is not taken into account, sulphate concentrations (controlled by gypsum or anhydrite) in Scenario 2 (Table 150) are not influenced by the Eh changes in groundwater produced by canister steel corrosion. Calculated speciation (Table 151) is very similar to the one obtained for Scenario 1.

Table 150: Sulphate Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2							
	Concentration (m)							
Solid phase	15°C	25°C	50°C	80°C				
CaSO ₄ ·2H ₂ O (Gypsum) ^{a)}	1.19·10 ⁻²	1.23·10 ⁻²						
CaSO₄(s) (Anhydrite) ^{a)}			1.17·10 ⁻²	7.94·10 ⁻³				

^a Mainly determined by gypsum solubility at T<40°C and anhydrite solubility at T>40°C. Further details provided in section 3.

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	SO ₄ ²⁻	58%	57%			
CaSO₄·2H₂O (Gypsum) ^{a)}	Ca(SO₄)(aq)	41%	41%			
	Mg(SO₄)(aq)	1%	1%			
	SO4 ²⁻			57%	58%	
CaSO₄(s) (Anhydrite) ^{a)}	Ca(SO₄)(aq)			41%	39%	
	Mg(SO₄)(aq)			2%	2%	

Table 151: Sulphate Speciation Under SCENARIO 2 Conditions

^a Mainly determined by gypsum solubility at T<40°C and anhydrite solubility at T>40°C. Further details provided in section 3.

4.21.3 S Solubility in Scenario 3

Calculated sulphate concentrations under Scenario 3 conditions, with solubility control exerted by gypsum or anhydrite, are reported in Table 152 and the corresponding aqueous speciation is summarized in Table 153. Total sulphate concentrations are not influenced by consideration of the interaction of groundwater with the bentonite buffer. However, changes in S speciation (in comparison with Scenario 2) are observed due to the bentonite ion exchange processes involving calcium and magnesium cations.

Table 152: Sulphate Concentrations Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

	SCENARIO 3									
	Concentration (m)									
		Cas	se A			Cas	se B			
	(Base case for Scenario 3)				(Sensitivity analysis for Scenario 3)					
Solid phase	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C		
CaSO₄·2H₂O (Gypsum) ^{a)}	1.19·10 ⁻²	1.23·10 ⁻²			1.19·10 ⁻²	1.23·10 ⁻²				
CaSO₄(s) (Anhydrite) ^{a)}			1.17·10 ⁻²	7.93·10 ⁻³			1.17·10 ⁻²	7.93·10 ⁻³		

^a Mainly determined by gypsum solubility at T<40°C and anhydrite solubility at T>40°C. Further details provided in section 3.

		SCENARIO 3							
		Case A			Case B			<u> </u>	
		(Base case for Scenario 3)			(Sensitivity analysis for Scenario 3			cenario 3)	
Solid phase	Speciation	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C
C2SO, 24.0	SO4 ²⁻	82%	82%			84%	84%		
$CaSU4 \cdot Z\Pi_2 U$	Ca(SO₄)(aq)	14%	13%			12%	12%		
(Gypsuiii)*/	Mg(SO₄)(aq)	4%	4%			4%	4%		
$C_{2}SO_{2}(c)$	SO4 ²⁻			83%	86%			84%	86%
CaSU4(S)	Ca(SO₄)(aq)			12%	10%			12%	10%
(Annyunte)*/	Mg(SO₄)(aq)			4%	4%			4%	4%

Table 153: Sulphate Speciation Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

^a Mainly determined by gypsum solubility at T<40°C and anhydrite solubility at T>40°C. Further details provided in section 3.

4.21.4 Uncertainties

Sulphate reduction to sulphide has not been taken into account in the calculations, as microbial activity is not taken into account. Furthermore, no sulphide concentrations are provided in the CR-10 groundwater. If sulphate reduction to sulphide is taken into account or sulphide is present in the groundwater, sulphide would impact the solubility and speciation of several elements such as Ag, Bi, Cd, Cu, Fe, Hg, Pb, Pd, Sb and Sn.

4.22 Sb

Antimony is a metalloid; its chemical properties are rather similar to non-metallic elements such as arsenic but also similar to other metals like silver.

Enthalpy data are available for all relevant solid and aqueous species in the calculations.

4.22.1 Sb Solubility in Scenario 1

 Sb_2O_3 (Valentinite) has been selected as the Sb solubility limiting phase under Scenario 1 conditions. Under Scenario 1 conditions, Sb solubility slightly increases as temperature increases (Table 154). The Sb solubility is observed to increase by half an order of magnitude from 15°C to 80°C. Antimony aqueous speciation remains identical at all studied temperatures, being $Sb(OH)_3(aq)$ the predominant species (Table 155).

Table 154: Antimony Solubility-Controlling Phase and Concentrations Under SCENARIO
1 Conditions

	SCENARIO 1						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
Sb ₂ O ₃ (Valentinite)	5.02·10 ⁻⁵	5.71·10 ⁻⁵	7.62·10 ⁻⁵	1.02.10-4			

Table 155: Antimony Speciation Under SCENARIO 1 Conditions

		SCENARIO 1					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
Sb ₂ O ₃ (Valentinite)	Sb(OH)₃(aq)	100%	100%	100%	100%		

4.22.2 Sb Solubility in Scenario 2

Neither the redox nor the iron concentration changes in groundwater affects antimony solubility and speciation, assuming Sb_2O_3 (Valentinite) as the solubility limiting phase. Thus, the solubility and speciation results obtained in Scenario 2 (Table 156 and Table 157) are almost equal to that obtained in Scenario 1.

Table 156: Antimony Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
Sb ₂ O ₃ (Valentinite)	5.02·10 ⁻⁵	5.71·10 ⁻⁵	7.62·10⁻⁵	1.02.10-4			

Table 157: Antimony Speciation Under SCENARIO 2 Conditions

		SCENARIO 2					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
Sb ₂ O ₃ (Valentinite)	Sb(OH)₃(aq)	100%	100%	100%	100%		

4.22.3 Sb Solubility in Scenario 3

The influence of bentonite buffer material on the groundwater chemistry (Scenario 3) is not affecting the antimony chemistry. The solubility and speciation results, assuming Sb_2O_3 (Valentinite) as the solubility limiting phase, are presented in Table 158 and Table 159.

Table 158: Antimony Solubility-Controlling Phase and Concentrations Under SCENARIO3 Conditions

	SCENARIO 3						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
Sb ₂ O ₃ (Valentinite)	5.00·10 ⁻⁵	5.61·10 ⁻⁵	7.59·10 ⁻⁵	1.02·10 ⁻⁴			

Table 159: Antimony Speciation Under SCENARIO 3 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
Sb ₂ O ₃ (Valentinite)	Sb(OH)₃(aq)	100%	100%	100%	100%	

4.22.4 Uncertainties

Although sulphides are not accounted for in the present study, under repository conditions it is expected that this ligand may have an important effect on antimony chemistry by the formation of aqueous species or solid phases such Stibnite ($Sb_2S_3(s)$) (see Table 207).

4.23 Se

Selenium is an oxoanionic element predominantly existing in the redox states -II, +IV and +VI. Se(-II) prevails under reducing conditions, whereas $SeO_3^{2^-}$ (or $HSeO_3^{-}$) and $SeO_4^{2^-}$ dominate under oxidant conditions (Figure 27). The parameters mostly affecting the selenium chemistry are the Eh and the iron concentration of the system (see the examples in Figure 28 and Figure 29).

Enthalpy data are available for all relevant solids and aqueous species in the calculations.



Figure 27: Eh vs pH Predominance Diagram at 25°C for Selenium Aqueous Species in Water, Calculated Using the Data Selection in the Present Work. $[Se]_T=10^{-7}$ M; Solids Are not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for Scenario 1 Groundwater at 25°C. Green Dotted Lines Stand for the Water Stability Field



Figure 28: Ferroselite (FeSe₂(s)) Solubility as a Function of Iron Concentration at 25°C and Eh=-0.19 V; the Effect of Other Ligands Is not Taken into Account in This Graph. Vertical Dotted Line Indicates $[Fe]_T=1.6\cdot10^{-4}$ M, Similar to Scenario 1 Conditions



Figure 29: $Fe_{1.04}Se(s)$ Solubility as a Function of Iron Concentration at 25°C and Eh=-0.6 V; the Effect of Other Ligands Is not Taken into Account in This Graph. Vertical Dotted Line Indicates [Fe]_T=3·10⁻⁴ M, Similar to Scenario 2 Conditions

4.23.1 Se Solubility in Scenario 1

Se solubility, assuming ferroselite ($FeSe_2(s)$), $Fe_{1.04}Se(s)$ or Se(s) as solubility limiting phases, for Scenario 1 is shown in Table 160. As described in Olin et al. (2005), the presence of iron in the aqueous solution may cause the precipitation of $FeSe_x(s)$ solid phases, which are expected to control the Se solubility in reducing environments where Fe(II) is present. Elemental selenium, Se(s), could also be stable under slightly reducing conditions (see Figure 30).

Under Scenario 1 conditions, ferroselite ($FeSe_2(s)$) seems to be the most likely Se solubility limiting phase (Table 160 and Figure 30). HSe⁻ is the predominant aqueous species under all the range of conditions studied (Table 161).

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Conditions	

	SCENARIO 1						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
Fe _{1.04} Se(s)	5.40·10 ⁻⁷	1.16·10 ⁻⁶	7.56·10⁻ ⁶	6.28·10 ⁻⁵			
FeSe ₂ (s) (Ferroselite)	5.53·10 ⁻¹¹	1.07·10 ⁻¹⁰	5.67·10 ⁻¹⁰	3.88·10 ⁻⁹			
Se(s)	1.01·10 ⁻⁸	1.03·10 ⁻⁸	1.28·10 ⁻⁸	2.05·10 ⁻⁸			

		SCENARIO 1					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
Fe _{1.04} Se(s)	HSe	100%	100%	100%	100%		
FeSe ₂ (s) (Ferroselite)	HSe ⁻	100%	100%	100%	100%		
Se(s)	HSe ⁻	100%	100%	100%	100%		

Table 161: Selenium Speciation Under SCENARIO 1 Conditions



Figure 30: log[Fe]_T vs Eh Diagram of Selenium at pH = 7.03, [Se]_T =1 \cdot 10⁻⁷ M, [Mg]_T = 2.5 \cdot 10⁻³ M, [Ca]_T = 5.5 \cdot 10⁻² M, [CO₃]_T =9 \cdot 10⁻⁴ M, [Na]_T =8 \cdot 10⁻² M, [CI]_T =1.7 \cdot 10⁻¹ M. Red Dot Indicates log[Fe]_T / Eh Conditions for Scenario 1 Groundwater at 25°C

4.23.2 Se Solubility in Scenario 2

The parameters mostly affecting the selenium chemistry are the Eh and the iron concentration. In Scenario 2, due to the steel canister corrosion, Fe concentration in solution increases and the Eh of the groundwater decreases. Under those conditions, Fe_{1.04}Se(s) seems to be the most likely Se solubility limiting phase (Figure 31). Se solubility increases as temperature increases (Table 162). HSe⁻ species is the predominant Se species at all studied temperatures (Table 163).

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Fe _{1.04} Se(s)	4.82·10 ⁻⁹	7.58·10 ⁻⁹	3.25·10 ⁻⁸	1.43·10 ⁻⁷		
FeSe ₂ (s) (Ferroselite)	2.63·10 ⁻⁶	3.73·10 ⁻⁶	8.45·10 ⁻⁶	1.98·10 ⁻⁵		

 Table 162: Selenium Solubility-Controlling Phase and Concentrations Under SCENARIO 2

 Conditions

Table 163: Selenium Speciation Under SCENARIO 2 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
Fe _{1.04} Se(s)	HSe	100%	100%	100%	100%	
FeSe ₂ (s) (Ferroselite)	HSe ⁻	100%	100%	100%	100%	



Figure 31: log[Fe]_T vs Eh Diagram of Selenium at pH = 8.46, [Se]_T =1·10⁻⁷ M, [Mg]_T = $2.5 \cdot 10^{-3}$ M, [Ca]_T = $5.5 \cdot 10^{-2}$ M, [CO₃]_T =4.5·10⁻⁵ M, [Na]_T =8·10⁻² M, [CI]_T =1.7·10⁻¹ M. Blue Dot Indicates log[Fe]_T / Eh Conditions for Scenario 2 Groundwater at 25°C

4.23.3 Se Solubility in Scenario 3

Se solubility and speciation results in Scenario 3 are presented in Table 164 and Table 165. $Fe_{1.04}Se(s)$ seems to be the most likely Se solubility limiting phase.

Scenario 3 solubility and speciation results are very similar to those of Scenario 2, although slightly higher Se solubilities have been obtained due to Fe incorporation into the bentonite exchanger, which reduces the amount of available iron in solution.

Table 164: Selenium Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

	SCENARIO 3				
		Concentr	ation (m)		
Solid phase	15°C	25°C	50°C	80°C	
Fe _{1.04} Se(s)	8.55·10 ⁻⁹	1.56·10 ⁻⁹	7.03·10 ⁻⁸	3.39·10 ⁻⁷	
FeSe ₂ (s) (Ferroselite)	5.28·10 ⁻⁶	7.66·10⁻ ⁶	1.86·10⁻⁵	4.67 ∙ 10 ⁻⁵	

Table 165: Selenium Speciation Under SCENARIO 3 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
Fe _{1.04} Se(s)	HSe	100%	100%	100%	100%	
FeSe ₂ (s) (Ferroselite)	HSe ⁻	100%	100%	100%	100%	

4.23.4 Uncertainties

The reduction of sulphate to sulphide (not considered in the present assessment) could affect the stabilities of both $Fe_{1.04}Se(s)$ and $FeSe_2(s)$. Given the similarities between the ionic radius of Se^{2-} and that of S^{2-} (0.191 nm vs. 0.184 nm, Shannon 1976), substitution of selenium for sulphur may occur.

Finally, there are some uncertainties related to Se(-II) speciation. Polynuclear Se aqueous species $Se_2^{2^2}$, $Se_3^{2^2}$ and $Se_4^{2^2}$ species have not been included in the calculations, as there is a lack of thermodynamic information related to their acid/base stabilities (Olin et al. 2005).

4.24 Sn

Tin is a pseudo-metallic, easily hydrolysable element normally existing in +II and +IV redox states (Figure 32). The available enthalpy data for relevant Sn solids and aqueous species is summarised in Table 166.



Figure 32: Eh vs pH Predominance Diagram at 25°C for Tin Aqueous Species in Water. [Sn]_T=10⁻⁸ M. Solids Are not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for Scenario 1 Groundwater at 25°C, Blue Dot Indicates pH/Eh Conditions for Scenario 2 Groundwater at 25°C. Green Dotted Lines Stand for the Water Stability Field

 Table 166: Available Enthalpy Data for Correcting Temperature Effects on Sn Behaviour

Soli	Available enthalpy data	
SnO₂(am)	×	
CaSn(OH)	×	
	Available	
Aqueous p	mase	enthalpy data
Sp(1II)	Sn(OH)₂(aq)	\checkmark
511(+11)	Sn(OH)₃ ⁻	\checkmark
	Sn(OH)₄(aq)	\checkmark
Sn(+IV)	Sn(OH)₅⁻	×
	Sn(OH) ₆ ²⁻	×

4.24.1 Sn Solubility in Scenario 1

Under Scenario 1 conditions, and following the Ostwald's rule, the amorphous phase $SnO_2(am)$ is the more likely solubility limiting solid. The Sn solubility and speciation, assuming $SnO_2(am)$ as the solubility limiting phase, are shown in Table 167 and Table 168. Under more alkaline conditions, the solid phase $CaSn(OH)_6(s)$ could also be formed.

The calculated results presented in these tables indicates that the Sn solubility decreases when temperature increases. However, the lack of enthalpy data (see Table 166) makes it difficult to verify the accuracy of the calculations at $T \neq 25^{\circ}$ C.

Table 167: Tin Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
SnO ₂ (am)	1.20·10 ⁻⁷	6.05·10 ⁻⁸	1.35∙10 ⁻⁸	3.18∙10 ⁻⁹		
CaSn(OH)₀(s)	3.21·10 ⁻⁶	4.09·10 ⁻⁶	4.98·10 ⁻⁶	4.80·10 ⁻⁶		

Table 168: Tin Speciation Under SCENARIO 1 Conditions

				SCEN	ARIO 1	
Solid phase	Sp	eciation	15°C	25°C	50°C	80°C
$SnO_{1}(am)$	Sn(11)/)	Sn(OH)₄(aq)	97%	96%	93%	83%
ShO ₂ (am)	51(+17)	Sn(OH)₅⁻	3%	4%	7%	17%
	Sn(11)/)	Sn(OH)₄(aq)	97%	96%	93%	83%
	31(+1V)	Sn(OH)₅ ⁻	3%	4%	7%	17%

4.24.2 Sn Solubility in Scenario 2

In Scenario 2, the groundwater pH is more alkaline than in Scenario 1. In this case, both $SnO_2(am)$ and $CaSn(OH)_6(s)$ may limit Sn solubility (Table 169).

Under Scenario 2 conditions, Sn solubility increases as temperature increases. This is related to the reducing characteristics of the groundwater and the formation of Sn(+II) aqueous species at high temperatures (Table 170 and Figure 33). However, the lack of enthalpy data (see Table 166) makes it difficult to verify the accuracy of the calculations at T \neq 25°C.

	SCENARIO 2						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
SnO₂(am)	2.52·10 ⁻⁷	1.57·10 ⁻⁷	2.83·10 ⁻⁷	1.94·10 ⁻⁶			
CaSn(OH)₀(s)	6.82·10 ⁻⁹	1.48⋅10 ⁻⁸	5.80·10 ⁻⁷	8.52·10 ⁻⁵			

Table 169: Tin Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

Table 170: Tin S	peciation Under	SCENARIO	2 Conditions
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			SCENARIO 2					
Solid phase	Sp	eciation	15°C	25°C	50°C	80°C		
-	-	Sn(OH)₄(aq)	46%	37%	4%	0%		
	Sn(+IV)	Sn(OH)₅	43%	38%	5%	0%		
SnO₂(am)		Sn(OH) ₆ ²⁻	5%	3%	0%	0%		
	Sp(1II)	Sn(OH) ₂ (aq)	4%	13%	53%	57%		
	51(+1)	Sn(OH)₃ ⁻	2%	9%	38%	43%		
		Sn(OH)₄(aq)	46%	37%	4%	0%		
	Sn(+IV)	Sn(OH)₅ ⁻	43%	38%	5%	0%		
CaSn(OH)₀(s)		Sn(OH) ₆ ²⁻	5%	3%	0%	0%		
	Sp(1II)	Sn(OH)₂(aq)	4%	13%	53%	57%		
	31(+1)	Sn(OH)₃ ⁻	2%	9%	38%	43%		



Figure 33: Tin Speciation Under Scenario 2 Conditions as a Function of Temperature. Sn(+IV) Species Are Represented in Green Colours and Sn(+II) Species in Orange-Yellow Colours. 4.24.3 Sn Solubility in Scenario 3

Solubility and speciation results obtained for Sn in Scenario 3 are very similar to those reported for Scenario 2. Solubility and speciation results are presented in Table 171 and Table 172. The lack of enthalpy data makes it difficult to verify the accuracy of the calculations at T≠25°C.

Table 171: Tin Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

	SCENARIO 3					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
SnO₂(am)	4.05·10 ⁻⁷	2.44·10 ⁻⁷	4.16·10 ⁻⁷	2.93·10⁻ ⁶		
CaSn(OH)₀(s)	1.10·10 ⁻⁸	2.30·10 ⁻⁸	8.25·10 ⁻⁷	-		

Table 172: Tin Speciation Under SCENARIO 3 Conditions

			SCENARIO 2				
Solid phase	Spe	eciation	15°C	25°C	50°C	80°C	
		Sn(OH)₄(aq)	28%	24%	3%	0%	
Sn(+IV) SnO₂(am) Sn(+II)	Sn(+IV)	Sn(OH)₅⁻	53%	49%	7%	0%	
		Sn(OH)₀²⁻	13%	7%	0%	0%	
	Sp(1II)	Sn(OH)₂(aq)	2%	9%	36%	37%	
	511(+11)	Sn(OH)₃ ⁻	3%	11%	53%	62%	
		Sn(OH)₄(aq)	28%	24%	3%	0%	
CaSn(OH)₀(s)	Sn(+IV)	Sn(OH)₅⁻	53%	49%	7%	0%	
		Sn(OH)₀²⁻	13%	7%	0%	0%	
	Sp(1II)	Sn(OH)₂(aq)	2%	9%	36%	37%	
	511(+11)	Sn(OH)₃⁻	3%	11%	53%	62%	

4.24.4 Uncertainties

The main uncertainty affecting Sn solubility and speciation calculations is the lack of enthalpy data (see Table 166). No additional literature data that can help to reduce this uncertainty has been identified.

Another uncertainty affecting the assessment of tin solubility and speciation refers to the reduction of sulphate to sulphide. In the presence of HS⁻, tin may precipitate as tin sulphides, which would affect its aqueous concentration (see section 5).

4.25 Sr

The alkaline-earth Sr is a non-redox sensitive element with a great affinity towards several ligands like carbonate and sulphate, thus its chemistry maybe be driven by interactions with them.

Enthalpy data are available for all relevant solids and aqueous species in the calculations.

4.25.1 Sr Solubility in Scenario 1

Celestite $(Sr(SO_4)(s))$ and strontianite $(Sr(CO_3)(s))$ are the two main solid phases that may control the solubility of strontium in Scenario 1. Sr solubility and speciation for this Scenario are shown in Table 173 and Table 174.

The solid phase exerting the solubility control basically depends on the SO_4^{2-}/CO_3^{2-} ratio of the water. Under Scenario 1 conditions, celestite is the more likely solubility limiting phase (Figure 34).



Figure 34: $\log[CO_3^{2^-}]_T$ vs $\log[SO_4^{2^-}]_T$ Diagram of Strontium at pH = 7.03, $[Sr]_T = 1 \cdot 10^{-3}$ M, $[Mg]_T = 2.5 \cdot 10^{-3}$ M, $[Ca]_T = 5.5 \cdot 10^{-2}$ M, $[Na]_T = 8 \cdot 10^{-2}$ M, $[K]_T = 4 \cdot 10^{-4}$ M, $[CI]_T = 1.7 \cdot 10^{-1}$ M. Red Dot Indicates $\log[CO_3^{2^-}]_T$ / $\log[SO_4^{2^-}]_T$ Conditions for Scenario 1 Groundwater at 25°C

Celestite is mainly affected by the presence of sulphate in the groundwater; an increase of sulphate concentration results in a decrease of celestite solubility, due to the common-ion effect (Figure 35).



Figure 35: Celesite Solubility (Solid Black Line) as a Function of Sulfate Concentration at 25°C, $[CI]_T=1.7\cdot10^{-1}$ M, $[Na]_T=8.4\cdot10^{-2}$ M, $[Ca]_T=5.5\cdot10^{-3}$ M, $[Mg]_T=2.5\cdot10^{-3}$ M, $[K]_T=3.9\cdot10^{-4}$ M, $[C]_T=9\cdot10^{-4}$ M, pH=7. Calcite and Gypsum Are not Allowed to Precipitate in This Calculation. Vertical Dotted Line Indicates $[SO_4]_T=1.2\cdot10^{-2}$ M, as Expected Under Scenario 1 Conditions

Sr solubility slightly increases as temperature increases, from $6.03 \cdot 10^{-4}$ m at 15° C to $1.05 \cdot 10^{-3}$ m at 80° C. Sr speciation in all the studied temperature range is governed by the free cation, Sr²⁺, with minor contributions from SrSO₄(aq) and SrCl⁺ species.

Table 173: Strontium Solubility-Controlling Phase and Concentrations Under SCENARIO
1 Conditions

	SCENARIO 1						
	Concentration (m)						
Solid phase	15°C	25°C	50°C	80°C			
SrSO₄(Celestite)	6.03·10 ⁻⁴	6.02·10 ⁻⁴	6.75·10 ⁻⁴	1.05⋅10 ⁻³			
SrCO ₃ (Strontianite)	8.92·10 ⁻³	1.06·10 ⁻²	1.53·10 ⁻²	2.39·10 ⁻²			

		SCENARIO 1				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
-	Sr ²⁺	86%	85%	84%	85%	
SrSO ₄ (Celestite)	Sr(SO₄)(aq)	7%	8%	8%	6%	
	SrCl⁺	6%	7%	7%	8%	
SrCO	Sr ²⁺	87%	86%	85%	87%	
SICU ₃ (Strontionito)	Sr(SO₄)(aq)	7%	7%	7%	5%	
(Submanite)	SrCl ⁺	6%	7%	7%	7%	

Table 174: Strontium Speciation Under SCENARIO 1 Conditions

4.25.2 Sr Solubility in Scenario 2

Sr solubility and speciation results, assuming celestite or strontianite as solubility limiting phase, for Scenario 2 are presented in Table 175 and Table 176. Celestite is the more likely solubility limiting phase. The effect of steel canister corrosion on Sr chemistry is small, as neither Eh/pH nor the iron content is affecting Sr solubility or speciation. Thus, Sr solubility and speciation results for Scenario 2 are similar to those of Scenario 1.

Table 175: Strontium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
SrSO₄ (Celestite)	6.01·10 ⁻⁴	5.98·10 ⁻⁴	6.69·10 ⁻⁴	1.04·10 ⁻³		
SrCO ₃ (Strontianite)	8.80·10 ⁻³	1.04·10 ⁻²	1.56·10 ⁻²	2.44·10 ⁻²		

Table 176: Strontium Speciation Under SCENARIO 2 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
-	Sr ²⁺	86%	85%	84%	86%	
SrSO₄ (Celestite)	Sr(SO₄)(aq)	7%	8%	8%	6%	
	SrCl ⁺	6%	7%	7%	8%	
S-CO	Sr ²⁺	87%	86%	86%	87%	
SILU3 (Strentionite)	Sr(SO₄)(aq)	7%	7%	7%	5%	
(Suomanite)	SrCl⁺	6%	7%	7%	8%	

The Sr solubility and speciation calculated in Scenario 3 conditions assuming celestite or strontianite as solubility limiting phase, are shown in Table 177 and Table 178. Solubility and speciation results indicate that taking into account the effect of the bentonite buffer on groundwater, only slight differences are observed from the solubility and speciation results of Scenario 1 and Scenario 2.

Table 177: Strontium Solubility-Controlling Phase and Concentrations Under SCENARIO3 Conditions

	SCENARIO 3					
		Concentr	ation (m)			
Solid phase	15°C	25°C	50°C	80°C		
SrSO₄ (Celestite)	4.78·10 ⁻⁴	4.67·10 ⁻⁴	4.96·10 ⁻⁴	7.35·10 ⁻⁴		
SrCO ₃ (Strontianite)	2.29·10 ⁻³	2.55 ⋅ 10 ⁻³	3.01·10 ⁻³	3.47·10 ⁻³		

Table 178: Strontium Speciation Under SCENARIO 3 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	Sr ²⁺	84%	83%	82%	83%	
SrSO ₄ (Celestite)	Sr(SO₄)(aq)	9%	10%	11%	9%	
	SrCl ⁺	6%	6%	7%	8%	
S*CO	Sr ²⁺	85%	84%	82%	83%	
SICU ₃ (Strontionito)	Sr(SO₄)(aq)	9%	10%	11%	8%	
(Strontianite)	SrCl ⁺	6%	6%	7%	8%	

4.25.4 Uncertainties

The main uncertainty affecting Sr solubility is the possible co-precipitation of Sr with other major solids present in the environment. For example, Bruno et al. (2001) suggested the formation of a solid solution between $SrCO_3(s)$ and $CaCO_3(s)$. The formation of such co-precipitates will lead to a lower Sr concentration in groundwater.

4.26 Tc

Technetium redox properties are very relevant to its chemical behaviour in nature. In the reducing groundwater conditions studied in this project, Tc(+IV) species will be predominant.

The available enthalpy data for relevant Tc solids and aqueous species is summarized in Table 179.

Solid phase	Available enthalpy data
TcO ₂ -1.63H ₂ O(s)	×
Aqueous phase	Available enthalpy data
TcO(OH)₂(aq)	\checkmark
Tc(OH)₂CO₃(aq)	×

4.26.1 Tc Solubility in Scenario 1

Tc solubility and speciation for Scenario 1 are shown in Table 180 and Table 181. The most likely solid phase limiting the Tc solubility is $TcO_2 \cdot 1.63H_2O(s)$, $TcO(OH)_2(aq)$ being the main aqueous species in solution.

Tc solubility is almost constant, $\sim 4 \cdot 10^{-9}$ m, independently of the system temperature. A small effect of temperature on Tc solubility was also predicted in the literature (see Lemire and Garisto 1992), although the lack of enthalpy data (see Table 179) makes it difficult to verify the accuracy of this affirmation.

Table 180: Technetium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1			
	Concentration (m)			
Solid phase	15°C	25°C	50°C	80°C
TcO ₂ -1.63H ₂ O(s)	4.07·10 ⁻⁹	4.16·10 ⁻⁹	4.61·10 ⁻⁹	5.74·10 ⁻⁹

Table 181: Technetium Speciation Under SCENARIO 1 Conditions

		SCENARIO 1			
Solid phase	Speciation	15°C	25°C	50°C	80°C
TcO ₂ -1.63H ₂ O(s)	TcO(OH)₂(aq)	98%	96%	87%	70%
	Tc(OH) ₂ CO ₃ (aq)	2%	4%	13%	30%

Tc(+IV) aqueous species and solid compounds are predominant under both the slightly reducing conditions of Scenario 1 and the strongly reducing conditions of Scenario 2. As a consequence, solubility and speciation results, assuming TcO₂·1.63H₂O(s) as the Tc solubility limiting phase, calculated in Scenario 2 (Table 182 and Table 183) are similar to the ones obtained under Scenario 1 conditions.

Table 182: Technetium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2			
	Concentration (m)			
Solid phase	15°C	25°C	50°C	80°C
TcO ₂ -1.63H ₂ O(s)	4.02·10 ⁻⁹	4.02·10 ⁻⁹	4.02·10 ⁻⁹	4.07·10 ⁻⁹

Table 183: Technetium Speciation Under SCENARIO 2 Conditions

		SCENARIO 2			
Solid phase	Speciation	15°C	25°C	50°C	80°C
TcO ₂ -1.63H ₂ O(s)	TcO(OH)₂(aq)	99%	99%	99%	98%
	Tc(OH)₂CO₃(aq)	0%	0%	0%	1%

4.26.3 Tc Solubility in Scenario 3

Tc solubility and speciation results, assuming $TcO_2 \cdot 1.63H_2O(s)$ as the Tc solubility limiting phase, in Scenario 3 (Table 184 and Table 185) are almost identical to those of Scenario 1 and Scenario 2.

Table 184: Technetium Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

	SCENARIO 3			
	Concentration (m)			
Solid phase	15°C	25°C	50°C	80°C
TcO ₂ -1.63H ₂ O(s)	4.06·10 ⁻⁹	4.06·10 ⁻⁹	4.05·10 ⁻⁹	4.10·10 ⁻⁹

		SCENARIO 2			
Solid phase	Speciation	15°C	25°C	50°C	80°C
TcO ₂ -1.63H ₂ O(s)	TcO(OH)₂(aq)	99%	99%	99%	98%
	Tc(OH) ₂ CO ₃ (aq)	0%	0%	0%	1%

Table 185: Technetium Speciation Under SCENARIO 3 Conditions

4.26.4 Uncertainties

Although a small effect of temperature on Tc solubility is observed, the lack of enthalpy data (see Table 179) makes it difficult to verify the accuracy of this affirmation.

The formation of Tc(cr) has not been considered in the calculations because of the slow precipitation kinetics usually associated to the formation of metals from solution.

The lack of information about the possible formation of very reduced Tc(III) species, and the consequent omission of these species from the thermodynamic database, may also introduce some uncertainty in the calculations

4.27 Th

Thorium is a non-redox actinide chemical element. Given the relatively high carbonate concentrations in the studied groundwater, it is expected that this ligand will control the aqueous speciation of thorium at neutral pH values, while hydrolyzed species will become more relevant at alkaline pH and lower carbonate concentrations (Figure 36).

The available enthalpy data for the relevant Th solid and aqueous species is summarised in Table 186.



Figure 36: Carbonate vs pH Predominance Diagram at 25°C for Thorium Aqueous Species. $[Th]_T=1\cdot10^{-9}$ M; $[Ca]_T=5\cdot10^{-2}$ M. Calcite Is not Allowed to Precipitate in the calculations. Red Dot Indicates pH/Carbonate Conditions for Scenario 1 Groundwater at 25°C; Blue Dot Indicates pH/Carbonate Conditions for Scenario 2

 Table 186: Available Enthalpy Data for Correcting Temperature Effects on Th Behaviour

Solid phase	Available enthalpy data
ThO ₂ (am, aged)	×
Aqueous phase	Available enthalpy data
Th(OH)₃⁺	\checkmark
Th(OH)₄(aq)	\checkmark
Th(OH) ₂ (CO ₃) ₂ ²⁻	×
Th(OH)₂(CO₃)(aq)	×
Th(OH)₃(CO₃) ⁻	×

4.27.1 Th Solubility in Scenario 1

Several oxo-hydroxide Th phases, with different solubilities due to the crystallinity variation, ageing effects, surface hydration, particle size variation and colloids formation, may control the Th solubility under the studied conditions. ThO₂(am, aged) seems the most likely solid controlling Th solubility under Scenario 1 conditions. The Th solubility and speciation, in equilibrium with the selected solid phase, for Scenario 1 are shown in Table 187 and Table 188.
The calculated Th solubility (Table 187) increases as the temperature increases; however, those calculations are not in complete agreement with some experimental data available in the literature (Grivé et al. 2017; Moon 1989; Neck and Kim 2001; Vandenborre et al. 2012). The general conclusion from those experiments is that, in the near neutral to alkaline pH range, the presence of an amorphous layer covering a bulk crystalline solid minimises the effect of temperature on Th solubility in the absence of carbonates. Data in the presence of carbonates is much scarcer. Grivé et al. (2017) reported solubility experiments at pH~9 at high carbonate concentration ($[CO_3]_T \approx 5 \cdot 10^{-2} M$); no significant differences on thorium oxo-hydroxide solubility at T=25°C and T=40°C were observed. Thus, the literature results illustrate that the calculations at T≠25°C in Table 187 and Table 188 must be used with caution, due to the lack of enthalpy data for the main aqueous species (Th(OH)₃(CO₃)⁻) and the solid (ThO₂(am, aged).

Table 187: Thorium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1				
	Concentration (m)				
Solid phase	15°C	25°C	50°C	80°C	
ThO ₂ (am, aged)	1.89·10 ⁻⁹	4.20·10 ⁻⁹	1.99·10 ⁻⁷	2.31·10 ⁻⁵	

Table 188: Thorium Speciation Under SCENARIO 1 Conditions

	SCENARIO 1				
Solid phase	Speciation	15°C	25°C	50°C	80°C
-	Th(OH) ₃ (CO ₃)	75%	47%	2%	0%
	Th(OH)₄(aq)	8%	30%	74%	79%
ThO₂(am, aged)	Th(OH)₃⁺	2%	9%	23%	21%
	Th(OH) ₂ (CO ₃) ₂ ²⁻	10%	9%	1%	0%
	Th(OH)₂(CO₃)(aq)	5%	5%	0%	0%

4.27.2 Th Solubility in Scenario 2

The Th solubility and speciation, assuming $ThO_2(am, aged)$ as the solubility limiting phase, for Scenario 2 are shown in Table 189 and Table 190. As Th is a non-redox sensitive element, the impact of steel canister corrosion on its solubility and aqueous chemistry is very small.

As in the Scenario 1, the results at T≠25°C must be used with caution given the lack of enthalpy data for the solid phase and relevant aqueous species.

	SCENARIO 2					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
ThO ₂ (am, aged)	1.93·10 ⁻¹⁰	1.33·10 ⁻⁹	1.50·10 ⁻⁷	1.90·10 ⁻⁵		

Table 189: Thorium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

Table 190: Thorium Speciation Under SCENARIO 2 Conditions

			SCENARIO 2			
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	Th(OH) ₃ (CO ₃) ⁻	23%	5%	0%	0%	
ThO₂(am, aged)	Th(OH)₄(aq)	76%	93%	98%	96%	
	Th(OH)₃⁺	1%	1%	2%	4%	

4.27.3 Th Solubility in Scenario 3

The Th solubility and speciation, assuming ThO₂(am, aged) as the solubility limiting phase, for Scenario 3 are shown in Table 191 and Table 192. Differences in the Th solubility and speciation behaviour between Scenario 2 and 3 are negligible. As in Scenario 1 and Scenario 2, the solubility results at T \neq 25°C must be used with caution due to the lack of enthalpy data for the solid phase and relevant aqueous species.

Table 191: Thorium Solubility-Controlling Phase and Concentrations Under SCENARIO 3 Conditions

	SCENARIO 3				
	Concentration (m)				
Solid phase	15°C	25°C	50°C	80°C	
ThO ₂ (am, aged)	2.39·10 ⁻¹⁰	1.40·10 ⁻⁹	1.48·10 ⁻⁷	1.85·10 ⁻⁵	

Table 192: Thorium Speciation Under SCENARIO 3 Conditions

		SCENARIO 2				
Solid phase	Speciation	15°C	25°C	50°C	80°C	
	Th(OH)₃(CO₃) ⁻	38%	11%	0%	0%	
ThO ₂ (am, aged)	Th(OH)₄(aq)	61%	88%	99%	98%	
	Th(OH)₃⁺	0%	1%	1%	2%	

4.27.4 Uncertainties

The main uncertainty affecting the Th solubility and speciation behaviour with temperature is the lack of enthalpy data for the main aqueous species $(Th(OH)_3(CO_3)^-)$ and the solid $(ThO_2(am, aged))$. Additional literature information pointed out that the effect of temperature on Th solubility is not as high as estimated in the calculations.

Another uncertainty is the effect of phosphate on Th solubility. For example, Östhols (1995) performed Th oxo-hydroxide batch solubility experiments in phosphate-rich solutions and observed that the solid used in the experiments had a small but measurable phosphate content after being in contact with the phosphate solution, suggesting the formation of a sparingly soluble thorium phosphate. Phosphate minerals such as monazite can also incorporate thorium into its structure. However, the lack of thermodynamic data for those systems (Rand et al. 2009) does not allow to evaluate its influence under the studied conditions.

4.28 U

Uranium is a redox sensitive actinide element that under the groundwater conditions of interest will be predominantly in the oxidation states +IV and +VI. Uranium has a great complexation affinity towards some of the ligands present in groundwaters, especially carbonate, and thus its aqueous chemistry could be driven by such interactions (Figure 37).



Figure 37: UO₂·2H₂O(am) Solubility (Solid Black Line) and Underlying Aqueous U Speciation (Dashed Lines) as a Function of Carbonate Concentration at 25°C, [Ca]_T= $5.5 \cdot 10^{-3}$ M, pH=7, Eh=-0.19 V. Calcite Is not Allowed to Precipitate in This Calculation. Vertical Dotted Line Indicates [C]_T= $9 \cdot 10^{-4}$ M, as Expected Under Scenario 1 Conditions

Recent works (e.g. Vercouter et al. 2015) indicate that alkaline earth ternary carbonate species of uranyl (and specially Ca(II)–U(VI)-CO₃ species) may dominate the uranyl speciation in natural waters and clay conditions. Stability constants for Ca-U(VI)-carbonate species $(CaUO_2(CO_3)_3^{2-}$ and Ca₂UO₂(CO₃)₃(aq)) are already included in the ThermoChimie version 10a thermodynamic database²; on the contrary, their corresponding enthalpy values are not included in ThermoChimie yet.

The effect of temperature on these species was studied by Endrizzi and Rao (2014) and Jo et al. (2019) using calorimetric techniques; results provided by both authors are in reasonable agreement. Considering the relevance of these species under the studied conditions, the corresponding $\Delta_r H^{\circ}_m$ was included in the calculations (Equation 12 and Equation 13).

 $UO_{2^{2+}} + 3CO_{3^{2-}} + Ca^{2+} = CaUO_{2}(CO_{3})_{3^{2-}} \qquad \begin{array}{l} \Delta_{r}H^{\circ}{}_{m} = -40.4 \text{ kJ/mol} \\ (Jo \text{ et al. 2019}) \\ \Delta_{r}H^{\circ}{}_{m} = -42.3 \text{ kJ/mol} \\ (Jo \text{ et al. 2019}) \end{array} \qquad \begin{array}{l} \text{Equation 12} \\ \text{Equation 13} \end{array}$

The available enthalpy data for the relevant U solid and aqueous species are summarised in Table 193.

Table 193: Available Enthalpy Data for Correcting Temperature Effects on U Behaviour

Solid phase		Available enthalpy data
UO ₂ .2H	2 O(am)	×
Aqueou	ıs phase	Available enthalpy data
	Ca ₂ UO ₂ (CO ₃) ₃ (aq)	Added in p.w.
U(+VI)	CaUO ₂ (CO ₃) ₃ ²⁻	Added in p.w.
	UO ₂ (CO ₃) ₂ ²⁻	\checkmark
U(+IV)	U(OH)₄(aq)	\checkmark

 $MgUO_2(CO_3)_3^{2-}$ and $Mg_2UO_2(CO_3)_3(aq)$ are not included in the ThermoChimie database yet. Although those species will not be as relevant as $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3(aq)$ under the conditions studied in the present work, they were however included in the database for completeness (Equation 14 and Equation 15).

$UO_2^{2+} + 3CO_3^{2-} + Mg^{2+} = MgUO_2(CO_3)_3^{2-}$	Log K°= 25.80±0.80 (Lee et al. 2017)	Equation 14
$UO_2^{2+} + 3CO_3^{2-} + 2Mg^{2+} = Mg_2UO_2(CO_3)_3(aq)$	Log K°= 27.10±0.60 (Lee et al. 2017)	Equation 15

² CaUO₂(CO₃)₃²⁻ and Ca₂UO₂(CO₃)₃(aq) stability constants are included in ThermoChimie database version 10a used in present work. However, they were not included in ThermoChimie database version 7b used in Duro et al. (2010). This results in significant differences in calculated U concentration in Scenario 1 conditions.

4.28.1 U Solubility in Scenario 1

In the conditions of Scenario 1, following the Ostwald's principle, the amorphous oxide $UO_2 \cdot 2H_2O(am)$ was selected instead of the crystalline oxide as the most likely solubility limiting phase. The U solubility and speciation, using the above-mentioned solid phase, for Scenario 1 is shown in Table 194 and Table 195. Ca-U(VI)-CO₃ complexes dominate the uranium aqueous chemistry. Mg-U(VI)-CO₃ complexes, which are less stable, are formed in minor amounts under those conditions.

The uranium solubility shown in Table 194 indicates a solubility increase as the temperature increases. As there are still some data gaps to evaluate the temperature influence on uranium solubility (specially the enthalpy data for the solid phase, see Table 193), the U solubility data at $T\neq 25^{\circ}$ C should be used with caution.

Table 194: Uranium Solubility-Controlling Phase and Concentrations Under SCENARIO 1 Conditions

	SCENARIO 1				
	Concentration (m)				
Solid phase	15°C	25°C	50°C	80°C	
UO ₂ -2H ₂ O(am)	2.47·10 ⁻⁸	1.25·10 ⁻⁷	3.69·10 ⁻⁶	5.78·10 ⁻⁵	

Table 195: Uranium Speciation Under SCENARIO 1 Conditions

			SCENARIO 1			
Solid phase		Speciation	15°C	25°C	50°C	80°C
		Ca ₂ UO ₂ (CO ₃) ₃ (aq)	90%	89%	86%	66%
	11/1/1	CaUO ₂ (CO ₃) ₃ ²⁻	7%	7%	9%	9%
UO ₂ -2H ₂ O(am)	0(+vi)	UO ₂ (CO ₃) ₂ ²⁻	0%	0%	1%	7%
		MgUO ₂ (CO ₃) ₃ ²⁻	0%	0%	1%	5%
	U(+IV)	U(OH)₄(aq)	3%	3%	3%	5%

4.28.2 U Solubility in Scenario 2

Under Scenario 2 conditions the Eh of the system is highly reducing due to the steel canister corrosion. As uranium is a redox sensitive element this process has an important impact on its aqueous chemistry. Therefore, the U aqueous chemistry is controlled by U(IV) species $(U(OH)_4(aq), see Table 197)$ instead of Ca-U(VI)-CO₃ complexes. As a consequence, the calculated U concentration in equilibrium with UO₂·2H₂O(am), the selected solubility limiting phase, in Scenario 2 (Table 196) is about 2 orders of magnitude lower than in Scenario 1.

As described in the case of thorium, in the near neutral to alkaline pH range, the presence of an amorphous layer covering a bulk crystalline solid has been reported in U(IV) oxides (Parks and Pohl 1988; Rai et al. 2003). This would minimize the effect of temperature on the solubility of

U(IV). A tentative explanation of this phenomena may be related with the prevalence of $U(OH)_4(aq)$ aqueous species in the near-neutral pH range, favoring a process like an "isocoulombic" reaction³ (Equation 16) where electrostatic interactions are not expected to bring a relevant contribution to possible temperature effects. Thus, the solubility increase with temperature would not be as significant as shown in Table 196. Calculated solubility results at T \neq 25°C should be used with caution.

$$UO_2 \cdot 2H_2O(am) = U(OH)_4(aq)$$
 Equation 16

Table 196: Uranium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2				
	Concentration (m)				
Solid phase	15°C	25°C	50°C	80°C	
UO ₂ ·2H ₂ O(am)	6.80·10 ⁻¹⁰	3.17·10 ⁻⁹	9.77·10 ⁻⁸	3.16·10⁻ ⁶	

Table 197: Uranium Speciation Under SCENARIO 2 Conditions

			SCENARIO 2			
Solid phase	Sp	eciation	15°C	25°C	50°C	80°C
UO ₂ -2H ₂ O(am)	U(+IV)	U(OH)₄(aq)	100%	100%	100%	100%

4.28.3 U Solubility in Scenario 3

Uranium solubility behaviour in Scenario 3, assuming $UO_2 \cdot 2H_2O(am)$ as the solubility limiting phase, is almost identical to that observed in Scenario 2. Furthermore, solubility and speciation results for Case A (base case for Scenario 3) and case B (used for the sensitivity analysis in Scenario 3) are identical (Table 198 and Table 199).

³ Isocoulombic reactions are defined as reactions in which the magnitude of the electrical charge of each individual species is balanced between reactants and products.

Table 198: Uranium Solubility-Controlling Phase and Concentrations Under SCENARIO 3Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Correspondsto a Sensitivity Analysis

	SCENARIO 3							
	Concentration (m)							
	Case A				Case B			
	(Ba	ase case fo	r Scenario	3)	(Sensitivity analysis for Scenario 3)			
Solid phase	15°C	25°C	50°C	80°C	15°C	25°C	50°C	80°C
UO ₂ ·2H ₂ O(am)	6.79·10 ⁻¹⁰	3.16·10 ⁻⁹	9.76·10 ⁻⁸	3.15·10⁻ ⁶	6.79·10 ⁻¹⁰	3.16·10 ⁻⁹	9.76∙10 ⁻⁸	3.15·10 ⁻⁶

Table 199: Uranium Speciation Under SCENARIO 3 Conditions. Case A Corresponds to the Base Case for Scenario 3; Case B Corresponds to a Sensitivity Analysis

			SCENARIO 3							
			Case A Case B							
			(Base	case fo	or Scena	rio 3)	(Sensitivity analysis for Scenario 3)			
Solid phase	Sp	eciation	15°C	15°C 25°C 50°C 80°C			15°C	25°C	50°C	80°C
UO₂∙2H₂O(am)	U(+IV)	U(OH)₄(aq)	100%	100%	100%	100%	100%	100%	100%	100%

4.28.4 Uncertainties

Additional literature information illustrates that the effect of temperature on U solubility would not be as high as estimated in the calculations. Thus, the main uncertainty affecting U solubility calculations is the parameters related to the calculation of temperature effect on solubility, specially a) the enthalpy data for Ca-U(VI)-CO₃ aqueous species and b) lack of enthalpy data for the amorphous solid $UO_2 \cdot 2H_2O(am)$.

4.29 Zr

Zirconium presents a low affinity towards most of the common ligands present in the studied groundwaters. It is expected that the Zr chemistry will be mainly governed by the hydrolysed species.

No enthalpy data for the main reaction that is expected to control the solubility (Equation 17) is available.

 $Zr(OH)_4(am, aged) = Zr(OH)_4(aq)$ Equation 17

4.29.1 Zr Solubility in Scenario 1

Two different Zr hydroxides, $Zr(OH)_4(am, aged)$ and $Zr(OH)_4(am, fresh)$, as well as a crystalline oxide (ZrO_2 , Baddeleyite) are included in the ThermoChimie database. Following the Ostwald's principle (as used for other tetravalent actinides) the amorphous hydroxide phase $Zr(OH)_4(am, aged)$ was selected as the solubility limiting phase for Zr in Scenario 1. Under such assumptions, the Zr solubility and speciation are shown in Table 200 and Table 201.

As seen in Table 200 and Table 201, the solubility of zirconium is calculated to be constant $(1.82 \cdot 10^{-8} \text{ m})$ independent of the studied temperatures, due to the lack of enthalpy data for the main reaction expected to control the Zr solubility (Equation 17). $Zr(OH)_4(aq)$ is the main aqueous species at all studied temperatures.

Table 200: Zirconium Solubility-Controlling Phase and Concentrations Under SCENARIO1 Conditions

	SCENARIO 1					
	Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C		
Zr(OH) ₄ (am, aged)	1.82·10 ⁻⁸	1.82·10 ⁻⁸	1.82∙10 ⁻⁸	1.82·10 ⁻⁸		

Table 201: Zirconium Speciation Under SCENARIO 1 Conditions

		SCENARIO 1					
Solid phase	Speciation	15°C	25°C	50°C	80°C		
Zr(OH)₄(am, aged)	Zr(OH)₄(aq)	100%	100%	100%	100%		

4.29.2 Zr Solubility in Scenario 2

Zirconium is not affected neither by iron content nor by the pH and pe conditions of the groundwater. Thus, assuming $Zr(OH)_4$ (am, aged) as the solubility limiting phase, no differences are observed between the solubility and speciation results obtained in Scenario 2 (see Table 202 and Table 203) and those obtained in Scenario 1.

Table 202: Zirconium Solubility-Controlling Phase and Concentrations Under SCENARIO 2 Conditions

	SCENARIO 2					
		Concentr	ation (m)			
Solid phase	15°C	25°C	50°C	80°C		
Zr(OH)₄(am, aged)	1.82∙10 ⁻⁸	1.82∙10 ⁻⁸	1.82·10 ⁻⁸	1.82∙10 ⁻⁸		

			SCEN	ARIO 2	
Solid phase	Speciation	15°C	25°C	50°C	80°C
Zr(OH)₄(am, aged)	Zr(OH)₄(aq)	100%	100%	100%	100%

Table 203: Zirconium Speciation Under SCENARIO 2 Conditions

4.29.3 Zr Solubility in Scenario 3

The calculated zirconium solubility and speciation, assuming $Zr(OH)_4(am, aged)$ as the solubility limiting phase, in Scenario 3 are presented in Table 204 and Table 205. The zirconium solubility and speciation results are the same as the ones calculated for Scenarios 1 and 2.

Table 204: Zirconium Solubility-Controlling Phase and Concentrations Under SCENARIO3 Conditions

	SCENARIO 3						
		Concentration (m)					
Solid phase	15°C	25°C	50°C	80°C			
Zr(OH)₄(am, aged)	1.82∙10 ⁻⁸	1.82∙10 ⁻⁸	1.82·10⁻ ⁸	1.82·10⁻ ⁸			

Table 205: Zirconium Speciation Under SCENARIO 3 Conditions

			SCEN	ARIO 2	
Solid phase	Speciation	15°C	25°C	50°C	80°C
Zr(OH)₄(am, aged)	Zr(OH)₄(aq)	100%	100%	100%	100%

4.29.4 Uncertainties

The main uncertainties in the evaluation of Zr solubility are the influence of temperature and the formation of polynuclear species.

The enthalpy data for the main reaction expected to control the Zr solubility (Equation 17) is not available. Nevertheless, as discussed in the case of Th and U (4.27.1 and 4.28.2), it is expected that the presence of an amorphous layer covering a bulk crystalline solid would minimize the effect of temperature on the solubility of Zr(IV).

The formation of polynuclear species (specially $Zr_4(OH)_{16}(aq)$) is also uncertain which has not been included in the calculations. If $Zr_4(OH)_{16}(aq)$ is taken into account in the calculation, an increase of zirconium solubility of about 3 orders of magnitude at 80°C is calculated. This is related to the fact that the enthalpy of reaction is available for the polynuclear species but not for the main reaction (Equation 17), leading to inconsistent results with temperature.





5. SUMMARY AND CONCLUSIONS

This work has assessed the solubility limits for Am, Ag, Bi, C, Ca, Cd, Cs, Cu, Fe, Hg, Mo, Nb, Np, Pa, Pb, Pd, Pu, Ra, Rn, Ru, S, Sb, Se, Sn, Sr, Tc, Th, U and Zr in a Canadian crystalline rock reference groundwater CR-10 under three different scenarios:

- Scenario 1: Groundwater CR-10 directly enters the canister without interacting with the bentonite buffer or the canister materials.
- Scenario 2: Groundwater interacts with the carbon-steel container prior to contacting the used nuclear fuel waste inside the container. Steel corrosion influences the chemical characteristics of the groundwater.
- Scenario 3: Groundwater interacts with both bentonite buffer and the C-steel container prior to contacting the used nuclear fuel waste inside the container.

All the calculations use the reference thermodynamic database ThermoChimie. Most of the elements of interest are already included in ThermoChimie. However, ThermoChimie does not include thermodynamic data for Bi, Cu, Hg, Rn and Ru. A review of the information available in the scientific literature has been carried out and a consistent set of thermodynamic data has been selected for these elements.

The effect of the near field on the CR-10 groundwater composition, considering the three different scenarios, has been assessed. In Scenario 1, the initial CR-10 water composition has been re-equilibrated with gypsum (at temperatures below 40°C), anhydrite (at temperatures above 40°C), calcite, quartz, magnetite, goethite and fluorite in order to avoid undesired effects due to initial groundwater re-equilibration in Scenario 2 and Scenario 3. The re-equilibrated composition is very similar to the initial CR-10 water composition.

In Scenario 2, the interaction of groundwater with C-steel and its corresponding corrosion products increases the alkalinity and the reducing character of the groundwater. In Scenario 3, the interaction with bentonite results in a slight pH increase (and a slight pe decrease) in comparison with the modified groundwater in Scenario 2.

In each one of the scenarios, four different temperatures (15°C, 25°C, 50°C and 80°C) have been considered. The temperature increase results in a pH decrease (and a pe increase) of groundwater which is consistent with the change of water properties with temperature.

Different sensitivity cases have been considered in Scenario 2 and Scenario 3 in order to deal with uncertainties in groundwater compositions related to parameters such as corrosion rates, bentonite porosity and density, as well as the maximum hydrogen fugacity. The results of the calculations have shown that the impact of these parameters on the final calculated groundwater compositions is not important in the range of conditions of interest.

The selection of the solid phase that most likely precipitates is mainly based on the expert judgement considering that the less crystalline phases are kinetically favoured. Microbiologically mediated processes (sulphate to sulphide reduction, and the reduction of carbonate to methane) are not considered in the calculations.

PHREEQC/PHREEQCI has been used to calculate the solubility and speciation in the different scenarios. The concentration of the element of interest is assumed to be controlled by the equilibrium with the selected solid phase under the given porewater composition at each temperature of interest.

A summary of the calculated solubility results for different scenarios at different temperatures is shown in Table 206. The main conclusions are:

- The differences in the element solubility and speciation between Scenario 1 and Scenario 2 are due to the increase in alkalinity and the decrease in Eh values of groundwater in Scenario 2 caused by canister steel corrosion. The most affected elements are the redox-sensitive ones, mainly Mo, Pu, Se and U.
- The differences in the element solubility and speciation between Scenario 2 and Scenario 3 are small, which demonstrates that the interaction of bentonite buffer with groundwater has a smaller influence than that of the steel canister corrosion. A fourth scenario where only the effect of bentonite is considered is beyond the scope of the work and has not been evaluated.

Element	Scenario	Solid phase*	Solubility (m) (25ºC)	Solubility (m) range with temperature (15-80ºC)	Main sensitive parameters	Main uncertainties	
	Scenario 1	AgCI(s)	1.08·10 ⁻⁵	6.28·10 ⁻⁶ - 1.26·10 ⁻⁴			
Ag	Scenario 2	AgCI(s)	1.08·10 ⁻⁵	6.28·10 ⁻⁶ - 1.26·10 ⁻⁴	Chloride	Formation of sulphides	
	Scenario 3	AgCI(s)	1.09·10 ⁻⁵	6.35·10 ⁻⁶ - 1.24·10 ⁻⁴			
		Am(CO ₃)(OH)(cr)	-				
	Scenario 1	Am(CO ₃)(OH)(am)	2.27·10 ⁻⁵	9.65·10 ⁻⁶ - 5.72·10 ⁻⁷		Lack of enthalpy data	
		Am ₂ (CO ₃) ₃ (s)	1.59·10 ⁻⁵				
		Am(CO ₃)(OH)(cr)	-				
Am	Seconaria 2	Am(CO ₃)(OH)(am)	1.01·10 ⁻⁵	6 01 10-7 5 90 10-5	рН		
	Scenano 2	Am(CO ₃)(OH)·0.5H ₂ O(cr)	-	0.91.10 - 5.60.10 -	Carbonate	Phosphate Solid solution of Am with coloito	
		Am(OH) ₃ (am)	3.72 · 10 ⁻⁶		Silicate		
		Am(CO ₃)(OH)(cr)	-				
	Secondria 2	Am(CO ₃)(OH)(am)	2.93·10 ⁻⁶	1.98·10 ⁻⁷ - 2.46·10 ⁻⁵			
	Scenario 3	Am(CO ₃)(OH)·0.5H ₂ O(cr)	-				
		Am(OH)₃(am)	1.07·10 ⁻⁶				
	Scenario 1	Bi ₂ O ₃ (s)	1.17·10 ⁻⁵	2.40·10 ⁻⁶ – n.s.l.		Look of optionality data	
Bi	Scenario 2	Bi ₂ O ₃ (s)	1.16·10 ⁻⁵	2.40·10 ⁻⁶ −n.s.l.		Eack of enthalpy data	
	Scenario 3	Bi ₂ O ₃ (s)	1.16·10 ⁻⁵	2.39·10 ⁻⁶ −n.s.l.		Formation of sulphides	
	Scenario 1	CaCO ₃ (Calcite)	9.07·10 ⁻⁴	8.00·10 ⁻⁴ - 1.06·10 ⁻³			
С	Scenario 2	CaCO ₃ (Calcite)	4.53·10 ⁻⁵	4.09·10 ⁻⁵ - 1.58·10 ⁻⁴	рн	Formation of C(-IV)	
	Scenario 3	CaCO ₃ (Calcite)	8.16·10 ⁻⁵	6.91·10 ⁻⁵ - 3.66·10 ⁻⁴	Calcium		
6.	Scenario 1	CaCO ₃ (Calcite) ^{a)}	5.52·10 ⁻²	5.11·10 ⁻² - 5.52·10 ⁻²	рН	Variations in carbonate and	
Ca	Scenario 2	CaCO ₃ (Calcite) ^{a)}	5.47·10 ⁻²	5.06·10 ⁻² - 5.47·10 ⁻²	Carbonate	sulphate concentration	

Table 206: Main Results and Conceptual Uncertainties of the Solubility Calculations

Element	Scenario	Solid phase*	Solubility (m) (25ºC)	Solubility (m) range with temperature (15-80ºC)	Main sensitive parameters	Main uncertainties
	Seconaria 2	CaCO (Calaita)a)	1 20 10-2	0 10 10-3 1 45 10-2	Sulphate	
	Scenario 3	CaCO ₃ (Calcile) ⁴	1.39.10-	9.16.10° - 1.45.10 -	lon-exchange	
	Scenario 1	n.s.l.	-	-		
Cs	Scenario 2	n.s.l.	-	-		Cation exchange
	Scenario 3	n.s.l.	-	-		
	Scenario 1	Cd(CO ₃)(s)	8.92·10 ⁻⁵	8.54·10 ⁻⁵ - 1.08·10 ⁻⁴		
Cd	Scenario 2	Cd(CO ₃)(s)	8.87·10 ⁻⁵	8.50·10 ⁻⁵ - 1.07·10 ⁻⁴	Chioride	Formation of sulphides
	Scenario 3	Cd(CO ₃)(s)	2.15·10 ⁻⁵	1.95·10 ⁻⁵ - 2.16·10 ⁻⁵		
	Scenario 1	Cu(cr)	1.52·10 ⁻⁸	5.27·10 ⁻⁹ - 1.01·10 ⁻⁶	-	
Cu	Scenario 2	Cu(cr)	1.21.10-14	3.11·10 ⁻¹⁵ - 6.68·10 ⁻¹²	En	Formation of sulphides
	Scenario 3	Cu(cr)	5.88·10 ⁻¹⁵	1.54·10 ⁻¹⁵ - 2.84·10 ⁻¹²	Chioride	
	Scenario 1	Goethite and magnetite	1.65.10-4	1.03·10 ⁻⁵ - 2.38·10 ⁻⁴		Formation of sulphides
Fe	Scenario 2	b)	3.06.10-4	2.67·10 ⁻⁴ - 3.10·10 ⁻⁴	Eh	
	Scenario 3	b,c)	8.56·10 ⁻⁵	5.35·10 ⁻⁵ - 9.32·10 ⁻⁵		
	Scenario 1	n.s.l.	-	-		Scarcity of thermodynamic data
Цa	Scenario 2	n.s.l.	-	-		Lack of enthalpy data
пд	Soonaria 2	nol				Organic ligands
	Scenario S	11.5.1.	-	-		Formation of sulphides
	Scopario 1	CaMoO ₄ (s)	3.44·10 ⁻⁶	3.24·10 ⁻⁶ - 5.61·10 ⁻⁶		
	Scenario I	MoO ₂ (s)	2.04·10 ⁻⁸	6.55·10 ⁻⁹ - 1.10·10 ⁻⁵		
Mo	Sconario 2	CaMoO ₄ (s)	3.46·10 ⁻⁶	3.25·10 ⁻⁶ - 5.35·10 ⁻⁶		Scarcity of thermodynamic data
INIC	Scenario 2	MoO ₂ (s)	6.73·10 ⁻¹⁵	2.26·10 ⁻¹⁵ - 5.43·10 ⁻¹³	En, pri	Formation of sulphides
	Sconario 2	CaMoO ₄ (s)	1.46·10 ⁻⁵	1.31·10 ⁻⁵ - 2.90·10 ⁻⁵		
	Scenario 3	MoO ₂ (s)	2.8410 ⁻¹⁴	9.13·10 ⁻¹⁵ - 2.89·10 ⁻¹²		
Nb	Scenario 1	Nb ₂ O ₅ (s)	1.00·10 ⁻⁷	1.00·10 ⁻⁷ - 1.24·10 ⁻⁷	рН	Scarcity of thermodynamic data

Element	Scenario	Solid phase*	Solubility (m) (25ºC)	Solubility (m) range with temperature (15-80ºC)	Main sensitive parameters	Main uncertainties
	Scenario 2	Nb ₂ O ₅ (s)	5.24·10 ⁻⁶	7.83·10 ⁻⁷ - 8.61·10 ⁻⁶		Formation of Ca-Nb phases
	Scenario 3	Nb ₂ O ₅ (s)	1.66·10 ⁻⁵	2.06·10 ⁻⁷ - 2.82·10 ⁻⁵		
	Scenario 1	NpO ₂ ·2H ₂ O(am)	1.08·10 ⁻⁹	8.74·10 ⁻¹⁰ - 3.70·10 ⁻⁹		
Np	Scenario 2	NpO ₂ ·2H ₂ O(am)	1.00·10 ⁻⁹	7.57·10 ⁻¹⁰ - 3.60·10 ⁻⁹		
	Scenario 3	NpO ₂ ·2H ₂ O(am)	1.00·10 ⁻⁹	7.60·10 ⁻¹⁰ - 3.59·10 ⁻⁹		
	Scenario 1	Pa ₂ O ₅ (s)	2.30·10 ⁻⁹	1.25·10 ⁻⁹ - 5.18·10 ⁻⁸		
Ра	Scenario 2	Pa ₂ O ₅ (s)	1.21·10 ⁻⁹	7.45·10 ⁻¹⁰ - 4.70·10 ⁻⁸	рН	Scarcity of thermodynamic data
	Scenario 3	Pa ₂ O ₅ (s)	1.35·10 ⁻⁹	1.03·10 ⁻⁹ - 4.64·10 ⁻⁸		
		PbCO ₃ (Cerussite)	3.10·10 ⁻⁶	1.82·10 ⁻⁶ - 3.71·10 ⁻⁵		
	Scenario 1	Pb ₃ (CO ₃) ₂ (OH) ₂ (Hydrocerussite)	8.27·10 ⁻⁶	5.62·10 ⁻⁶ - 3.56·10 ⁻⁵		
		PbCO ₃ (Cerussite)	5.91·10 ⁻⁶	3.28·10 ⁻⁶ - 7.06·10 ⁻⁵	Chloride	
Pb	Scenario 2	Pb ₃ (CO ₃) ₂ (OH) ₂ (Hydrocerussite)	1.74·10 ⁻⁶	1.01·10 ⁻⁶ - 2.07·10 ⁻⁵	Carbonate	Formation of sulphides
		PbCO ₃ (Cerussite)	2.67·10 ⁻⁶	1.55·10 ⁻⁶ - 2.56·10 ⁻⁵		
	Scenario 3	Pb ₃ (CO ₃) ₂ (OH) ₂ (Hydrocerussite)	7.91·10 ⁻⁷	4.78·10 ⁻⁷ - 7.75·10 ⁻⁶		
	Scenario 1	Pd(OH) ₂ (s)	4.14·10 ⁻⁶	2.89·10 ⁻⁶ - 2.39·10 ⁻⁵		
Pd	Scenario 2	Pd(OH) ₂ (s)	3.98·10 ⁻⁶	2.67·10 ⁻⁶ - 2.39·10 ⁻⁵		Quality of thermodynamic data
	Scenario 3	Pd(OH) ₂ (s)	3.98·10 ⁻⁶	2.67·10 ⁻⁶ - 2.39·10 ⁻⁵		Formation of sulphides
	Scenario 1	PuO ₂ ·2H ₂ O(s)	1.69·10 ⁻⁸	1.19·10 ⁻⁸ - 5.26·10 ⁻⁶		
	Soonaria 2	PuO ₂ ·2H ₂ O(s)	1.46·10 ⁻⁷	6.64·10 ⁻⁸ - 1.38·10 ⁻⁴	Eh	Uncertainties in Pu(II)/Pu(IV)
Pu	Scenario 2	Pu(OH) ₃ (cr)	5.66·10 ⁻⁸	5.35·10 ⁻⁹ - 4.17·10 ⁻³	Carbonate	Lack of enthalpy data
	Soonaria 2	PuO ₂ ·2H ₂ O(s)	3.95·10 ⁻⁸	1.71·10 ⁻⁸ - 1.66·10 ⁻⁴	Sulphate	Phosphate
	Scenario 3	Pu(OH)₃(cr)	1.53·10 ⁻⁸	1.37·10 ⁻⁹ - 1.77·10 ⁻³		
Ra	Scenario 1	Ra(SO ₄)(s)	1.53·10 ⁻⁷	8.57·10 ⁻⁸ - 3.36·10 ⁻⁶	Sulphate	Formation of solid-solutions

Element	Scenario	Solid phase*	Solubility (m) (25ºC)	Solubility (m) range with temperature (15-80ºC)	Main sensitive parameters	Main uncertainties
	Scenario 2	Ra(SO ₄)(s)	1.24·10 ⁻⁷	7.05·10 ⁻⁸ - 2.46·10 ⁻⁶		
	Scenario 3	Ra(SO₄)(s)	1.52·10 ⁻⁷	8.56·10 ⁻⁸ - 3.35·10 ⁻⁶		
Rn		water/air partitior	n coefficient		Temperature	
			4.05.40.9		Ionic strength	
	Scenario 1	Ru(OH) ₃ ·2H ₂ O(s)	1.65.10-9	1.65.10 ⁻⁹ - 7.34.10 ⁻⁹	***	
Ru	Scenario 2	Ru(OH) ₃ ·2H ₂ O(s)	2.23·10 ⁻⁹	2.80·10 ⁻¹⁰ - 1.32·10 ⁻⁶	Eh	Scarcity of thermodynamic data
	Scenario 3	Ru(OH) ₃ .2H ₂ O(s)	1.82·10 ⁻⁹	1.26·10 ⁻¹⁰ - 1.11·10 ⁻⁶		
	Scenario 1	Gypsum/anhydrite ^{d)}	1.23·10 ⁻²	7.93·10 ⁻³ - 1.23·10 ⁻²	-	
S	Scenario 2	Gypsum/anhydrite ^{d)}	1.23·10 ⁻²	7.94·10 ⁻³ - 1.23·10 ⁻²	Calcium	Formation of sulphides
	Scenario 3	Gypsum/anhydrite ^{d)}	1.23·10 ⁻²	7.93·10 ⁻³ - 1.23·10 ⁻²		
	Scenario 1	Sb ₂ O ₃ (Valentinite)	5.71·10 ⁻⁵	5.02·10 ⁻⁵ - 1.02·10 ⁻⁴		
Sb	Scenario 2	Sb ₂ O ₃ (Valentinite)	5.71·10 ⁻⁵	5.02·10 ⁻⁵ - 1.02·10 ⁻⁴		Formation of sulphides
	Scenario 3	Sb ₂ O ₃ (Valentinite)	5.61·10 ⁻⁵	5.00·10 ⁻⁵ - 1.02·10 ⁻⁴		
		Fe _{1.04} Se(s)	1.16·10 ⁻⁶	5.40·10 ⁻⁷ - 6.28·10 ⁻⁵		
	Scenario 1	FeSe ₂ (Ferroselite)	1.07·10 ⁻¹⁰	5.53·10 ⁻¹¹ - 3.88·10 ⁻⁹		
		Se(s)	1.03·10 ⁻⁸	1.01·10 ⁻⁸ - 2.05·10 ⁻⁸		
Se	Seconaria 2	Fe _{1.04} Se(s)	7.58·10 ⁻⁹	4.82·10 ⁻⁹ - 1.43·10 ⁻⁷		Polynuclear Se aqueous
	Scenario 2	FeSe ₂ (Ferroselite)	3.73·10 ⁻⁶	2.63·10 ⁻⁶ - 1.98·10 ⁻⁵	IION	
	Connaria 2	Fe _{1.04} Se(s)	1.56·10 ⁻⁹	1.56·10 ⁻⁹ - 3.39·10 ⁻⁷		
	Scenario 3	FeSe ₂ (Ferroselite)	7.66·10 ⁻⁶	5.28·10 ⁻⁶ - 4.67·10 ⁻⁵		
	Connaria 1	SnO ₂ (am)	6.05·10 ⁻⁸	3.18·10 ⁻⁹ - 1.20·10 ⁻⁷		
	Scenario I	CaSn(OH)₀(s)	4.09·10 ⁻⁶	3.21·10 ⁻⁶ - 4.98·10 ⁻⁶		Leals of onthe law date
Sn	O a su a si a O	SnO ₂ (am)	1.57·10 ⁻⁷	1.57·10 ⁻⁷ - 1.94·10 ⁻⁶	Eh, pH	Lack of enthalpy data
	Scenario 2	CaSn(OH)₀(s)	1.48·10 ⁻⁸	6.82·10 ⁻⁹ - 8.52·10 ⁻⁵		Formation of sulphides
Sc	Scenario 3	SnO ₂ (am)	2.44·10 ⁻⁷	2.44·10 ⁻⁷ - 2.93·10 ⁻⁶		

Element	Scenario	Solid phase*	Solubility (m) (25ºC)	Solubility (m) range with temperature (15-80ºC)	Main sensitive parameters	Main uncertainties
		CaSn(OH) ₆ (s)	2.30·10 ⁻⁸	1.10·10 ⁻⁸ – 8.25·10 ⁻⁷ (15°C-50°C)		
	Connaria 1	SrSO ₄ (Celestite)	6.02·10 ⁻⁴	6.02·10 ⁻⁴ - 1.05·10 ⁻³		
	Scenano I	SrCO ₃ (Strontianite)	1.06·10 ⁻²	8.92·10 ⁻³ - 2.39·10 ⁻²		
Sr	O a su a si a O	SrSO ₄ (Celestite)	5.98·10 ⁻⁴	5.98·10 ⁻⁴ - 1.04·10 ⁻³	Sulphate	Co-precipitation with other major solids
	Scenario 2	SrCO ₃ (Strontianite)	1.04·10 ⁻²	8.80·10 ⁻³ - 2.44·10 ⁻²	Carbonate	
	Scenario 3	SrSO ₄ (Celestite)	4.67·10 ⁻⁴	4.67·10 ⁻⁴ - 7.35·10 ⁻⁴	-	
		SrCO ₃ (Strontianite)	2.55·10 ⁻³	2.29·10 ⁻³ - 3.47·10 ⁻³		
Тс	Scenario 1	TcO ₂ -1.63H ₂ O(s)	4.16·10 ⁻⁹	4.07·10 ⁻⁹ - 5.74·10 ⁻⁹		Lack of enthalpy data
	Scenario 2	TcO ₂ .1.63H ₂ O(s)	4.02·10 ⁻⁹	4.02·10 ⁻⁹ - 4.07·10 ⁻⁹	Eh	Formation of Tc(cr) Formation of Tc(III) species
	Scenario 3	TcO ₂ .1.63H ₂ O(s)	4.06·10 ⁻⁹	4.05·10 ⁻⁹ - 4.10·10 ⁻⁹	~	
	Scenario 1	ThO ₂ (am, aged)	4.20·10 ⁻⁹	1.89·10 ⁻⁹ - 2.31·10 ⁻⁵		Lack of enthalpy data Phosphate
Th	Scenario 2	ThO ₂ (am, aged)	1.33·10 ⁻⁹	1.93·10 ⁻¹⁰ - 1.90·10 ⁻⁵	pH Corbonata	
	Scenario 3	ThO ₂ (am, aged)	1.40·10 ⁻⁹	2.39·10 ⁻¹⁰ - 1.85·10 ⁻⁵	Carbonate	
U	Scenario 1	UO ₂ ·2H ₂ O(am)	1.25·10 ⁻⁷	2.47·10 ⁻⁸ - 5.78·10 ⁻⁵		Lack of enthalpy data
	Scenario 2	UO₂·2H₂O(am)	3.17·10 ⁻⁹	6.80·10 ⁻¹⁰ - 3.16·10 ⁻⁶	En, pH	
	Scenario 3	UO₂·2H₂O(am)	3.16·10 ⁻⁹	6.79·10 ⁻¹⁰ - 3.15·10 ⁻⁶	Carbonale	
	Scenario 1	Zr(OH) ₄ (am, aged)	1.82·10 ⁻⁸	1.82.10-8		Lack of enthalpy data
Zr	Scenario 2	Zr(OH)₄(am, aged)	1.82·10 ⁻⁸	1.82·10 ⁻⁸		Formation of polynuclear
	Scenario 3	Zr(OH)₄(am, aged)	1.82·10 ⁻⁸	1.82·10 ⁻⁸	species	species

* n.s.l. – Not solubility limited.
^a Calcium concentration is mainly determined by calcite solubility and also gypsum.
^b Controlled by iron corrosion processes.
^c The effect of the bentonite exchanger influences iron aqueous concentration.
^d Allowing the precipitation of gypsum (CaSO₄·2H₂O) at temperature 15°C and 25°C and anhydrite (CaSO₄) at temperature 50°C and 80°C.

A qualitative analysis of the uncertainties affecting solubility calculations has also been made. Some uncertainties are related to the thermodynamic data itself. This is not a weakness of the database, but a lack of relevant information in the literature, normally related to the difficulty of working with some elements in the laboratory. Specifically:

- Lack of thermodynamic data especially for Mo, Nb, Pa, Ru and Tc.
- Lack of enthalpy data needed for temperature correction at T≠25°C is identified for some elements. In some cases, the lack of enthalpy data affects relevant aqueous species (Am, Hg, Np, Ru). In other cases, the lack of enthalpy data affects amorphous solubility limiting solids (Bi, Sn, U). In the case of Pa, Tc, Th and Zr, the lack of enthalpy data affects both aqueous species and solubility limiting solid phases. This uncertainty can be qualitatively reduced with supporting literature data in the case of amorphous tetravalent oxides.

Other uncertainties are related to the conceptual model used in the calculations.

Microbial activity is not taken into account in this work, thus the reduction of sulphate to sulphide is not considered in the calculation. Sulphide concentrations are not provided in the CR-10 groundwater. If sulphides are assumed to be in thermodynamic equilibrium with sulphates, the concentration of $S(-II) \sim 10^{-6}$ m is calculated in Scenario 1 at 25°C. Under such conditions, the formation of sulphide solids could significantly decrease the solubility of elements such as Ag, Cd, Cu, Fe, Hg, Mo, Pb and Sb (see Table 207), although the formation of such insoluble phases could be limited by kinetic constrains. The lack of thermodynamic data prevents a quantitative analysis for Bi, Mo, Pd, and Sn.

		Base case	Sensitivity case: Sulphide ^{a)}		
Element	Scenario	Solid phase*	Solubility (m) (25ºC)	Solid phase	Solubility (m) (25ºC)
Ag	Scenario 1	AgCI(s)	1.08·10 ⁻⁵	Ag ₂ S(Acanthite)	~10 ⁻¹¹
Cd	Scenario 1	Cd(CO ₃)(s)	8.92·10 ⁻⁵	CdS(s)	~10 ⁻¹⁴
Cu	Scenario 1	Cu(cr)	1.52·10 ⁻⁸	CuS(s)	~10 ⁻¹⁰
Fe	Scenario 1	Goethite, Magnetite	1.65·10 ⁻⁴	FeS ₂ (Pyrite)	~10 ⁻¹¹
Hg	Scenario 1	n.s.l.	-	HgS(s)	~10 ⁻¹³
Мо	Sconaria 1	CaMoO ₄ (s)	3.44·10 ⁻⁶	Mask	10-14
WO Scenario i	MoO ₂ (s)	2.04·10 ⁻⁸	10033(5)	~10 14	
		PbCO ₃ (Cerussite)	3.10·10 ⁻⁶		
Pb	Scenario 1	Pb ₃ (CO ₃) ₂ (OH) ₂ (Hydrocerussite)	8.27·10 ⁻⁶	PbS(s) (Galena)	~10 ⁻¹⁴
Sb	Scenario 1	Sb_2O_3 (Valentinite)	5.71·10 ⁻⁵	Sb ₂ S ₃ (Stibnite)	~10 ⁻⁹

Table 207: Comparison of Solubility Results for Ag, Cd, Cu, Fe, Hg, Mo, Pb and Sb at 25°C in the Absence (Base Case) and Presence (Sensitivity Case) of Sulphide

* n.s.l. – Not solubility limited.

^a Sulphide concentrations (~10⁻⁶ m in Scenario 1) are calculated allowing thermodynamic equilibrium for sulphate to sulphide reduction in groundwater.

Phosphate concentrations are not measured in the CR-10 groundwater. Concentrations of phosphate in groundwaters are in many cases likely to be controlled by equilibrium with hydroxyapatite (Bruno et al. 2001). By assuming that the concentration of phosphate in the groundwater is given by equilibrium with this calcium phosphate solid, the resulting P aqueous concentrations will be range from $5 \cdot 10^{-10}$ to $3 \cdot 10^{-8}$ m, depending on the pH and calcium concentration of each Scenario (see Table 208). If P concentration is taken into account, formation of phosphate solids may affect the solubility of Am (for which the solubility could be decreased 2-3 orders of magnitude) and Pu (for which solubility could be decreased approximately one order of magnitude).

		Base case		Sensitivity case: Phosphate			
Element	Scenario	Solid phase	Solubility (m) (25ºC)	[P] ^{a)} (M)	Solid phase	Solubility (m) (25ºC)	
Am	Scenario 1	Am(CO ₃)(OH)(am)	2.27·10 ⁻⁵	3∙10 ⁻⁸	Am(PO ₄):xH ₂ O(am)	1.59·10 ⁻⁹	
		Am ₂ (CO ₃) ₃ (s)	1.59·10 ⁻⁵				
	Scenario 2	Am(CO ₃)(OH)(am)	1.01·10 ⁻⁵	5 10 -10		5.75·10 ⁻⁸	
		Am(OH)₃(am)	3.72·10 ⁻⁶	5.10	Am(PO4).xn ₂ O(am)		
	Scenario 3	Am(CO ₃)(OH)(am)	2.93·10 ⁻⁶	1.10 ⁻⁹	Am(PO ₄):xH ₂ O(am)	1.64·10 ⁻⁸	
		Am(OH)₃(am)	1.07·10 ⁻⁶				
D	Scenario 1	PuO ₂ ·2H ₂ O(s)	1.69·10 ⁻⁸	3·10 ⁻⁸	b)		
	Scenario 2	PuO ₂ ·2H ₂ O(s)	1.46·10 ⁻⁷	5,10-10	$Pu(PO_{i})(e_{i}byd)$	1 66, 10-8	
Fu		Pu(OH)₃(cr)	5.66·10 ⁻⁸	5.10	Fu(FO4)(S,IIyu)	1.00.10	
	Scenario 3	PuO₂·2H₂O(s)	3.95·10 ⁻⁸	1·10 ⁻⁹	PuO ₂ ·2H ₂ O(s)	4.47·10 ⁻⁹	

Table 208: Comparison of the Results for Am and Pu at 25°C in the Absence (Base Case)and Presence (Sensitivity Case) of Phosphates

^a Phosphate concentrations in groundwaters calculated in equilibrium with hydroxyapatite. ^b Pu(III)-solid phosphate is not expected to form in this Scenario.

Finally, some elements present specific chemical characteristics that result in the following additional uncertainties:

- Some elements (as Hg) may be expected to form strong complexes with organics, which will modify their mobility.
- In this work, only precipitation of pure solid phases has been considered in calculations. However, some elements are expected to be limited by the formation of solid solutions or co-precipitation; this is especially relevant in the case of Ra.
- Rn is noble gas, so its assessment is not based in the equilibrium with a solid phase but the partitioning coefficient of radon gas between water and air.

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APPENDIX A: INFORMATION PROVIDED BY NWMO

The following information (required in order to calculate groundwater compositions in Scenario 2 and Scenario 3 conditions) was provided by NWMO:

- Carbon steel container surface reactive area = 21.2 m², including:
 - Steel vessel inner surface area = 3.6 m²
 - \circ Total steel surface area of used fuel container basket = 17.6 m²
- Total amount of bentonite in the buffer box: 2.3085 m³
- Bentonite properties:
 - Porosity of highly compacted bentonite (HCB) at saturation within the Buffer Box: 38.2% (density = 1700 kg·m⁻³)
 - Porosity of HCB for Placement Room and tunnel seals = 41.8% (density = 1600 kg·m⁻³)
- Maximum hydrogen pressure to define the final point for the corrosion rate:
 - In the crystalline rock setting, the nominal swelling pressure of HCB at saturation within the Buffer Box is 6.4 MPa.
 - In the crystalline rock setting, the nominal swelling pressure of HCB for Placement Room and tunnel seals is 3.8 MPa.

	ę	SCENARIO	2 – CASE 1	l
Temperatur	15°C	25°C	50°C	80°C
е				
рН	8.73	8.46	7.81	7.17
ре	-9.63	-9.36	-8.71	-8.07
Solutes (m)				
Na	8.38·10 ⁻²	8.37·10 ⁻²	8.37·10 ⁻²	8.37·10 ⁻²
Κ	3.89·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴
Ca	5.44·10 ⁻²	5.47·10 ⁻²	5.42·10 ⁻²	5.06·10 ⁻²
Mg	2.51·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³
HCO ₃	4.09·10 ⁻⁵	4.53·10 ⁻⁵	7.61·10 ⁻⁵	1.58·10 ⁻⁴
SO ₄	1.19·10 ⁻²	1.23·10 ⁻²	1.17·10 ⁻²	7.94·10 ⁻³
CI	1.74⋅10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹
Sr	2.90·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴
F	5.85·10 ⁻⁵	6.97·10 ⁻⁵	1.06·10 ⁻⁴	1.73·10 ⁻⁴
Si	1.34·10 ⁻⁴	1.81·10 ⁻⁴	3.50·10 ⁻⁴	6.84·10 ⁻⁴
Fe	3.10·10 ⁻⁴	3.06·10 ⁻⁴	2.93·10 ⁻⁴	2.67·10 ⁻⁴

APPENDIX B: RESULTS OF GROUNDWATER COMPOSITION OF ALL CASES FOR SCENARIO 2

 Table B1: Groundwater Composition for Scenario 2 - Case 1

Table DZ. Gloundwaler Composition for Scenario Z - Case Z

	SCENARIO 2 – CASE 2					
Temperature	15°C	25°C	50°C	80°C		
рН	8.72	8.43	7.78	7.13		
pe	-9.50	-9.21	-8.56	-7.92		
Solutes (m)						
Na	8.36·10 ⁻²	8.36·10 ⁻²	8.36·10 ⁻²	8.36·10 ⁻²		
Κ	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴		
Ca	5.43·10 ⁻²	5.47·10 ⁻²	5.42·10 ⁻²	5.06·10 ⁻²		
Mg	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10⁻³		
HČO₃	4.15·10 ⁻⁵	4.80·10 ⁻⁵	8.20·10 ⁻⁵	1.72·10 ⁻⁴		
SO₄	1.19·10 ⁻²	1.23·10 ⁻²	1.17·10 ⁻²	7.93⋅10 ⁻³		
CI	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹		
Sr	2.89·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴		
F	5.84·10 ⁻⁵	6.96·10 ⁻⁵	1.06.10-4	1.73·10 ⁻⁴		
Si	1.34·10 ⁻⁴	1.81·10 ⁻⁴	3.50.10-4	6.84·10 ⁻⁴		
Fe	3.09·10 ⁻⁴	3.05·10 ⁻⁴	2.92·10 ⁻⁴	2.66·10 ⁻⁴		

		SCENARIO	2 – CASE 3	3
Temperature	15°C	25°C	50°C	80°C
рН	8.73	8.46	7.81	7.17
ре	-9.63	-9.36	-8.71	-8.07
Solutes (m)				
Na	8.38·10 ⁻²	8.37·10 ⁻²	8.37·10 ⁻²	8.38·10 ⁻²
K	3.89·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.89·10 ⁻⁴
Ca	5.44·10 ⁻²	5.47·10 ⁻²	5.42·10 ⁻²	5.07·10 ⁻²
Mg	2.51·10 ⁻³	2.50·10⁻³	2.50·10 ⁻³	2.51 ⋅ 10 ⁻³
HCO ₃	4.09·10 ⁻⁵	4.53·10 ⁻⁵	7.61·10 ⁻⁵	1.58·10 ⁻⁴
SO ₄	1.19·10 ⁻²	1.23·10 ⁻²	1.17·10 ⁻²	7.95 ⋅ 10 ⁻³
CI	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹
Sr	2.90·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴	2.90·10 ⁻⁴
F	5.85·10 ⁻⁵	6.97·10 ⁻⁵	1.06·10 ⁻⁴	1.73·10 ⁻⁴
Si	1.34·10 ⁻⁴	1.81·10 ⁻⁴	3.50.10-4	6.86·10 ⁻⁴
Fe	3.10·10 ⁻⁴	3.06·10 ⁻⁴	2.93·10 ⁻⁴	2.67·10 ⁻⁴

 Table B3: Groundwater Composition for Scenario 2 - Case 3

 Table B4: Groundwater Composition for Scenario 2 - Case 4

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		SCENARIO	2 – CASE 4	1
Temperature	15°C	25°C	50°C	80°C
рН	8.72	8.43	7.78	7.13
ре	-9.50	-9.21	-8.56	-7.92
Solutes (m)				
Na	8.36·10 ⁻²	8.36·10 ⁻²	8.36·10 ⁻²	8.36·10 ⁻²
Κ	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴
Ca	5.43·10 ⁻²	5.47·10 ⁻²	5.42·10 ⁻²	5.06·10 ⁻²
Mg	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³
HČO₃	4.15·10 ⁻⁵	4.80·10 ⁻⁵	8.20·10 ⁻⁵	1.72·10 ⁻⁴
SO ₄	1.19·10 ⁻²	1.23·10 ⁻²	1.17·10 ⁻²	7.93·10 ⁻³
CI	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹
Sr	2.89·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴
F	5.84·10 ⁻⁵	6.96·10 ⁻⁵	1.06·10 ⁻⁴	1.73·10 ⁻⁴
Si	1.34·10 ⁻⁴	1.81·10 ⁻⁴	3.50·10 ⁻⁴	6.84·10 ⁻⁴
Fe	3.09·10 ⁻⁴	3.05·10 ⁻⁴	2.92·10 ⁻⁴	2.66·10 ⁻⁴

	ļ	SCENARIO	2 – CASE 5	5
Temperature	15°C	25°C	50°C	80°C
рН	8.73	8.46	7.81	7.17
ре	-9.63	-9.36	-8.71	-8.07
Solutes (m)				
Na	8.38·10 ⁻²	8.37·10 ⁻²	8.37·10 ⁻²	8.37·10 ⁻²
K	3.89·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴
Ca	5.44·10 ⁻²	5.47·10 ⁻²	5.42·10 ⁻²	5.06·10 ⁻²
Mg	2.51 ⋅ 10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³
HCO ₃	4.09·10⁻⁵	4.53·10 ⁻⁵	7.61·10 ⁻⁵	1.58·10 ⁻⁴
SO4	1.19·10 ⁻²	1.23·10 ⁻²	1.17·10 ⁻²	7.94·10 ⁻³
CI	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹
Sr	2.90·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴
F	5.85·10⁻⁵	6.97·10 ⁻⁵	1.06.10-4	1.73·10 ⁻⁴
Si	1.34·10 ⁻⁴	1.81·10 ⁻⁴	3.50.10-4	6.84·10 ⁻⁴
Fe	3.10·10 ⁻⁴	3.06·10 ⁻⁴	2.93·10 ⁻⁴	2.67·10 ⁻⁴

 Table B5: Groundwater Composition for Scenario 2 - Case 5

Table B6: Groundwater Composition for Scenario 2 - Case 6

		SCENARIO	<u>2 – CASE 6</u>	5
Temperature	15°C	25°C	50°C	80°C
рН	8.72	8.43	7.78	7.13
ре	-9.50	-9.21	-8.56	-7.92
Solutes (m)				
Na	8.36·10 ⁻²	8.36·10 ⁻²	8.36·10 ⁻²	8.36·10 ⁻²
Κ	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴	3.88·10 ⁻⁴
Ca	5.43·10 ⁻²	5.47·10- ²	5.42·10 ⁻²	5.06·10 ⁻²
Mg	2.50∙10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³	2.50·10 ⁻³
HČO₃	4.15·10 ⁻⁵	4.80·10 ⁻⁵	8.20·10 ⁻⁵	1.72·10 ⁻⁴
SO ₄	1.19·10 ⁻²	1.23·10 ⁻²	1.17·10 ⁻²	7.93·10 ⁻³
CI	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹	1.74·10 ⁻¹
Sr	2.89·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴	2.89·10 ⁻⁴
F	5.84·10 ⁻⁵	6.96·10 ⁻⁵	1.06·10 ⁻⁴	1.73·10 ⁻⁴
Si	1.34·10 ⁻⁴	1.81·10 ⁻⁴	3.50.10-4	6.84·10 ⁻⁴
Fe	3.09·10 ⁻⁴	3.05·10 ⁻⁴	2.92·10 ⁻⁴	2.66·10 ⁻⁴

APPENDIX C: QUALITY ASSURANCE

Calculations have been performed following the requirements in the Project Quality Plan Project NWMO_Solub_2020 version 4 (3242_NWMO_Solub_A21_PQP_v4; NWMO document PM-PLAN-01913-0384-R000).

PhreeqC/PhreeqCl Interactive version 3.6.2 (released January 28, 2020) has been used in order to calculate the groundwater compositions in the different scenarios and cases. Additional calculations Spana (Chemical Equilibrium Diagrams) program version 2020-Feb-05 (released February 8, 2020) have been performed for verification purposes only.

The database used in the calculations is a modified version of the ThermoChimie database version 10a, including the modifications described in section 2.2 and decoupling of sulphate/sulphide and C(+4)/methane reactions as described in the text.