Radionuclide Solubility Calculations (Phase 2)

NWMO-TR-2022-11

March 2022

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ABSTRACT

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Abstract

The project: "NWMO Radionuclides Solubility Calculation (Phase 2)" aims at calculating the solubility limits for several chemical elements in a Canadian sedimentary rock reference groundwater (SR-290-PW). The work within this project 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.

The reference groundwater is highly saline, and the Pitzer model is preferred for ion activity correction in the calculations. Although the Pitzer model approach is used in some thermodynamic databases, none is complete enough to fulfill the needs of the extensive element list to be studied. Therefore, a specific thermodynamic database to be used in the calculations has been developed, and its advantages and limitations have been evaluated.

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 three different scenarios are evaluated. The radionuclide solubility limits and the corresponding speciation are calculated; a semiquantitative description of the main associated uncertainties in solubility and speciation calculations is provided.



TABLE OF CONTENTS

Page

AE	STRACT		.iii
1.			1
2.		THERMODYNAMIC DATABASE	3
	2.1	AG	5
	2.2	AM	5
	2.3	BI	6
	2.4	C	7
	2.5	CA	7
	2.6	CD	7
	2.7	CS	8
	2.8	CU	8
	2.9	FE	9
	2.10	HG	10
	2.11	MO	10
	2.12	NB	11
	2.13	NP	11
	2.14	PA	13
	2.15	PB	13
	2.16	PD	14
	2.17	PU	15
	2.18	RA	17
	2.19	RN	18
	2.20	RU	19
	2.21	S	20
	2.22	SB	20
	2.23	SE	20
	2.24	SN	21
	2.25	SR	21
	2.26	TC	22
	2.27	ТН	22
	2.28	U	25
	2.29	ZR	27
	2.30	HIGHLY CHARGED SPECIES An(CO ₃) ₅ ⁶⁻	27
2			
CC	MPOSITIC	N	30
	3 1	SCENARIO 1	30
	3.1		21
	3.2		31
	3.5	SUMMARY	30
	J. T		53
4.		RADIONUCLIDE SOLUBILITY CALCULATIONS	40
	4.1	SOLUBILITY CALCULATION RESULTS	41

Ag......41 4.1.1 4.1.1.1 4.1.1.2 Ag Solubility in Scenario 242 4.1.1.3 Ag Solubility in Scenario 342 4.1.1.4 Am43 4.1.2 4.1.2.1 Am Solubility in Scenario 143 4.1.2.2 Am Solubility in Scenario 345 4.1.2.3 4.1.2.4 4.1.3 4.1.3.1Bi Solubility in Scenario 1......46 4.1.3.2 Bi Solubility in Scenario 2......46 4.1.3.3 Bi Solubility in Scenario 3......47 4.1.3.4C......48 4.1.4 4.1.4.1 C Solubility in Scenario 148 4.1.4.2 4.1.4.3 4.1.4.4 4.1.5 4.1.5.1 4.1.5.2 4.1.5.3 4.1.5.4 4.1.6 Cd......51 Cd Solubility in Scenario 151 4.1.6.1 4.1.6.24.1.6.3 4.1.6.4 4.1.7 Cs......54 4.1.7.1 Cs Solubility in Scenario 154 4.1.7.2 Cs Solubility in Scenario 254 4.1.7.3 4.1.7.4 4.1.8 Cu......55 4.1.8.1 Cu Solubility in Scenario 155 4.1.8.24.1.8.3 4.1.8.4 4.1.9 Fe58 4.1.9.1 Fe Solubility in Scenario 1......58 Fe Solubility in Scenario 2......59 4.1.9.2 4.1.9.3 4.1.9.4 4.1.10 Hg......60 4.1.10.1 Hg Solubility in Scenario 161 4.1.10.2 Hg Solubility in Scenario 363 4.1.10.3 4.1.10.4 Uncertainties......64 4.1.11

4.1.11.1	Mo Solubility in Scenario 1	.65
4.1.11.2	Mo Solubility in Scenario 2	66
4.1.11.3	Mo Solubility in Scenario 3	.67
4.1.11.4	Uncertainties	.67
4.1.12	Nb	.67
4.1.12.1	Nb Solubility in Scenario 1	.68
4.1.12.2	Nb Solubility in Scenario 2	.68
4.1.12.3	Nb Solubility in Scenario 3	.69
4.1.12.4	Uncertainties	.70
4.1.13	Np	.70
4.1.13.1	No Solubility in Scenario 1	.70
4.1.13.2	Np Solubility in Scenario 2	.71
4.1.13.3	No Solubility in Scenario 3	72
4.1.13.4	Uncertainties	72
4 1 14	Pa	73
4 1 14 1	Pa Solubility in Scenario 1	73
4 1 14 2	Pa Solubility in Scenario 2	73
4 1 14 3	Pa Solubility in Scenario 3	74
4 1 14 4	Incertainties	75
4.1.1 4 .4	Ph	75
4 1 15 1	Ph Solubility in Scenario 1	75
1 1 15 2	Ph Solubility in Scenario 2	76
4.1.15.2	Dh Solubility in Scenario 3	76
4.1.15.5	Lineartaintias	77
4.1.15.4	Dd	77
4.1.10	Pd Solubility in Sconario 1	77
4.1.10.1	Pu Solubility in Scenario 2	77
4.1.10.2	Pu Solubility in Scenario 2	70
4.1.10.3	Lineartaintica	70
4.1.10.4		.10
4.1.17	PU	.78
4.1.17.1	Pu Solubility in Scenario 1	.79
4.1.17.2	Pu Solubility in Scenario 2	.79
4.1.17.3	Pu Solubility in Scenario 3	.80
4.1.17.4	Uncertainties	.80
4.1.18		.81
4.1.18.1		.81
4.1.18.2	Ra Solubility in Scenario 2	.82
4.1.18.3	Ra Solubility in Scenario 3	.82
4.1.18.4	Uncertainties	.83
4.1.19	Rn	.83
4.1.19.1	Rn Solubility in Scenarios 1, 2 and 3	.84
4.1.19.2		.84
4.1.20	Ru	.84
4.1.20.1	Ru Solubility in Scenario 1	.85
4.1.20.2	Ru Solubility in Scenario 2	.86
4.1.20.3	Ru Solubility in Scenario 3	.86
4.1.20.4	Uncertainties	.87
4.1.21	S	.87
4.1.21.1	S Solubility in Scenario 1	.87
4.1.21.2	S Solubility in Scenario 2	.88
4.1.21.3	S Solubility in Scenario 3	88

AP	PENDIX A	: Pu(IV) Thermodynamic Data	124
RE	FERENCE	S	116
5.		CONCLUSIONS	109
	4.2.2	Effect of phosphate	107
	4.2.1	Effect of sulphide	
	4.2	SENSITIVITY ANALYSIS: SULPHIDE OR PHOSPHATE EFFECT	
	4.1.29.4	Uncertainties	
	4.1.29.3	Zr Solubility in Scenario 3	
	4.1.29.2	Zr Solubility in Scenario 2	
	4.1.29.1	Zr Solubility in Scenario 1	
	4.1.29	Zr	
	4.1.28.4	Uncertainties	104 104
	4 1 28 3	U Solubility in Scenario 3	103 104
	4.1.20.1 1.1.28.2	U Solubility in Scenario 2	102 102
	4.1.20 1 1 20 1	U U Solubility in Scopario 1	101 102
	4.1.27.4		
	4.1.27.3	Th Solubility in Scenario 3	
	4.1.27.2	Th Solubility in Scenario 2	
	4.1.27.1	Th Solubility in Scenario 1	98
	4.1.27	Th	98
	4.1.26.4	Uncertainties	
	4.1.26.3	Tc Solubility in Scenario 3	
	4.1.26.2	Tc Solubility in Scenario 2	
	4.1.26.1	Tc Solubility in Scenario 1	
	4.1.26	Тс	96
	4.1.20.3 4 1 25 <i>1</i>	Uncertainties	9690 AD
	4.1.25.2	Sr Solubility in Scenario 3	95 0e
	4.1.25.1	Sr Solubility in Scenario 1	
	4.1.25	Sr	
	4.1.24.4		95
	4.1.24.3	Sn Solubility in Scenario 3	94
	4.1.24.2	Sn Solubility in Scenario 2	94
	4.1.24.1	Sn Solubility in Scenario 1	93
	4.1.24	Sn	
	4.1.23.4	Uncertainties	
	4.1.23.3	Se Solubility in Scenario 3	
	4.1.23.1 1 2 2 2	Se Solubility in Scenario 2	90 01
	4.1.23	Se Solubility in Seenerie 1	
	4.1.22.4	Uncertainties	90
	4.1.22.3	Sb Solubility in Scenario 3	89
	4.1.22.2	Sb Solubility in Scenario 2	89
	4.1.22.1	Sb Solubility in Scenario 1	89

4.1.21.4 4.1.22

PPENDIX B: Th(IV) Thermodynamic Data125

LIST OF TABLES

Table 1: Composition of the Reference Porewater SR-290-PW (Density 1.175 g·mL ⁻¹)1
Table 2: Pitzer Coefficients in the System Ag(I)/Cl ⁻ Included in Phase2-TDB5
Table 3: Pitzer Coefficients in the System Cu(I)/Cl ⁻ Included in Phase2-TDB9
Table 4: Pitzer Coefficients in the Hg(II) System Included in Phase2-TDB10
Table 5: Stability Constants for the Formation of PbCl _n ⁽²⁻ⁿ⁾ Species. Those in Bold Have
Table 6: Pitzer Coefficients in the Pb(II) System Included in Phase2-TDB
Table 7: Pitzer Coefficients in the System M(II)/Cl ⁻ (M(II) = Alkaline Earth Element)
Included in Phase2-TDB
Table 8: Parameters a_1 to b_3 Reported in Schubert et al. (2012)
Table 9: An(IV)-OH-CO ₃ Species and Associated Stability Constants in Phase2-1DB27
Table 10: Comparison Among Distance Between the Center of the Metal and
(at Coordination Number of Ω) for Tetravalent Actinides (from Neck and Kim
Table 11: Pitzer Coefficients for $An(CO_2)$ -6- Species Included in Phase2-TDB Values
Have Been Obtained from THEREDA
Table 12: Parameters Used for the Different Cases in Scenario 2 First Colum (Case 1
in Green) Indicates the Base Case
Table 13: SCENARIO 2: Groundwater Composition after Interaction with C-Steel
Container
Table 14: Mineralogical Composition of the Clay Fraction of Bentonite MX-80. from
SKB (2004)
Table 15: 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
Table 16: 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⋅m³36
Table 17: Initial Exchange Composition of MX-80 Bentonite (meq 100 g ⁻¹) 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
Table 18: C-steel Corrosion Parameters Used for Two Cases in Scenario 3. Case A
Corresponds to Porosity of 0.382 and Density of 1700 kg·m°; Case B
Table 10: SCENAPIO 3: Groundwater Composition after Interaction with Pontenite and
Table 13. SOLIVARIO 3. STOULIUWALET COMPOSITION ATTEL INTERACTION WITH DENTOMICE AND C-Steel Container. Case Δ Corresponde to Porosity of 0.382 and Donsity
of 1700 kg.m ⁻³ . Case B Corresponds to Porceity of 0.418 and Density of
1600 kg·m ⁻³
Table 20: Groundwater Compositions in Scenario 1. 2 and 3

Table Of		40
Table 21:	Silver Solid Phase and Concentration under Scenario 1 Conditions	42
Table 22:	Silver Speciation under Scenario 1 Conditions	42
Table 23:	Silver Solid Phase and Concentration under Scenario 2 Conditions	42
Table 24:	Silver Speciation under Scenario 2 Conditions	42
Table 25	Silver Solid Phase and Concentration under Scenario 3 Conditions	43
Table 26:	Silver Speciation under Scenario 3 Conditions	13
Table 20.	Americation and Concentration under Scenario 4 Conditions	43
	Americium Solid Phase and Concentration under Scenario 1 Conditions	44
Table 28:	Americium Speciation under Scenario 1 Conditions	44
Table 29:	Comparison of Calculated AmOHCO ₃ (s) Solubilities and Speciation with	
1	Different Databases under Scenario 1 Conditions	44
Table 30:	Americium Solid Phases and Concentrations under Scenario 2 Conditions.	
-	The Bold Corresponds to the Most Likely Solubility Controlling Solid and	
(Solubility	45
Table 31.	Amaricium Spaciation under Scanaria 2 Conditions	15
	Americium Speciation under Scenario 2 Conditions	4J
	Americium Solid Phases and Concentrations under Scenario 3 Conditions.	
	The Bold Corresponds to the Most Likely Solubility Controlling Solid and	
ę	Solubility	45
Table 33:	Americium Speciation under Scenario 3 Conditions	45
Table 34:	Bismuth Solid Phase and Concentration under Scenario 1 Conditions	46
Table 35:	Bismuth Speciation under Scenario 1 Conditions	46
Table 36	Bismuth Solid Phase and Concentration under Scenario 2 Conditions	47
Table 30.	Dismuth Speciation under Sconario 2 Conditions	47
	Distriction Speciation under Scenario 2 Conditions	47
Table 38:	Bismuth Solid Phase and Concentration under Scenario 3 Conditions	41
Table 39:	Bismuth Speciation under Scenario 3 Conditions	47
Table 40:	Carbon Concentration and Speciation under Scenario 1 Conditions	48
Table 41:	Carbon Concentration and Speciation under Scenario 2 Conditions	49
Table 42:	Carbon Concentration and Speciation under Scenario 3 Conditions	49
Table 43:	Calcium Concentration and Speciation under Scenario 1 Conditions	50
	Calcium Concentration and Speciation under Scenario 2 Conditions	50
Table 44.	Calcium Concentration and Speciation under Scenario 2 Conditions	JU EA
Table 45:	Calcium Concentration and Speciation under Scenario 3 Conditions	21
Table 46:	Cadmium Solid Phase and Concentration under Scenario 1 Conditions	52
Table 47:	Cadmium Speciation under Scenario 1 Conditions	52
Table 48:	Cadmium Solid Phase and Concentration under Scenario 2 Conditions	53
Table 49:	Cadmium Speciation under Scenario 2 Conditions	53
Table 50:	Cadmium Solid Phase and Concentration under Scenario 3 Conditions	53
Table 51:	Cadmium Speciation under Scenario 3 Conditions	53
Table 57:	Cosium Solid Phase and Concentration under Scenario 1 Conditions	51
	Cesium Solid Fliase and Concentration under Scenario T Conditions	54
Table 53:	Cesium Speciation under Scenario 1 Conditions	54
Table 54:	Cesium Solid Phase and Concentration under Scenario 2 Conditions	54
Table 55:	Cesium Speciation under Scenario 2 Conditions	54
Table 56:	Cesium Solid Phase and Concentration under Scenario 3 Conditions	55
Table 57:	Cesium Speciation under Scenario 3 Conditions	55
Table 58: (Copper Solid Phase and Concentration under Scenario 1 Conditions	56
Table 59:	Conner Speciation under Scenario 1 Conditions	56
Table 60.	Conner Solid Phase and Concentration under Scenario 2 Conditions	57
	Copper Sond Flase and Concentration under Stendito 2 Conditions	51
	Copper Speciation under Scenario 2 Conditions	3/ 5-
Table 62: 0	Copper Solid Phase and Concentration under Scenario 3 Conditions	57
Table 63:	Copper Speciation under Scenario 3 Conditions	57
Table 64:	Iron Concentration and Speciation under Scenario 1 Conditions	58
Table 65:	Iron Concentration and Speciation under Scenario 2 Conditions	59
Table 66:	Iron Concentration and Speciation under Scenario 3 Conditions.	60

Table 67:	Mercury Solid Phases and Concentrations under Scenario 1 Conditions	62
Table 68:	Mercury Speciation under Scenario 1 Conditions	62
Table 69:	Mercury Solid Phase and Concentration under Scenario 2 Conditions	63
Table 70:	Mercury Speciation under Scenario 2 Conditions	63
Table 71:	Mercury Solid Phase and Concentration under Scenario 3 Conditions	64
Table 72:	Mercury Speciation under Scenario 3 Conditions	64
Table 73:	Molybdenum Solid Phases and Concentrations under Scenario 1 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and	~~
Table 74	Solubility	60
Table 74:	Molybdenum Speciation under Scenario 1 Conditions	00
Table 75:	The Bold Corresponds to the Most Likely Solubility Controlling Solid and	66
Table 76	Solubility	67
Table 70.	Molybdenum Speciation under Scenario 2 Conditions	07
	Morybuenum Sonu Filases and Concentrations under Scenario 5 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and	
	Solubility	67
Table 78:	Molybdenum Speciation under Scenario 3 Conditions	67
Table 79:	Niobium Solid Phase and Concentration under Scenario 1 Conditions	68
Table 80:	Niobium Speciation under Scenario 1 Conditions	68
Table 81:	Niobium Solid Phase and Concentration under Scenario 2 Conditions	68
Table 82:	Niobium Speciation under Scenario 2 Conditions	68
Table 83:	Niobium Solid Phase and Concentration under Scenario 3 Conditions	69
Table 84:	Niobium Speciation under Scenario 3 Conditions	69
Table 85:	Comparison of Calculated Np(OH)4(am) Solubilities and Speciation with	
l	Different Databases under Scenario 1 Conditions	71
Table 86:	Neptunium Solid Phase and Concentrations under Scenario 1 Conditions	71
Table 87:	Neptunium Speciation under Scenario 1 Conditions	71
Table 88:	Neptunium Solid Phase and Concentrations under Scenario 2 Conditions	72
Table 89:	Neptunium Speciation under Scenario 2 Conditions	72
Table 90:	Neptunium Solid Phase and Concentrations under Scenario 3 Conditions	72
Table 91:	Neptunium Speciation under Scenario 3 Conditions	72
Table 92:	Protoactinium Solid Phase and Concentration under Scenario 1 Conditions	73
Table 93:	Protoactinium Speciation under Scenario 1 Conditions	73
Table 94:	Protoactinium Solid Phase and Concentration under Scenario 2 Conditions	73
Table 95:	Protoactinium Speciation under Scenario 2 Conditions	73
Table 96:	Protoactinium Solid Phase and Concentration under Scenario 3 Conditions	74
Table 97:	Protoactinium Speciation under Scenario 3 Conditions	74
Table 98:	Lead Solid Phase and Concentration under Scenario 1 Conditions	75
Table 99:	Lead Speciation under Scenario 1 Conditions	75
Table 100	: Lead Solid Phases and Concentrations under Scenario 2 Conditions	76
Table 101	: Lead Speciation under Scenario 2 Conditions	76
Table 102	: Lead Solid Phase and Concentration under Scenario 3 Conditions	76
Table 103	: Lead Speciation under Scenario 3 Conditions	76
Table 104	: Palladium Solid Phase and Concentration under Scenario 1 Conditions	77
Table 105	: Palladium Speciation under Scenario 1 Conditions	77
Table 106	: Palladium Solid Phase and Concentration under Scenario 2 Conditions	77
Table 107	: Palladium Speciation under Scenario 2 Conditions	78
Table 108	: Palladium Solid Phase and Concentration under Scenario 3 Conditions	78
Table 109	: Palladium Speciation under Scenario 3 Conditions	18 70
	. Futonium Sond Phase and Concentration under Scenario 1 Conditions	19

Table 111: P	Plutonium Speciation under Scenario 1 Conditions	.79
Table 112: P	Plutonium Solid Phase and Concentration under Scenario 2 Conditions.	
T	he Bold Corresponds to the Most Likely Solubility Controlling Solid and	
S	Solubility	.79
Table 113: P	Plutonium Speciation under Scenario 2 Conditions. The Bold Corresponds	~~
	b the most Likely Solubility Controlling Solid and Speciation	.80
Table 114: P	Viutonium Solid Phases and Concentrations under Scenario 3 Conditions.	
1	ne Bold Corresponds to the Most Likely Solubility Controlling Solid and	00
Jahla 115. D	Olubility	.80
	Autonium Speciation under Scenario 3 Conditions. The Bold Corresponds	00
Table 116, B	o the Most Likely Solubility Controlling Solid and Speciation	00. 00
Table 110. R	adium Speciation under Scenario 1 Conditions	20. רס
	adjum Solid Phase and Concentration under Scenario 2 Conditions	20. רס
Table 110. N	Adulum Sond Filase and Concentration under Scenario 2 Conditions	20. 20
Table 119. N	Adulum Speciation under Scenario 2 Conditions	20. 20
Table 120. N	Adulum Sociation under Sconario 3 Conditions	נס. גם
Table 121. N	Padon K	03. ۸۵
Table 122. N	$\gamma_{\text{warr under}}$ of Calculated Ru(OH), HeO Solubilities and Speciation with	.04
	Different Databases under Scenario 1 Conditions	86
Table 124. C	C_{O} comparison of Calculated Ru(OH) $_{2}$ H ₂ O Solubility and Speciation with	.00
	Different Databases under Scenario 2 Conditions	86
Table 125: C	C_{OM} comparison of Calculated Ru(OH) ₃ , H ₂ O Solubility and Speciation with	.00
	Different Databases under Scenario 3 Conditions	87
Table 126: S	Sulphate Concentration and Speciation under Scenario 1 Conditions	.07 87
Table 127: S	Sulphate Concentration and Speciation under Scenario 2 Conditions	.07 88
Table 128: S	Sulphate Concentration and Speciation under Scenario 2 Conditions	.00 88
Table 129: A	Antimony Solid Phase and Concentration under Scenario 1 Conditions	.89
Table 130: A	Antimony Speciation under Scenario 1 Conditions	.89
Table 131: A	Antimony Solid Phase and Concentration under Scenario 2 Conditions	.89
Table 132: A	Antimony Speciation under Scenario 2 Conditions	.89
Table 133: A	Antimony Solid Phase and Concentration under Scenario 3 Conditions	.90
Table 134: A	Antimony Speciation under Scenario 3 Conditions	.90
Table 135: S	Selenium Solid Phases and Concentrations under Scenario 1 Conditions.	
Т	The Bold Corresponds to the Most Likely Solubility Controlling Solid and	
Š	Solubility	.90
Table 136: S	Selenium Speciation under Scenario 1 Conditions	.91
Table 137: S	Belenium Solid Phases and Concentrations under Scenario 2 Conditions.	
т	he Bold Corresponds to the Most Likely Solubility Controlling Solid and	
S	Solubility	.91
Table 138: S	Selenium Speciation under Scenario 2 Conditions	.91
Table 139: S	Selenium Solid Phases and Concentrations under Scenario 3 Conditions.	
Т	he Bold Corresponds to the Most Likely Solubility Controlling Solid and	
S	Solubility	.91
Table 140: S	Selenium Speciation under Scenario 3 Conditions	.92
Table 141: T	in Solid Phases and Concentrations under Scenario 1 Conditions.	
Т	he Bold Corresponds to the Most Likely Solubility Controlling Solid and	
S	Solubility	.93
Table 142: T	in Speciation under Scenario 1 Conditions	.93
Table 142. T	in Solid Phases and Concentrations under Scenarie 2 Conditions	

Table 143: Tin Solid Phases and Concentrations under Scenario 2 Conditions.

The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility94
 Table 144: Tin Speciation under Scenario 2 Conditions
Table 145: Tin Solid Phases and Concentrations under Scenario 3 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility94 Table 146: Tin Speciation under Scenario 3 Conditions95 Table 147: Strontium concentration and Speciation under Scenario 1 Conditions95 Table 148: Strontium Concentration and Speciation under Scenario 2 Conditions.......96 Table 150: Technetium Solid Phase and Concentration under Scenario 1 Conditions97 Table 152: Technetium Solid Phase and Concentration under Scenario 2 Conditions97 Table 154: Technetium Solid Phase and Concentration under Scenario 3 Conditions98 Table 156: Thorium Solid Phase and Concentration under Scenario 1 Conditions98 Table 158: Comparison of Calculated Th(OH)₄(am) Solubilities and Speciation with Table 159: Thorium Solid Phase and Concentration under Scenario 2 Conditions100 Table 160: Thorium Speciation under Scenario 2 Conditions101 Table 161: Thorium Solid Phase and Concentration under Scenario 3 Conditions101 Table 162: Thorium Speciation under Scenario 3 Conditions101 Table 163: Comparison of Calculated U(OH)₄(am) Solubilities and Speciation with Table 164: Uranium Solid Phase and Concentration under Scenario 1 Conditions.......103 Table 165: Uranium Speciation under Scenario 1 Conditions103 Table 166: Uranium Solid Phase and Concentration under Scenario 2 Conditions.......103 Table 167: Uranium Speciation under Scenario 2 Conditions103 Table 168: Uranium Solid Phase and Concentration under Scenario 3 Conditions.......104 Table 170: Zirconium Solid Phase and Concentration under Scenario 1 Conditions105 Table 172: Zirconium Solid Phase and Concentration under Scenario 2 Conditions105 Table 174: Zirconium Solid Phase and Concentration under Scenario 3 Conditions105 Table 176: Comparison of Solubility Results in the Absence (Base Case) and Presence (Sensitivity Case) of Sulphide for Scenario 1107 Table 177: Comparison of Solubility Results in the Absence (Base Case) and Presence (Sensitivity Case) of Phosphate......108 Table 178: Main Results and Conceptual Uncertainties of the Solubility Calculations ...111

LIST OF FIGURES

Figure 1:	Periodic Table Showing the Elements of Interest in Present Work (in Colour). Purple: Elements for which Data Are Already Included in YMP Database
	data0 ypf R2. Grey: Elements not Included in YMP Database data0 ypf R24
Figure 2:	Speciation Diagram for Americium at $[Am]_T = 1.10^{-9}$ m, with the Groundwater
U	Composition of SR-290-PW, Using Phase2-TDB (Left) and Using YMP
	data0 vpf R2 (Right)
Fiaure 3:	Speciation Diagram for Bismuth in Equilibrium with Bi ₂ O ₃ (s) in NaCl Solution.
0	Calculated Using Phase2-TDB
Figure 4:	Eh vs pH Predominance Diagram at I = 0 m for Copper Aqueous Species in
•	Pure Water, Calculated Using Phase2-TDB. $[Cu]_T = 10^8$ m; Solids Are not
	Allowed to Precipitate in the Calculation. Green Dashed Lines Stand for the
	Water Stability Field
Figure 5:	Experimental CuCl(s) Solubility Reported by Fritz (1982) and Calculated
	Values Using Phase2-TDB9
Figure 6:	Speciation Diagram for Neptunium at $[Np]_T = 1.10^{-9}$ m and Eh = -0.15 V, with
	the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left) and
	Using YMP data0_ypf_R2 Database (Right). The Dotted Lines Indicate Np(IV)
	Species
Figure 7:	Speciation Diagram for Neptunium at $[Np]_T = 1.10^{-9}$ m and Eh = -0.60 V, with
	the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left) and
	Using YMP data0_ypt_R2 Database (Right). The Dotted Lines Indicate Np(IV)
E !	Species
Figure 8:	Speciation Diagram for Palladium in Equilibrium with Pd(OH) ₂ (s) in NaCl
	Solution, Calculated Using Phase2-1DB
Figure 9.	specialion Diagram for Fluconium at $[Fu]_T = 1 \cdot 10^{-1}$ in and En = -0.15 V, with the Groundwater Composition of SP-200 PW Using Phase 2-TDP (Loft) and
	Lising VMP Database data0 whf P2 (Pight) The Solid and Dotted Lines
	Indicate Pu(III) and Pu(IV) Species Respectively 16
Figure 10.	Speciation Diagram for Plutonium at $[Pu]_{T} = 1.10^{-9}$ m and Fh = -0.36 V with
rigure re.	the Groundwater Composition of SR-290-PW. Using Phase2-TDB (Left), and
	Using YMP Database data0 vpf R2 (Right). The Solid and Dotted Lines
	Indicate Pu(III) and Pu(IV) Species, Respectively
Figure 11:	Speciation Diagram for Plutonium at $[Pu]_T = 1.10^{-9}$ m and Eh = -0.60 V, with
U	the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left), and
	Using YMP Database data0_ypf_R2 (Right). The Solid and Dotted Lines
	Indicate Pu(III) and Pu(IV) Species, Respectively
Figure 12:	Eh vs pH Predominance Diagram at I = 0 m for Ruthenium Aqueous Species
	in Pure Water, Calculated Using Phase2-TDB. $[Ru]_T = 10^{-6}$ m; Solids Are Not
	Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh
	Conditions for SR-290-PW. Green Dashed Lines Stand for the Water Stability
	Field
Figure 13:	Eh vs pH Predominance Diagram at I = 0 m for Selenium Aqueous Species
	in Pure Water, Calculated Using Phase2-TDB. [Se] _T = 10^{-7} m; Solids Are not
	Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh
	Conditions for SK-290-PW. Green Dasned Lines Stand for the Water
Figure 14.	Stability Field
Figure 14:	\Box is predominance Diagram at $I = 0$ in for reconcetium Aqueous

Species in Pure Water, Calculated Using Phase2-TDB. $[Tc]_{T} = 10^{-9}$ m: Solids Are not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for SR-290-PW. Green Dashed Lines Stand for the Water Figure 15: Speciation Diagram for Thorium at $[Th]_T = 1.10^{-9}$ m with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left), and Using YMP data0 ypf R2 (Right)......23 Figure 16: Solubility of Thorium Hydroxide at I = 4 m and $[C]_T = 0.02$ m (NaHCO₃-Na₂CO₃-NaCl). Symbols: Experimental Data from Altmaier et al. (2006). Lines: Calculated Using Phase2-TDB (Blue Lines) or THEREDA (Orange Line)24 Figure 17: Calculated Underlying Speciation for Thorium Hydroxide as in Table 23 Calculated Using Phase2-TDB (Left) or THEREDA (Right)25 Figure 18: Speciation Diagram for Uranium at $[U]_T = 1 \cdot 10^{-9}$ m and Eh = -0.15 V, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left) and Using YMP data0 ypf R2 (Right).....26 Figure 19: Speciation Diagram for Uranium at $[U]_T = 1 \cdot 10^{-9}$ m and Eh = -0.36 V, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left) and Using YMP data0_ypf_R2 (Right).....26 Figure 20: Correlation Among An(OH)₄(aq) (Left) or An(CO₃)₅⁶⁻ (Right) Stability Constants (log K°) and the Distance Between the Center of the Metal and Coordinated Water (d_{M-OH2})......28 Figure 21: Saturation Index of the Most Relevant Solid Phases under SR-290-PW Figure 22: Summary of the Different Cases Evaluated for Scenario 2. Cases with the Figure 24: AgCl(cr) Solubility (Solid Black Line) and Underlying Aqueous Ag Speciation (Dashed Lines) in NaCl Solution as a Function of Chloride Concentration, pH = 5.5. Vertical Dotted Line Indicates $[CI]_T = 5.5$ m, as Expected in the Studied Porewater (Table 1)......41 Figure 25. Cd(CO₃)(s) Solubility (Solid Black Line) and Underlying Aqueous Cd Speciation (Dashed Lines) as a Function of Chloride Concentration under Scenario 1 Conditions. Vertical Dotted Line Indicates [CI]_T = 5.5 m, as Expected in the Porewater (Table 1)......52 Figure 26: Cu(cr) Solubility (Solid Black Line) and Underlying Aqueous Cu Speciation (Dashed Lines) as a Function of Chloride Concentration at 25°C under Scenario 2 Conditions. Vertical Dotted Line indicates $[CI]_T = 5.5$ m, as expected in the Porewater (Table 20)56 Figure 27. Eh vs pH Predominance Diagram for Iron Calculated Using Scenario 1 Groundwater Composition. Red Dot Represent pH/Eh Conditions for Scenario 1. Green Dashed Lines Stand for the Water Stability Field58 Figure 28. Eh vs pH Predominance Diagram for Iron Calculated Using Scenario 2 Groundwater Composition. Red Dot Represent pH/Eh Conditions for Figure 29. Eh vs pH Predominance Diagram for Mercury System in Water, Calculated Using the Thermodynamic Data Selected in the Present Work Phase 2-TDB. $[CI]_T = 5 m; [Hg]_T = 10^{-6} m.$ Red Dots Indicates pH/Eh Conditions for Scenario 1, 2 and 3 Groundwaters. Green Dashed Lines Stand for the Water Stability Field61 Figure 30: Hg₂Cl₂(cr) Solubility (Solid Black Line) and Underlying Aqueous Hg Speciation (Dashed Lines) as a Function of Chloride Concentration,

under Scenario 1 Conditions. Vertical Dotted Line Indicates $[CI]_{T} = 5.5$ m. As Expected in the Porewater (see Table 1)62 Figure 31: Hg₂Cl₂(cr) Solubility (Solid Black Line) and Underlying Aqueous Hg Speciation (Dashed Lines) as a Function of Chloride Concentration at 25°C under Scenario 2 Conditions. Vertical Dotted Line Indicates $[CI]_T = 5.5 \text{ m}$. as Expected in the Porewater (Table 20).....63 Figure 32. Eh vs pH Predominance Diagram for Molybdenum Aqueous Species in Water, Calculated Using the Data Selection in the Present Work Phase 2-TDB. $[Ca]_T = 1.1 \text{ m}; [Mo]_T = 10^{-6} \text{ m}.$ Red Dots Indicates pH/Eh Conditions for Scenario 1, 2 and 3 Groundwater. Green Dashed Lines Stand for the Water Stability Field65 Figure 33: Nb₂O₅(s) Solubility (Solid Black Line) and Underlying Aqueous Nb Speciation (Dashed Lines) as a Function of pH. Vertical Dotted Line Indicates pH = 7.82, as Expected in the Scenario 2 Porewater (Table 20)69 Figure 34: Pa₂O₅(s) Solubility (Solid Black Line) and Underlying Aqueous Pa Speciation (Dashed Lines) as a Function of pH in 5.5 m NaCl Solution. Vertical Dotted Lines Indicate the pH Expected in the Different Scenario Groundwaters (Table 20)......74 Figure 35: Ra(SO₄)(s) Solubility (Solid Black Line) and Underlying Aqueous Ra Speciation (Dashed Lines) as a Function of Sulphate Concentration under Scenario 1 Conditions. Vertical Dotted Line Indicates $[SO_4]_T = 3.1 \cdot 10^{-3}$ m, as Expected in the Porewater (Table 1).....81 Figure 36: Dependence of the Partitioning Coefficient of Radon Gas between Water and Air (K_{w/air}) with Salinity......84 Figure 37. Ru(OH)₃·H₂O(s) Solubility (Solid Black Line) and Underlying Agueous Ru Speciation (Dashed Lines) as a Function of Chloride Concentration at 25°C under Scenario 1 Conditions, Calculated with Phase2-TDB. Vertical Dotted Figure 38. Eh vs pH Predominance Diagram for Tin Calculated Using Phase2-TDB. $[Ca]_T = 1.1 \text{ m}; [CI] = 5.5 \text{ m}; [Sn]_T = 10^{-6} \text{ m}. \text{ Red Dots Indicates pH/Eh}$ Conditions for Scenario 1. 2 and 3 Groundwaters at 25°C. Green Dashed Lines Stand for the Water Stability Field......93 Figure 39. Solubility of Hydrous Th(IV) Oxide in 3 m NaCl Solution and Underlying Calculated Speciation. Symbols: Experimental Data from Felmy et al. (1991). Lines: Calculated using Phase2-TDB (Left) or Modified ThermoChimie Figure 40: Periodic Table Showing the Elements of Interest in Present Work (in Colour). Green: Elements for which a Reasonable Amount of Thermodynamic Data are Available. Yellow: Elements for Which Relevant Pitzer Data are Lacking. Red: Elements for which the Lack of Thermodynamic Data is a Handicap110 Figure 41: Periodic Table Showing the Elements of Interest in Present Work (in Colour). Brown: Elements for which the Concentration is that Calculated for the Groundwater at Each Scenario. Blue: Elements for which Chloride Complexation Dominates the Aqueous Chemistry. Green: Elements for which the Formation of An(CO₃)₅⁶⁻ Species has been Discussed. Red: Elements for which the Lack of Thermodynamic Data is a Handicap. Grey:



1. INTRODUCTION

The objective of the "Radionuclides Solubility Calculation" project is to calculate the solubility limit values and speciation for the following elements: 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 support to the preparation of safety assessments and safety cases for a deep geological repository in a Canadian crystalline or sedimentary environment. The main goal of the present phase (Phase 2) is to calculate the solubility limit values for these elements in a Canadian reference porewater (SR-290-PW) representing groundwater chemistry of sedimentary rocks at repository depth. Table 1 describes the compositions of the reference porewater SR-290-PW.

	SR-290-PW
Nominal pH	5.5
Nominal Eh (mV)	-200
Solutes (mmol-kg ⁻¹ water)	
Na	2512
К	250
Са	1165
Mg	336
С	0.30
S(+VI)	3.10
CI	5531
Br	32
Sr	14
Li	1.48
F	0.02
I	0.12
В	16.50
Si	0.023
Fe	0.1

Table 1: Composition of the Reference Porewater SR-290-PW¹ (Density 1.175 g·mL⁻¹)

The reference groundwater is highly saline. The Pitzer model is preferred for ion activity correction in the calculations; although this approach is used in some thermodynamic databases, none is complete enough to fulfill the deal with the extensive element list described above. Therefore, a specific thermodynamic database has been developed.

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

- Scenario 1 (SC1). Groundwater enters the canister without interacting with the bentonite buffer or the canister materials.
- Scenario 2 (SC2). Groundwater interacts with the carbon-steel container prior to contacting the waste. The main component of C-steel is Fe(0). In the absence of other

¹ As indicated by NWMO

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 waste.

The thermodynamic database and the calculated groundwater compositions are then used in the solubility assessment.

The present document contains:

- A description of the thermodynamic database used in the calculations (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 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.

2. THERMODYNAMIC DATABASE

There are several approaches to deal with the ionic strength effect in thermodynamic data. For concentrated, high ionic strength solutions, the Pitzer model is frequently used. In the Pitzer model, the following parameters are needed to calculate the activity coefficients:

- $\beta^{(0)}, \beta^{(1)}$ and C^{ϕ} to describe cation-anion interactions;
- θ to describe cation-cation or anion-anion interactions;
- Ψ to describe triple interactions where the ions are not all of the same sign;
- λ to describe interactions for ion-neutral pairs;
- an additional parameter $\beta^{(2)}$ (correlated with the corresponding stability constant) is needed between cations and anions with charges 2 or higher.

Detailed equations of the Pitzer model can be found in Grenthe et al. (1997).

The main limitation of the application of the Pitzer approach to deal with radionuclide and toxic metal chemistry is the lack of information. The more extensive Pitzer database is the Yucca Mountain Pitzer (YMP) dataset data0.ypf.R2 (Jove-Colon et al. 2007), but it only contains some thermodynamic and Pitzer data for some of the elements of interest in present work (Figure 1). To complete and enlarge the thermodynamic database for present work, three different additional sources have been used:

- The THEREDA database (*www.thereda.de;* Altmaier et al. 2014) which uses the Pitzer approach for activity corrections and is intended for modeling of aqueous electrolyte solutions up to high concentrations. It contains a complete set of thermodynamic data and associated Pitzer parameters for some major elements (e.g., sodium, chloride, calcium, carbonate, sulphate) and several radionuclides (e.g., trivalent americium and tetravalent plutonium). Although THEREDA is the most recent and updated Pitzer database including radionuclides, some relevant major species (such as iron) and radionuclides (such as trivalent plutonium) are not included. Most of the toxic elements of interest in present work (copper, silver, palladium, lead, tin) are not included. The version of the database used in present work was released early in 2020.
- The Modified ThermoChimie database (www.thermochimie-tdb.com; Giffaut et al. 2014; Grivé et al. 2015). ThermoChimie is a complete and updated TDB for the purpose of modelling needs in performance assessments of high, low and intermediate level radioactive nuclear waste repositories. Most of the elements of interest for this study are included in ThermoChimie version 10a, except Bi, Cu, Hg, Rn and Ru (see Colàs et al. 2021a, were a review of the available thermodynamic data in the scientific literature for these elements was performed). However, ThermoChimie uses the Specific ion Interaction Theory (SIT) for ionic strength correction, not the Pitzer approach, and is not intended for its application in concentrated, high ionic strength systems.
- Available literature information focused on Pitzer thermodynamic data.



Figure 1: Periodic Table Showing the Elements of Interest in Present Work (in Colour). Purple: Elements for which Data Are Already Included in YMP Database data0_ypf_R2. Grey: Elements not Included in YMP Database data0_ypf_R2

The thermodynamic database used in the calculations is then a modified version of Yucca Mountain Pitzer database data0_ypf_R2 (hereafter named "Phase2-TDB") and its development has been performed with the following steps for each of the elements of interest.

- i. Evaluation of the data (stability constants and Pitzer coefficients) available in YMP database for each element of interest.
- ii. Literature review of additional available data in other thermodynamic databases (e.g., THEREDA or ThermoChimie) or in the open literature.
- iii. Selection of the reliable thermodynamic data.
- iv. Evaluation of the impact of the thermodynamic data modifications (using speciation, solubility and benchmark calculations).
- v. Identification of remaining uncertainties and data gaps.

The sections below contain a description of the thermodynamic data selection for each element, with a special emphasis on stability constants and Pitzer coefficients (when available). Speciation and solubility calculations at high ionic strength values have been performed with PhreeqC/PhreeqCl Interactive version 3.6.2 (released on January 28, 2020; Parkhurst and Appelo 2013) to evaluate the effect of database modifications on the calculations. To increase the reliability of the data selection and reduce the inconsistencies, comparisons with other thermodynamic databases and with experimental data (when available) are also reported. Finally, in those cases where the required data are not available, a discussion about the identified uncertainties and data gaps is provided.

2.1 AG

Silver is not included in YMP data0_ypf_R2 database, neither in THEREDA.

ThermoChimie contains a thermodynamic data selection for most relevant silver aqueous species and solid compounds, including stability constants for silver hydroxides and chlorides (Baes and Mesmer 1976; Ball and Nordstrom 1991). Those have been added to Phase2-TDB.

At high chloride concentrations, the formation of silver chloride complexes will play a key role in silver solubility and behaviour. Pitzer data associated to Ag(I) aqueous species is scarce in the open literature, although Fritz (1985) reported several Pitzer parameters for the Ag⁺/Cl⁻ system. Those values (Table 2) have been added to the silver thermodynamic data selection to be used in the calculations.

	Fritz (1985)				
	β ⁽⁰⁾	β ⁽¹⁾	Cφ		
Ag⁺/Cl⁻	0.0599	0.1800	0.03283		
Na⁺/AgCl₂⁻	0.1480	0.2930	-0.01520		
Na ⁺ /AgCl ₃ ²⁻	0.1288	1.2000	-0.01076		
Na⁺/AgCl₄ ³⁻	0.3436	4.0000	-0.01951		

Table 2: Pitzer Coefficients in the System Ag(I)/Cl⁻ Included in Phase2-TDB

2.2 AM

YMP data0_ypf_R2 database includes the following aqueous americium species:

- The stability constants of the four americium hydrolysis species: Am(OH)_n³⁻ⁿ; n = 0 to 4 and associated Pitzer parameters.
- The stability constants for the Am carbonate species: $Am(CO_3)n^{3-2n}$; n = 1 to 4.
- The stability constants for the Am chloride species: $AmCl^{2+}$ and $AmCl_{2^+}$ and associated $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} coefficients.
- The stability constants for the Am sulfate species: Am(SO₄)⁺ and Am(SO₄)₂⁻.

We have modified the YMP database in order to complete it with missing Pitzer coefficients for some americium species. The complete set of Pitzer coefficients for the Am(CO₃)⁺ and the Ψ and θ coefficients for the carbonate and chloride species from THEREDA have been added.

Related to the americium solid phases relevant for the present study, YMP database includes stability constants for $Am(OH)_3(cr)$, $Am(OH)_3(am)$, $AmOHCO_3$ and $Am_2(CO_3)_3$. These solid phases, together with their stability constants have been kept in the modified YMP database to maintain the consistency with the hydrolysis and carbonate systems.

With the aim to evaluate the implications of those changes, americium speciation calculations have been performed with the Phase2-TDB and the results are compared with the diagrams obtained using the YMP data0_ypf_R2 database (without modification). For this purpose, fraction diagrams of [Am] = 10^{-9} m have been calculated considering the pore water composition

detailed in Table 1 and a pH range of 5 to 9. The comparison between the speciation diagrams in Figure 2 indicates that the Phase2-TDB provides similar results as the YMP data0_ypf_R2 database.



Figure 2: Speciation Diagram for Americium at $[Am]_T = 1 \cdot 10^{-9}$ m, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left) and Using YMP data0_ypf_R2 (Right)

2.3 BI

Bismuth is not included in YMP data0_ypf_R2 database, neither in THEREDA nor in ThermoChimie. The most complete thermodynamic dataset for Bi is those reported by Lothenbach et al. (1999), which is the one used in the Phase 1 of the present project; selected data include the stability constants of Bi(III) aqueous species with hydroxide and chloride and oxide solid compounds (see Colàs et al. 2021a). Those have been added to the Phase2-TDB.

Bismuth is known to form strong complexes with chloride (Lothenbach et al. 1999; Rai et al. 2010). At high NaCl concentrations, species such as $BiCl_5^{2-}$ or $BiCl_6^{3-}$ can be formed (see Figure 3). However, due to the scarce experimental data, the stability constants associated to $BiCl_5^{2-}$ and $BiCl_6^{3-}$ are only tentative (see Lothenbach et al. 1999). This, and the lack of Pitzer parameters for the Bi-Cl system, are the main uncertainties affecting the selected data under the studied conditions.



Figure 3: Speciation Diagram for Bismuth in Equilibrium with Bi₂O₃(s) in NaCl Solution, Calculated Using Phase2-TDB

2.4 C

Stability constants and consistent Pitzer parameters for relevant carbonate aqueous species such as $CO_3^{2^\circ}$, HCO_3^{-} and $CO_2(aq)$ are already included in the YMP database data0_ypf_R2. Calcite (CaCO₃(s)) is also included in the database. The selection for the carbonate system is reported in Jove-Colon et al. (2007).

CH₄(g) is included in the database, but the reduction of carbonate to methane is neglected in the present work, as methanogenesis is normally microbiologically mediated and the microbial activity has not been considered in this study.

2.5 CA

Stability constants and consistent Pitzer parameters for relevant calcium aqueous species such as $CaCO_3(aq)$, $CaSO_4(aq)$, $CaCI^+$ and $CaCl_2(aq)$ are already included in YMP data0_ypf_R2 database. Gypsum ($CaSO_4 \cdot 2H_2O(s)$) is also included in the database. The selection for the calcium system is reported in Jove-Colon et al. (2007).

2.6 CD

Cadmium is not included in YMP data0_ypf_R2 database, neither in THEREDA. Data selection including Pitzer coefficients has not been identified in open literature.

ThermoChimie contains a thermodynamic data selection for most relevant cadmium aqueous species and solid compounds, including stability constants for cadmium hydroxides and chlorides (Baes and Mesmer 1976; Rai et al. 1991). Those have been added to the Phase2-TDB.

Aqueous cadmium chloride complexes will be formed at high chloride concentrations. The lack of Pitzer parameters for those complexes will be one of the main uncertainties affecting the calculations.

2.7 CS

Overall, caesium aqueous chemistry is weakly affected by the groundwater changes as its reactivity is relatively limited, being the free cation Cs^+ the dominant species. Cesium data selection in YMP data0_ypf_R2 includes Cs^+ as the master species and Cs^+/Cl^- and Cs^+/SO_4^{2-} Pitzer coefficients.

2.8 CU

Although no copper aqueous species or solid phases are incorporated in YMP data0_ypf_R2 database, Pitzer coefficients for free Cu²⁺ ion (Cu²⁺/Cl⁻, Cu²⁺/SO₄²⁻ and others) are included. However, Cu(I) (not Cu(II)) will dominate copper chemistry under reducing conditions (see Figure 4). Copper thermodynamic data are neither included in THEREDA nor in ThermoChimie.



Figure 4: Eh vs pH Predominance Diagram at I = 0 m for Copper Aqueous Species in Pure Water, Calculated Using Phase2-TDB. $[Cu]_T = 10^{-8}$ m; Solids Are not Allowed to Precipitate in the Calculation. Green Dashed Lines Stand for the Water Stability Field

Thus, the Cu data selection (aqueous and solid Cu species and their associated stability constants) from Phase 1 of the project has been maintained in present work. Selected Log K° values are mainly from Puigdomènech and Taxén (2000), who performed one of the most extensive and accurate data compilations for copper, including chlorides, carbonates, phosphates, sulphates, sulphides and redox aqueous species. The exception are the stability constants of the Cu(I) species Cu(OH)(aq) and Cu(OH)₂⁻, that have been selected from Palmer (2011) (see Colàs et al. 2021a).

Pitzer data associated to Cu(I) aqueous species is scarce in the open literature. Fritz (1981, 1982) studied CuCl(s) solubility (Figure 5) and reported several Pitzer parameters for the Cu⁺/Cl⁻ system which are detailed in Table 3; those values have been added to the Phase2-TDB.

	Fritz (1981)
β ⁽⁰⁾	B ⁽¹⁾	Cφ

0.0747

0.0619

Na⁺/CuCl₂⁻

Na⁺/CuCl₃²⁻

Table 3: Pitzer Coefficients in the System Cu(I)/Cl⁻ Included in Phase2-TDB

0.2052

0.9999

0.0107

0.0254

	1.0 -	
		CuCl(s) solubility
	0.5 -	•
_	0.0 -	
	-0.5 -	and the second se
log [CL	-1.0 -	and the second sec
	-1.5 -	• Fritz (1982)
	-2.0 -	Phase2-TDB
	-2.5 -	· · · ·
	-	1 -0.5 0 0.5 1 log [NaCl] (m)

Figure 5: Experimental CuCl(s) Solubility Reported by Fritz (1982) and Calculated Values Using Phase2-TDB

2.9 FE

Data for Fe(II)/Fe(III) redox and stability constants for Fe(II) and Fe(III) aqueous species such as $FeCI^+$, $FeOH^+$, $FeCI_2^+$, $Fe(OH)_2^+$, $Fe(OH)_3(aq)$ and relevant iron solids as magnetite

(Fe₃O₄(s)), ferrihydrite (Fe(OH)₃(s)) or siderite (FeCO₃(s) are included in YMP data0_ypf_R2 database. Pitzer parameters for Fe(II) interactions such as Fe^{2+}/CI^{-} or Fe^{2+}/SO_4^{2-} are also included.

Relevant Fe-sulphide aqueous and solid species as Pyrite (FeS₂(s)) are not reported in YMP data0_ypf_R2. Microbial activity is not considered in present work, thus the reduction of sulphate to sulphide should be kinetically hindered. Sulphide concentration in the reference water is below the detection limit; however, $1.6 \cdot 10^{-5}$ m was defined by NWMO as an upper bound (maximum) for its use in model parameterizations and will be used in some sensitivity calculations (see Section 4.2.1). To fulfill this objective, the stability constants for Fe-sulphide species already included in ThermoChimie have been added to Phase2-TDB.

2.10 HG

Mercury is not included in the YMP data0_ypf_R2 database, neither in THEREDA nor in ThermoChimie. The Hg data selection (aqueous and solid mercury species and their associated stability constants) from Phase 1 of the project have been maintained in present work (see Colàs et al. 2021a).

Mercury has two redox states in aqueous solution, Hg(II) as Hg²⁺ (formed under oxidizing conditions) and Hg(I) as Hg₂²⁺ (formed under reducing conditions). Redox data for Hg²⁺/Hg₂²⁺ has been selected from Bard et al. (1985). Data selection for Hg(II) chemistry is mainly based on the work by Powell et al. (2005), who made a critical evaluation of the complex formation reactions between aqueous Hg(II) and common environmental inorganic ligands such as OH⁻, Cl⁻, CO₃²⁻ or SO₄²⁻. 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). Those data have been included in the Phase2-TDB.

González-Dávila et al. (2007) calculated Pitzer parameters for Hg(II) in NaClO₄ system. As discussed by the authors, those data sets are consistent with the stability constants selection made by Powell et al. (2005); thus, the Pitzer coefficients in Table 4 have been added to Phase2-TDB.

	González-Dávila et al. (2007)			
	β ⁽⁰⁾	β ⁽¹⁾	Cφ	λ
Na⁺/HgCl₂(aq)⁺				-0.6500
Na⁺/HgCl₃ (aq)	-0.3979		0.0772	
Na ⁺ /HgCl ₄ ²⁻ (aq)	-0.3489		0.0576	
Na⁺/HgOHCl(aq)				-0.1957

Table 4:	Pitzer Co	efficients i	n the	Hq(II)	System	Included i	n Phase2-TDB
		•••••••••••					

2.11 MO

Molybdenum is a redox sensitive element. Mo(IV) and Mo(VI) are the most common oxidation states in nature.

The most relevant Mo(VI) aqueous species, $MoO_4^{2^-}$, is already included in YMP data0_ypf_R2 database; the most relevant Pitzer coefficients for this species (Na⁺/ MoO_4²⁻ and Ca²⁺/ MoO_4²⁻) and relevant solids (Powellite, CaMoO_4(s)) are also included. To complete the database, solid $MoO_2(s)$ and its associated stability constant (as reported in ThermoChimie) has been added to the Phase2-TDB.

2.12 NB

Niobium is not included in YMP data0_ypf_R2 database, neither in THEREDA. Data selection including Pitzer coefficients has not been identified in other open literature.

ThermoChimie contains stability constants for niobium oxides and hydroxides (Peiffert et al. 1997) which are expected to dominate Nb chemistry under the studied conditions; those data have been added to the Phase2-TDB.

2.13 NP

YMP data0_ypf_R2 database includes data for the following aqueous neptunium species:

- The master species of the different neptunium oxidation states: Np³⁺, Np⁴⁺, NpO₂⁺ and NpO₂²⁺ and their associated Pitzer coefficients.
- The hydrolysis system of Np(IV): Np(OH)_n⁴⁻ⁿ; n = 1 to 4 and some associated Pitzer parameters.
- The hydrolysis system of Np(V): NpO₂OH and NpO₂(OH)₂ and some associated Pitzer parameters.
- Main carbonate species of Np(V): NpO₂CO₃⁻, NpO₂(CO₃)₂³⁻ and NpO₂(CO₃)₃⁵⁻ and some associated Pitzer parameters.

THEREDA database contains a more updated and extensive Np(IV) thermodynamic data selection than YMP data0_ypf_R2. Taking into account that Np(IV) is expected to be the more relevant neptunium oxidation state under the studied conditions, the following actions have been undertaken in the Phase2-TDB:

- The aqueous species and Pitzer coefficients of Np(III), Np(V) and Np(VI) system from YMP data0_ypf_R2 database have been kept in the Phase2-TDB.
- The hydrolysis species and corresponding Pitzer coefficients of Np(IV) selected in THEREDA database have been included in the Phase2-TDB.
- The carbonates species and corresponding Pitzer coefficients of Np(IV) selected in THEREDA database (Np(CO₃)₅⁶⁻ and Np(OH)₂(CO₃)₂²⁻) have been included in the Phase2-TDB.
- The chloride species and corresponding Pitzer coefficients of Np(IV) selected in THEREDA database (NpCl³⁺) have been included in the Phase2-TDB.
- Np(OH)₄(am) and its associated stability constant from THEREDA has been included in the Phase2-TDB.

Figure 6 and Figure 7 show Np speciation diagrams at Eh = -0.15 V and Eh = -0.60 V as a function of pH, calculated using the Phase2-TDB (left) or YMP data0_ypf_R2 (right). In all cases total carbonate concentration is $3 \cdot 10^{-4}$ m. The main difference in the calculations is the

predominant role of the highly charged species, $Np(CO_3)_5^{6-}$, in the calculations performed with the Phase2-TDB; see discussion in Section 2.30.



Figure 6: Speciation Diagram for Neptunium at $[Np]_T = 1 \cdot 10^{-9}$ m and Eh = -0.15 V, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left) and Using YMP data0_ypf_R2 Database (Right). The Dotted Lines Indicate Np(IV) Species



Figure 7: Speciation Diagram for Neptunium at $[Np]_T = 1 \cdot 10^{-9}$ m and Eh = -0.60 V, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left) and Using YMP data0_ypf_R2 Database (Right). The Dotted Lines Indicate Np(IV) Species

2.14 PA

Protactinium mainly occurs in the oxidation states Pa(IV) and Pa(V), although Pa(IV) is very sensitive to oxidation and it is only stable under strong acid media and low Eh values.

Protactinium is not included in YMP data0_ypf_R2 database, neither in THEREDA. ThermoChimie contains a thermodynamic data selection (stability constants) for Pa(IV) aqueous hydroxides and solid oxides, and Pa(V) aqueous hydroxides and sulphates and solid oxides (Baes and Mesmer 1976; Fourest et al. 2004; Di Giandomenico et al. 2007). Those have been added to Phase2-TDB.

The lack of thermodynamic information related to Pa is one of the main handicaps when performing calculations for this element, even at low ionic strengths.

2.15 PB

Lead is not included in YMP data0_ypf_R2 database, neither in THEREDA.

ThermoChimie contains a thermodynamic data selection for most relevant lead aqueous species and solid compounds, including stability constants for lead hydroxides and chlorides (Sverjensky et al. 1997). Those have been added to the Phase2-TDB, with the modification described below.

Aqueous lead chloride complexes will be formed at high chloride concentrations. Several authors, including Sverjensky et al. (1997), Lothenbach et al. (1999) and Felmy et al. (2000), have reported stability constants for those species; data are compared in Table 5. As seen in the table, the stability constants for PbCl⁺, PbCl₂(aq) and PbCl₃⁻ are similar in all publications. However, Felmy et al. (2000) suggested a significantly different log K° value for PbCl₄²⁻. As log K° (PbCl₄²⁻) = 1.40 was considered only a rough, preliminary estimate by the original authors (Seward 1984), the log K° (PbCl₄²⁻) = 0.14 from Felmy et al. (2000) is preferred in Phase2-TDB.

Nevertheless, Powell et al. (2009) provided an extensive review on the formation of $PbCl_4^{2-}$ and reported conflicting results in the literature about its associated formation constant and even about the existence of the species itself. Thus, the role of this species in concentrated chloride systems may be overestimated; an evaluation of the uncertainty related to the formation of $PbCl_4^{2-}$ and its effects in solubility calculations is provided in Section 4.

Table 5: Stability Constants for the Formation of PbCl _n ⁽²⁻ⁿ⁾ Species.	Those in Bold
Have Been Included in Phase2-TDB	

	Sverjensky et al. (1997)	Lothenbach et al. (1999)	Felmy et al. (2000)
Species	Log K°	Log K°	Log K°
PbCl⁺	1.44	1.55	1.48
PbCl ₂ (aq)	2.00	2.00	2.03
PbCl ₃	1.69	2.01	1.88
PbCl ₄ ²⁻	1.40	1.35	0.14

The Pitzer data reported by Xiong et al. (2013), Xiong et al. (2015) and Xiong et al. (2018) have been included in Phase2-TDB (Table 6).

	Х	liong et al.	(2013), Xio	ng (2015), Xi	ong et al. (20)18)
	β ⁽⁰⁾	β ⁽¹⁾	Cφ	λ	θij	Ψ_{ijk}
Na ⁺ /Pb(CO ₃) ₂ ²⁻	0.20	1.74	-0.21			
Mg ²⁺ /PbCl ₃ ⁻	1.43	1.74	0.00			
Pb ²⁺ /Cl ⁻	0.26	1.64	0.09			
PbCl ⁺ /Cl ⁻	0.15	0.00	0.00			
Na⁺/PbCl₃⁻	-0.06	0.00	0.09			
H ⁺ /Pb(OH) ₃ ⁻	0.27	-0.63	0.00			
Pb(OH)⁺/Cl⁻	0.00	0.00	0.00			
Pb(CO ₃)(aq)/Na⁺				0.00		
PbCl ₂ (aq)/Mg ²⁺				-0.07		
PbCl₂(aq)/Na⁺				-0.11		
Pb(OH)₂(aq)/Na⁺				0.00		
Pb(CO ₃)(aq)/Cl ⁻				-0.02		
Pb(OH) ₂ (aq)/SO ₄ ²⁻				-0.56		
Pb(OH) ₂ (aq)/Cl ⁻				-0.17		
PbCl ₂ (aq)/Cl ⁻				-0.14		
Mg ²⁺ /PbCl ⁺					-0.13	
Na ⁺ /Pb ²⁺					0.10	
Na⁺/PbCl⁺					0.00	
HCO ₃ ⁻ /Pb(CO ₃) ₂ ²⁻					0.15	
CI ⁻ /PbCl ₃ ⁻					0.74	
SO ₄ ²⁻ /Pb(OH) ₃ ⁻					-0.40	
$CO_{3}^{2}/Pb(CO_{3})_{2}^{2}$					0.22	
Mg ²⁺ /PbCl ⁺ /Cl ⁻						-0.41
Cl ⁻ /PbCl ₃ ⁻ /Mg ²⁺						0.00

Table 6: Pitzer Coefficients in the Pb(II) System Included in Phase2-TDB

2.16 PD

Palladium is not included in YMP data0_ypf_R2 database, neither in THEREDA. Data selection including Pitzer coefficients has not been identified in open literature.

ThermoChimie contains a thermodynamic data selection for most relevant palladium aqueous species and solid compounds, including stability constants for cadmium hydroxides and chlorides (Nabivanets and Kalabina 1970; Lothenbach et al. 1999). Those have been added to the Phase2-TDB.

As in the case of other metals such as cadmium, lead, etc., aqueous palladium chloride complexes will be formed at high chloride concentrations (Figure 8). The lack of Pitzer parameters for those complexes will be one of the main uncertainties affecting the calculations.



Figure 8: Speciation Diagram for Palladium in Equilibrium with Pd(OH)₂(s) in NaCl Solution, Calculated Using Phase2-TDB

2.17 PU

YMP data0_ypf_R2 database includes data for the following aqueous plutonium species:

- Master species: Pu³⁺, Pu⁴⁺, PuO₂⁺ and PuO₂²⁺.
- Hydrolysis system of Pu(III): $Pu(OH)_n^{3-n}$; n = 1 to 3.
- Hydrolysis system of Pu(IV): $Pu(OH)_n^{4-n}$; 1 = 0 to 4.
- Pu(III) carbonates species: Pu(CO₃)_n³⁻²ⁿ; n = 1 to 4.
- Pu(VI) carbonate species: $PuO_2(CO_3)_n^{2-2n}$; n = 1 to 3.
- Pu(III) sulphate species: $Pu(SO_4)^+$ and $Pu(SO_4)_2^-$.
- Pu(III) chloride species: PuCl²⁺ and PuCl₂⁺.

THEREDA database contains a more updated and extensive Pu(IV) thermodynamic data selection than YMP data0_ypf_R2 database. Taking into account that Pu(IV) is expected to be very relevant under the studied conditions, the following actions have been undertaken in the Phase2-TDB:

- The aqueous species and Pitzer coefficients of Pu(III), Pu(V) and Pu(VI) system from YMP data0_ypf_R2 database have been kept in Phase2-TDB.
- The whole set of aqueous species and Pitzer coefficients of Pu(IV) in Phase2-TDB have been selected from THEREDA database.
- The stability constants of the Pu(IV) solid phases already included in YMP data0_ypf_R2 database have been modified in agreement with those in THEREDA.

A summary of Pu(IV) thermodynamic data included in Phase2-TDB is provided in Appendix A.

Figure 9 shows Pu speciation diagrams at Eh = -0.15 V as a function of pH, calculated using the Phase2-TDB (left) or YMP data0_ypf_R2 database (right). In all cases, total carbonate concentration is $3 \cdot 10^{-4}$ m. The main difference in the calculations is the predominant role of the Pu(IV) highly charged species, Pu(CO₃)₅⁶⁻, in the calculations performed with the Phase2-TDB. Due to the high stability of this species, Pu(IV) dominates the aqueous Pu chemistry in the calculations using Phase2-TDB; on the contrary, using the YMP data0_ypf_R2 database, Pu(III) species are expected to dominate the aqueous chemistry of the system at pH below about 7.7.



Figure 9: Speciation Diagram for Plutonium at $[Pu]_T = 1 \cdot 10^{-9}$ m and Eh = -0.15 V, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left), and Using YMP Database data0_ypf_R2 (Right). The Solid and Dotted Lines Indicate Pu(III) and Pu(IV) Species, Respectively

Similar results are obtained under more reducing conditions (Eh = -0.36 V, Figure 10, and Eh = -0.60 V, Figure 11). Even under those reducing conditions, the Pu(IV) species $Pu(CO_3)_5^{6-1}$ dominates the aqueous chemistry using Phase2-TDB database.

A more detailed discussion about the role of tetravalent $An(CO_3)_5^{6-}$ species is provided in Section 2.30.


Figure 10: Speciation Diagram for Plutonium at $[Pu]_T = 1 \cdot 10^{-9}$ m, and Eh = -0.36 V, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left), and Using YMP Database data0_ypf_R2 (Right). The Solid and Dotted Lines Indicate Pu(III) and Pu(IV) Species, Respectively



Figure 11: Speciation Diagram for Plutonium at $[Pu]_T = 1 \cdot 10^{-9}$ m and Eh = -0.60 V, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left), and Using YMP Database data0_ypf_R2 (Right). The Solid and Dotted Lines Indicate Pu(III) and Pu(IV) Species, Respectively

2.18 RA

Radium is not included in YMP data0_ypf_R2 database, neither in THEREDA.

ThermoChimie contains a thermodynamic data selection for most relevant radium aqueous species and solid compounds, including stability constants for aqueous and solid chlorides, carbonates and sulphates (Scherbaum 1999; Langmuir and Riese 1985). Those have been added to Phase2-TDB.

Rosenberg et al. (2011) proposed a set of Pitzer coefficients to describe $RaSO_4$ behaviour in NaCl solutions. The data set for Ra^{2+}/Cl^{-} interactions is consistent with the Pitzer data included in YMP data0_ypf_R2 database for other alkaline earth elements (see Table 7). Thus, those data have been included in Phase2-TDB.

	β ⁽⁰⁾	β ⁽¹⁾	Cφ	Reference
Mg ²⁺ /Cl ⁻	0.35	1.65	0.0065	data0_ypf_R2
Ca ²⁺ /Cl ⁻	0.30	1.70	0.0012	data0_ypf_R2
Sr ²⁺ /Cl ⁻	0.28	1.63	-0.00089	data0_ypf_R2
Ba ²⁺ /Cl ⁻	0.26	1.50	-0.01938	data0_ypf_R2
Ra²⁺/Cl⁻	0.25	1.48	-0.023	Rosenberg et al. (2011)

Table 7: Pitzer Coefficients in the System M(II)/Cl⁻ (M(II) = Alkaline Earth Element) Included in Phase2-TDB

2.19 RN

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 partitioning coefficient $K_{w/air}$ is related to the Bunsen coefficient β and the temperature (in Kelvin) with Eq. 1.

$$K_{w/air} = \beta * \frac{T}{273.15}$$
 Eq. 1

The Bunsen coefficient depends on salinity (S); the dependence can be calculated using Eq. 2 derived by Weiss (Weiss et al. 1970, 1971; Weiss and Kyser 1978) for other noble gases (He, Ne, Ar and Kr).

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

Schubert et al. (2012) performed a series of Rn solubility laboratory experiments (up to 50°C and 360 % NaCl) that were used to determine the a₁ to b₃ parameters needed to apply Eq. 2.

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

|--|

*The data set corresponds to the most recommendable one reported in Table 1 of Schubert et al. (2012)

2.20 RU

Ruthenium is not included in YMP data0_ypf_R2, neither in THEREDA or in ThermoChimie. The Ru data selection (aqueous and solid Ru species and their associated stability constants) from Phase 1 of the project have been maintained in present work.

Thermodynamic data for Ru is quasi-inexistent in the literature. This, and its complex redox behaviour (Ru can form compounds with valences up to VIII, see Figure 12) complicates the thermodynamic data selection, even at low ionic strengths.



Figure 12: Eh vs pH Predominance Diagram at I = 0 m for Ruthenium Aqueous Species in Pure Water, Calculated Using Phase2-TDB. $[Ru]_T = 10^{-6}$ m; Solids Are Not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for SR-290-PW. Green Dashed Lines Stand for the Water Stability Field

Sassani and Shock (1998) discussed thermodynamic data for platinum group elements, including lower Ru oxidation states (Ru(II) and Ru(III)). 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)₂²⁺, Ru(OH)₄(aq) and the polymeric species Ru₄(OH)₁₂⁴⁺, in agreement with the discussion in Rard (1987).

No Pitzer data has been identified in the open literature.

2.21 S

Stability constants and consistent Pitzer parameters for relevant sulphate aqueous species (such as Pitzer parameters for Na⁺/SO₄²⁻, Ca²⁺/SO₄²⁻) are already included in YMP database data0_ypf_R2. Gypsum (CaSO₄·2H₂O(s)) is also included.

Microbial activity is not considered in present work, thus the reduction of sulphate to sulphide should be kinetically hindered. Sulphide concentration in the reference water is below the detection limit; however, $1.6 \cdot 10^{-5}$ m was defined by NWMO as an upper bound (maximum) for its use in model parameterizations and will be used in some sensitivity calculations (see Section 4.2.1). To fulfill this objective, basic sulphide chemistry needs to be included in the database.

Stability constants associated to SO_4^{2-} reduction to HS⁻ are already included in YMP database data0_ypf_R2. The acid/base sulphide chemistry (HS⁻/S²⁻ and HS⁻/H₂S(aq) stability constants) from ThermoChimie have been added to Phase2-TDB. The stability constants for Fe-sulphide species already included in ThermoChimie have also been included in the database (see Section 2.9). Due to the scarce information available, no Pitzer parameters for sulphide species are included in Phase2-TDB.

2.22 SB

Antimony is not included in YMP data0_ypf_R2 database, neither in THEREDA. Data selection including Pitzer coefficients has not been identified in open literature.

ThermoChimie contains a thermodynamic data selection for most relevant antimony aqueous species and solid compounds, including stability constants for Sb(III) oxides, hydroxides and chlorides, and Sb(V) oxides and hydroxides (Baes and Mesmer 1976; Lothenbach et al. 1999). Those have been added to Phase2-TDB.

2.23 SE

Selenium is not included in YMP data0_ypf_R2 database, neither in THEREDA.

ThermoChimie contains a thermodynamic data selection for most relevant Se(VI), Se(IV) and Se(-II) aqueous species and solid compounds; most of the data corresponds to the NEA-TDB selection (Olin et al. 2005). Those species and its related stability constants have been added to Phase2-TDB.

Due to the chemical analogies between selenate, SeO_4^{2-} , and sulphate, SO_4^{2-} , some Pitzer data are available in the literature for Se(VI) main aqueous species (e.g., Rai et al. 2014). Nevertheless, Se(-II), and not Se(VI), is expected to be the predominant Se redox state under the conditions of interests (see Figure 13). No reliable Pitzer data for Se(-II) have been identified.



Figure 13: Eh vs pH Predominance Diagram at I = 0 m for Selenium Aqueous Species in Pure Water, Calculated Using Phase2-TDB. $[Se]_T = 10^{-7}$ m; Solids Are not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for SR-290-PW. Green Dashed Lines Stand for the Water Stability Field

2.24 SN

Tin is not included in YMP data0_ypf_R2 database, neither in THEREDA.

ThermoChimie contains a thermodynamic data selection for most relevant Sn(IV) and Sn(II) aqueous species and solid compounds; most of the data corresponds to the NEA-TDB selection (Gamsjäger et al. 2012). No reliable Pitzer data have been identified.

2.25 SR

Stability constants and consistent Pitzer parameters for relevant strontium aqueous species (Pitzer parameters for Sr^{2+}/Cl^{-}) are already included in YMP database data0_ypf_R2. Strontianite ($SrCO_3(s)$) and celestite ($SrSO_4(s)$) are also included.

2.26 TC

YMP data0_ypf_R2 database includes the following aqueous and solid technetium complexes:

- Tc(VII) master species, TcO₄, and a set of associated Pitzer parameters.
- The redox reaction from TcO_4 (Tc(VII)) to TcO^{2+} (Tc(IV)).
- Several solid species, including Tc(VII) and Tc(IV) oxides and hydroxides.

The main redox state expected under the studied conditions is Tc(IV); hydrolysed species (and not TcO²⁺) are expected to dominate the aqueous speciation (see Figure 14). Thus, Phase2-TDB has been modified in order to include Tc(VII)/Tc(IV) redox reaction and the species TcO²⁺, TcO(OH)⁺, TcO(OH)₂(aq) and TcO(OH)₃⁻ from ThermoChimie. The redox reaction from TcO₄⁻ (Tc(VII)) to TcO₄²⁻ (Tc(VI)) has also been included. No relevant Pitzer data for Tc(IV) system has been identified.

The lack of thermodynamic information related to Tc is one of the main handicaps when performing calculations for this element, even at low ionic strengths.



Figure 14: Eh vs pH Predominance Diagram at I = 0 m for Technetium Aqueous Species in Pure Water, Calculated Using Phase2-TDB. $[Tc]_T = 10^{-9}$ m; Solids Are not Allowed to Precipitate in the Calculation. Red Dot Indicates pH/Eh Conditions for SR-290-PW. Green Dashed Lines Stand for the Water Stability Field

2.27 TH

YMP data0_ypf_R2 database includes the following aqueous thorium species:

- The stability constants of the four thorium hydrolysis species: $Th(OH)_n^{4-n}$; n = 0 to 4.

- The polynuclear hydrolysis species: Th₂(OH)₂⁶⁺, Th₄(OH)₈⁸⁺, Th₄(OH)₁₂⁴⁺, Th₆(OH)₁₅⁹⁺.
- The carbonate species: Th(CO₃)₅⁶⁻.
- The Th sulfate species: Th(SO₄)₂, Th(SO₄)₃²⁻ and Th(SO₄)₄⁴⁻.

In Phase2-TDB, the following changes have been performed to improve the database:

- The polynuclear hydrolysis species have been excluded from the calculations.
- The Th(IV)-CO₃ system has been substituted for the one in THEREDA, which includes stability constants and Pitzer interaction parameters for both Th(CO₃)₅⁶⁻ and Th(OH)₃(CO₃)⁻.

Appendix B summarizes Th(IV) hydroxide, carbonate and hydroxycarbonate aqueous species and its associated Log K^o values included in different databases in comparison with the thermodynamic data in Phase2-TDB.

Related to the thorium solid phases relevant for the present study, YMPdata0_ypf_R2 database includes stability constants for three different thorium oxides phases with crystallinity increasing in the order $ThO_2(am) < Th(OH)_4(am) < ThO_2(cr)$. These solid phases, together with their stability constants have been kept in the modified version of Yucca Mountain Pitzer database to maintain the consistency with the hydrolysis system.

Figure 15 indicates different predominant species as a function of pH calculated using two databases. With Phase2-TDB, Th(OH)³⁺ appears as the predominant species at pH < 6.5, at the pH range 6.5 < pH < 8 the main aqueous species is Th(CO₃)₅⁶⁻ and at higher pH the dominant aqueous species is Th(OH)₃(CO₃)⁻. Using the YMP data0_ypf_R2 database, the predicted main aqueous species is Th(CO₃)₅⁶⁻.



Figure 15: Speciation Diagram for Thorium at $[Th]_T = 1 \cdot 10^{-9}$ m with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left), and Using YMP data0_ypf_R2 (Right)

Altmaier et al. (2006) studied thorium hydroxide solubility at ionic strength (I) = 4 m in a closed system at a total carbonate concentration of 0.02 m (NaHCO₃-Na₂CO₃-NaCl) and at the pH range of 8 to 11. Figure 16 shows the experimental data from Altmaier et al. (2006) modelled with Phase2-TDB (blue lines) and THEREDA (orange lines) respectively. The difference among the experimental and the calculated data provides an indication of the uncertainty encountered in this type of models.

Figure 17 shows the underlying speciation diagrams; the main difference is the slightly higher predominance of $Th(OH)_3CO_3^-$ when using Phase2-TDB.

Attempts to model the data using YMP data0_ypf_R2 database failed. The YMP data0_ypf_R2 database includes Th polynuclear species, and the stability constant associated to $Th(CO_3)_5^{6-}$ is two orders of magnitude higher than the one selected in THEREDA database. As a consequence, the calculated solubility resulted in excessively high thorium dissolved concentrations, corroborating the need to i) exclude the polymeric species and, ii) to select the thorium carbonate species from THEREDA database in Phase2-TDB.



Figure 16: Solubility of Thorium Hydroxide at I = 4 m and $[C]_T = 0.02$ m (NaHCO₃⁻ Na₂CO₃-NaCI). Symbols: Experimental Data from Altmaier et al. (2006). Lines: Calculated Using Phase2-TDB (Blue Lines) or THEREDA (Orange Line)



Figure 17: Calculated Underlying Speciation for Thorium Hydroxide as in Table 23 Calculated Using Phase2-TDB (Left) or THEREDA (Right)

Further discussion on the role of $An(CO_3)_5^{6-}$ species is provided in Section 2.30.

2.28 U

THEREDA database contains a more updated data set for uranium than YMP data0_ypf_R2. Furthermore, recent works (e.g., Vercouter et al. 2015) indicate that alkaline earth ternary carbonate species of uranyl (and especially Ca(II)-U(VI)-CO₃ species) have to be taken into account in calculations relevant for clay conditions. Thus, the following modifications were performed to Phase2-TDB:

- The complete set of data (stability constants and consistent Pitzer parameters) from THEREDA for uranium aqueous species were selected.
- Thermodynamic data for the aqueous species: Ca₂UO₂(CO₃)₃ and CaUO₂(CO₃)₃⁻², from ThermoChimie v10a, were included in Phase2-TDB.
- The solid uranium phases included in YMP data0_ypf_R2 database were kept but their stability constants were changed for those from THEREDA.

Figure 18 shows uranium speciation diagram at Eh = -0.15 V as a function of pH, calculated using the Phase2-TDB (left) and YMP database data0_ypf_R2 (right). The U(IV) highly charged species, $U(CO_3)_5^{6-}$, dominates the calculations performed with the Phase2-TDB at pH < 7.5. On the contrary, using the YMP data0_ypf_R2 database, the U(VI) species $UO_2(CO_3)_3^{4-}$ predominates in all the studied pH range.



Figure 18: Speciation Diagram for Uranium at $[U]_T = 1 \cdot 10^{-9}$ m and Eh = -0.15 V, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left) and Using YMP data0_ypf_R2 (Right)

Figure 19 shows a similar uranium speciation diagram at Eh = -0.36 V. The U(IV) highly charged species $U(CO_3)_5^{6-}$ dominates the aqueous chemistry in the calculations performed with the Phase2-TDB. On the contrary, using the YMP data0_ypf_R2 database, U(IV) aqueous hydroxides and the U(VI) highly charged polymeric species $(UO_2)_3(CO_3)_6^{6-}$ are formed.

Further discussion on the role of $An(CO_3)_5^{6-}$ species is provided in Section 2.30.



Figure 19: Speciation Diagram for Uranium at $[U]_T = 1 \cdot 10^{-9}$ m and Eh = -0.36 V, with the Groundwater Composition of SR-290-PW, Using Phase2-TDB (Left) and Using YMP data0_ypf_R2 (Right)

2.29 ZR

Zirconium is not included in YMP data0_ypf_R2 database, neither in THEREDA. Data selection including Pitzer coefficients has not been identified in open literature.

ThermoChimie contains a thermodynamic data selection for most relevant zirconium aqueous species and solid compounds, including stability constants for zirconium hydroxides (Brown et al. 2005). Those have been added to the Phase2-TDB.

2.30 HIGHLY CHARGED SPECIES An(CO₃)₅⁶⁻

Chemical properties of tetravalent radionuclides (Th(IV), U(IV), Np(IV), Pu(IV)) (for example stability constants, see Table 9) usually follow a trend with the ionic radii or other related properties of different ions (Table 10), being Th the most different in behaviour. Examples of those correlations are shown in Figure 20.

Table 9: An(IV)-OH-CO₃ Species and Associated Stability Constants in Phase2-TDB

		Lo	g K°	
Reaction	Th(IV)	U(IV)	Np(IV)	Pu(IV)
$An^{4+} + 3H_2O = An(OH)_3^+ + 3H^+$	-11.00	-4.70	-2.80	-2.30
$An^{4+} + 4H_2O = An(OH)_4(aq) + 4H^+$	-17.50	-10.00	-8.30	-8.50
$An^{4+} + 5CO_3^{2-} = An(CO_3)_5^{6-}$	29.10	32.35	35.61	35.65
$An^{4+} + 2H_2O + 2CO_3^{2-} = An(OH)_2(CO_3)_2^{2-} + 2H^+$	-	14.36	16.95	18.24
$An^{4+} + 3H_2O + CO_3^{2-} = An(OH)_3(CO_3)^- + 3H^+$	-1.72	-	-	-

Table 10: Comparison Among Distance Between the Center of the Metal and Coordinated Water (d_{M-OH2}), Effective Ionic Radius (r_m), and Crystal Radius (at Coordination Number of 9) for Tetravalent Actinides (from Neck and Kim 1999)

Actinide	d _{м-он2} (Å)	r _м (Å)	Crystal radius (Å)
Th ⁴⁺	2.46 ± 0.02	1.08 ± 0.02	1.09 (CN=9)
U ⁴⁺	2.42 ± 0.02	1.04 ± 0.02	1.05 (CN=9)
Np ⁴⁺	2.40 ± 0.01	1.02 ± 0.02	1.03 (CN=9)
Pu ⁴⁺	2.39 ± 0.01	1.01 ± 0.02	1.01 (CN=9)



Figure 20: Correlation Among An(OH)₄(aq) (Left) or An(CO₃)₅⁶⁻ (Right) Stability Constants (log K°) and the Distance Between the Center of the Metal and Coordinated Water (d_{M-OH2})

The stability of the species $An(CO_3)_5^{6-}$ (An = U, Pu, Np and Th) have been studied by different authors. For example, both $Th(CO_3)_5^{6-}$ and $Th(OH)_3CO_3^{--}$ were considered in the solubility calculations of microcrystalline ThO_2 under 10%-100% CO₂ partial pressures (Östhols et al. 1994). The dissociation of the complex $U(CO_3)_5^{6-}$ to $U(CO_3)_4^{4-}$ was studied by Bruno et al. (1989) using spectroscopy under 1, 10, 50 and 100% CO₂ partial pressures. The structures of $An(CO_3)_5^{6-}$ have been defined by spectroscopic measurements (Clark et al. 1998; Capdevila et al. 1996; Rai et al. 1994; Rai et al. 1999a; Rai et al. 1999b; Bruno et al. 1989; Felmy et al. 1997). $Th(CO_3)_5^{6-}$ and $Th(OH)_3CO_3^{--}$ were also identified by X-ray adsorption spectroscopy by Felmy et al. (1997). Thus, the existence of these species seems to be confirmed, and their associated stability constants seem reliable.

However, the evaluation of the role of the species $An(CO_3)_5^{6-}$ in a complex, highly concentrated media is challenging. Highly-charged species such as $An(CO_3)_5^{6-}$ will interact strongly with their environment, and the inclusion of Pitzer mixing terms θ ($An(CO_3)_5^{6-}/CI^-$) and Ψ ($An(CO_3)_5^{6-}/CI^-$ /Na⁺) can be very important in order to predict aqueous thermodynamics (Felmy and Rai 1999). Unfortunately, these values are hardly available, except for Th(IV) (see Table 11); and the extrapolation of this information to other tetravalent elements is problematic, as Th is the most different one in ionic radii and in the chemical behaviour.

	Th(IV)	U(IV)	Np(IV)	Pu(IV)
β⁽⁰⁾ (An(CO ₃) ₅ ⁶⁻ /Na ⁺)	1.31	1.5	1.5	1.5
β ⁽¹⁾ (An(CO ₃) ₅ ⁶⁻ /Na ⁺)	30	31.3	31.3	31.3
β⁽²⁾ (An(CO ₃)₅ ⁶⁻ /Na⁺)	0	0	0	0
C ^ϕ (An(CO ₃) ₅ ⁶⁻ /Na ⁺)	0	0	0	0
θ (An(CO ₃) ₅ ⁶⁻ /Cl ⁻)	1.8	-	-	-
Ψ (An(CO ₃) ₅ ⁶⁻ /Cl ⁻ /Na ⁺)	0.3	-	-	-

Table 11: Pitzer Coefficients for An(CO₃)₅⁶⁻ Species Included in Phase2-TDB. Values Have Been Obtained from THEREDA

Thus, the role of these species in concentrated systems with limited carbonate concentration (Sections 2.13, 2.17, 2.27 and 2.28 above) may be overestimated. An evaluation of the uncertainty related to the formation of $An(CO_3)_5^{6-}$ and their effects in solubility calculations is provided in Section 4.

3. EFFECT OF THE NEAR FIELD ON SR-290-PW GROUNDWATER COMPOSITION

PhreeqC/PhreeqCl Interactive version 3.6.2 (released on January 28, 2020) (Parkhurst and Appelo 2013) has been used to calculate the influence of steel corrosion and the influence of steel corrosion and bentonite in the different scenarios. The database used is the "Phase2-TDB" described in Section 2.

Sulphide and phosphate concentrations in the reference water are below the detection limit and will not be considered in the base case calculations for the groundwater composition in the different scenarios. Furthermore, it has been assumed that sulphate to sulphide reduction does not occur; this phenomenon is expected to be microbiologically mediated (Abrahamsen-Mills and Small 2019) and the microbial activity has not been considered in this study. The reduction of carbonate to methane and the reduction of nitrate to ammonium or $N_2(g)$ have also been neglected.

Details for the different scenarios are provided in the following sections.

3.1 SCENARIO 1

In Scenario 1, groundwater (SR-290-PW) enters the canister without interacting with the bentonite buffer or the canister materials.

In this Scenario, the water composition is the same as the initial SR-290-PW (see Table 1). It has been verified that all relevant solid phases are under saturated as it is shown in Figure 21. This is in agreement with the porewater characteristics described in Raven et al. (2011).



Figure 21: Saturation Index of the Most Relevant Solid Phases under SR-290-PW Groundwater Conditions

Note that sulphide, phosphate or organics compounds, whose concentrations in the initial groundwater composition are not available, have not been included in the calculations.

3.2 SCENARIO 2

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

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 chloride concentration of the system. To evaluate the uncertainty associated to those parameters, and based on the results of literature research, the corrosion rates presented below have been used in the calculations:

- The aerobic corrosion rate selected in all calculations is 2 μm·y⁻² as reported in King (2007) (NWMO TR-2007-01).
- For the anaerobic corrosion rate, and to evaluate if this parameter has a significant influence in the results of the calculations, three different values have been considered:
 - A reference value of 2 µm·y⁻¹, which is the reference corrosion rate for carbon steel corrosion at pH < 10.5 reported in Diomidis (2014). This is similar to the value of 1 µm·y⁻¹, the mean corrosion rate for Base Case simulations in King and Kolar (2012) (NWMO TR-2012-07).
 - A high corrosion rate of 5 μm·y⁻¹, as reported in Diomidis (2014) for pH < 10.5. The high corrosion rate reported in King and Kolar (2012) (NWMO TR-2012-07) is also 5 μm·y⁻¹.
 - For the sake of conservativism, the low corrosion rate used in Phase 1 of the project (0.005 μ m·y⁻¹, from Smart and Hochs 2006) has been increase to 0.1 μ m·y⁻¹ (minimum corrosion rate reported in Diomidis (2014) for pH < 10.5).

Notice that, according to Diomidis (2014), the corrosion rate is mostly independent on the chloride concentration.

To perform the calculations at 25°C, we have scaled the corrosion values described above by a factor of 1.14 (aerobic corrosion) and by a factor of 0.69 (anaerobic corrosion) (Smart and Hoch 2010).

Due to the input characteristics of the geochemical code PhreeqC/PhreeqCl (Parkhurst and Appelo 2013), the C-steel corrosion rate in $\mu m \cdot y^{-1}$ must be converted to mol(Fe)·m⁻²·s⁻¹. A C-steel density of 7860 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 calculations². By considering the porosity of the bentonite (38.2%) and the total amount of bentonite in the buffer box² (2.3085 m³), 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.

It has been assumed that the initial amount of steel in the media is sufficiently high not to be exhausted in any case.

The generation of hydrogen shown in Reaction 1 is important to consider; the final composition of the groundwater retained for the solubility calculation is set to achieve a maximum hydrogen pressure. Two different limiting hydrogen pressures² have been used in the calculations, as follows:

- 2.7 MPa, corresponding to the nominal swelling pressure of Highly Compacted Bentonite, HCB, at saturation within the Buffer Box; and
- 1.4 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 12 and Figure 22.

	Case 1 SC2 Base Case	Case 2	Case 3	Case 4	Case 5	Case 6
Temperature (°C)	25	25	25	25	25	25
Aerobic corrosion rate*	2 µm⋅y⁻¹ (x 1.14)	2 µm⋅y⁻¹ (x 1.14)	2 µm⋅y⁻¹ (x 1.14)	2 µm⋅y⁻¹ (x 1.14)	2 µm₊y⁻¹ (x 1.14)	2 µm⋅y⁻¹ (x 1.14)
Anaerobic corrosion rate*	2 µm⋅y⁻¹ (x 0.69)	2 µm₊y⁻¹ (x 0.69)	5 µm₊y⁻¹ (x 0.69)	5 µm∙y⁻¹ (x 0.69)	0.1 µm₊y⁻¹ (x 0.69)	0.1 µm∙y⁻¹ (x 0.69)
Steel surface area exposed to corrosion	0.02 m ^{2.} dm ⁻³					
Maximum H₂(g) pressure	2.7 MPa	1.4 MPa	2.7 MPa	1.4 MPa	2.7 MPa	1.4 MPa

Table 12: Parameters Used for the Different Cases in Scenario 2. First Colum (Case 1in Green) Indicates the Base Case

* Must be converted to $mol(Fe) \cdot m^2 \cdot s^{-1}$ for PhreeqC/PhreeqCI calculations.

² Indicated by NWMO



Figure 22: Summary of the Different Cases Evaluated for Scenario 2. Cases with the Same Colour Provide Exactly the Same Results

The parameters in Table 12 have been used to obtain the calculated groundwater composition for Scenario 2. Detailed analysis of the results indicates that calculated groundwater compositions are very similar for all cases. Cases with the same colour in Figure 22 provide the same results. The only parameter having a small influence on the simulated groundwater composition is the maximum hydrogen pressure (2.7 MPa or 1.4 MPa) 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, as summarized in Table 13.

	SCENARI	0 2
	2.7 MPa (SC2 Base Case)	1.4 MPa
Temperature	25°C	25°C
рН	7.82	7.78
ре	-8.54	-8.35
Solutes (m)		
Na	2.51	2.51
K	0.25	0.25
Ca	1.17	1.17
Mg	0.34	0.34
HČO₃	2.46·10⁻⁵	2.60·10 ⁻⁵
SO ₄	3.10·10 ⁻³	3.10·10 ⁻³
CI	5.54	5.54
Br	3.20·10 ⁻²	3.20·10 ⁻²
Li	1.48·10 ⁻³	1.48·10 ⁻³
Sr	1.40·10 ⁻²	1.40·10 ⁻²
F	2.00·10 ⁻⁵	2.00·10 ⁻⁵
I	1.20·10 ⁻⁴	1.20·10 ⁻⁴
В	1.65·10 ⁻²	1.65·10 ⁻²
Si	2.30·10 ⁻⁵	2.30·10 ⁻⁵
Fe	6.66·10 ⁻³	6.49·10 ⁻³

Table 13: SCENARIO 2: Groundwater Composition after Interaction with C-Steel Container

The comparison of Scenario 1 groundwater (Table 1) and Scenario 2 groundwater (Table 13) indicates that the interaction with C-steel and its corresponding corrosion products increases the alkalinity and the reducing character of the groundwater.

The groundwater composition summarized in Table 13 and labeled as Base Case will be used in the solubility calculations under Scenario 2 conditions (see Section 4).

3.3 SCENARIO 3

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

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 2004) has been used in the calculations in the present work and is reported in Table 14.

Table 14: Mineralogical Composition of the Clay Fraction of Bentonite MX-80, from SKB (2004)

	Mineral (wt%)
Montmorillonite	87 ± 3*
Quartz	3.0 ± 0.5
Cristobalite	2.0 ± 0.5
Mica	4 ± 1
Albite	3 ± 1
Anortoclasse	0 ± 1
Calcite+siderite	0 ± 1
Pyrite	0.07 ± 0.05
Gypsum	0.7 ± 0.2

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

Details on how bentonite mineralogical composition has been handled in the calculations are provided below and summarized in Table 15.

The main component of bentonite is montmorillonite. However, its dissolution rate is very low under near neutral pH (Cama et al. 2000) so that, it has been considered that montmorillonite dissolution is a minor process that will hardly affect the geochemical evolution of the system. Therefore, montmorillonite dissolution has not been explicitly included in the calculations.

It has not been distinguished between cristobalite and quartz in the calculations. Groundwater compositions are equilibrated with 5 wt% of SiO_2 (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 (2004), 0.7 wt% of calcite and 0.7 wt% of siderite have been considered in the calculations. The inclusion of those carbonates is done 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 $CaSO_4 \cdot 2H_2O$ (gypsum) has been considered in the 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) (Eq. 3).

$$\begin{aligned} & \mathsf{FeS}_2(\mathsf{s}) + 3.75\mathsf{O}_2(\mathsf{g}) + 3.5\mathsf{H}_2\mathsf{O} \leftrightarrow \mathsf{Fe}(\mathsf{OH})_3(\mathsf{s}) + 2\mathsf{SO}_4^{2^*} + 4\mathsf{H}^+ & \mathsf{Reaction} \ \mathbf{2} \\ & R_{py} \left(mol \cdot m^{-2} \cdot s^{-1} \right) = 10^{-8.19(\pm 0.10)} \frac{[O_2(aq)]^{0.50(\pm 0.04)}}{[H^+]^{0.11(\pm 0.01)}} & \mathsf{Eq. 3} \end{aligned}$$

To obtain the moles of mineral per dm³ shown in Table 15, two different cases have been considered³:

- Scenario 3 Case A corresponds to porosity of 38.2% and density of 1700 kg·m⁻³.
- 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, ferrihydrite, magnetite) have been allowed to precipitate if oversaturated.

Table 15: 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.

³ The porosity and density data were indicated by NWMO

$>$ sOH + H ⁺ \leftrightarrow $>$ sOH ₂ ⁺	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 (listed in Table 16) from the analyses of batch titration experiments on dispersed systems. 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.

Table 16: 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

			Site ca			
Surface	Log <i>K</i>	Cas	Case A		Case 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 _{W1} OH \leftrightarrow $>$ s _{W1} O ⁻ + H ⁺	-7.9					
s _{W2} OH		4.00·10 ⁻²	0.15	4.00·10 ⁻²	0.13	
$>$ SW2OH + H ⁺ \leftrightarrow $>$ SW2OH ₂ ⁺	6.0					
$>$ s _{W2} OH \leftrightarrow $>$ s _{W2} O ⁻ + H ⁺	-10.5					

The cation exchange capacity of the MX-80 bentonite used in Duro et al. (2010) (from SKB (2004)) reported in Table 17 has been used in the calculations. The values agree with the values suggested in NWMO-TR-2019-07 (Dixon 2019), which 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.

Selectivity exchange coefficients for cation exchange reactions (**Error! Reference source not found.**, **Error! Reference source not found.** and **Error! Reference source not found.**) have also been selected from Bradbury and Baeyens (2002). Partial substitution of interlayer major cations by Fe²⁺ in montmorillonite would also be expected, according to **Error! Reference source not found.**. We have used an average value of 0.4 (Charlet and Tournassat 2005).

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

Table 17: Initial Exchange Composition of MX-80 Bentonite (meq-100 g⁻¹) 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

CEC (meq⋅100 g ⁻¹)	Dixon (2019)* >75	SKB (2004) 75±2		
	meq ·100 g ⁻¹	meq ∙100 g ⁻¹	Case A mol⋅dm ⁻³	Case B mol·dm ⁻³
NaX	>50	54	2.09	1.80
KX		1.5	0.058	0.050
MgX ₂	<6	6	0.116	0.100
CaX ₂	<15	13.5	0.261	0.225
FeX ₂		0	0	0

* Provided for comparison purposes only

C-steel corrosion processes (see Section 3.2) have also been included in the calculations; the parameters are summarized in Table 18.

Table 18: C-steel Corrosion Parameters Used for Two 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	25	25
Aerobic corrosion rate*	2 µm₊y⁻¹ (x 1.14)	2 µm₊y⁻¹ (x 1.14)
Anaerobic corrosion rate*	2 µm₊y⁻¹ (x 0.69)	2 µm₊y⁻¹ (x 0.69)
Steel surface area exposed to corrosion	0.01 m ^{2.} dm ⁻³	0.01 m ^{2.} dm ⁻³
Maximum H₂(g) pressure	2.7 MPa	1.4 MPa

* Must be converted to mol(Fe)·m²·s⁻¹ for PhreeqC/ PhreeqCl calculations

As a result of the different conditions and parameters described above, two different cases summarized in Figure 23 have been calculated; the corresponding groundwater compositions are summarized in Table 19.

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. Results for Scenario 3 - Case

A (green squares in Figure 23) will be used in the solubility calculations under Scenario 3 conditions (see Section 4).



Figure 23: Summary of the Different Cases Evaluated for Scenario 3

Table 19: SCENARIO 3: Groundwater Composition 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

	SCENARIO 3		
	2.7 MPa	1.4 MPa	
	(Case A)	(Case B)	
Temperature	25°C	25°C	
рН	7.17	7.12	
ре	-7.88	-7.69	
Solutes (m)			
Na	2.63	2.63	
K	0.08	0.08	
Ca	1.10	1.09	
Mg	0.37	0.37	
HCO ₃	9.09·10 ⁻⁵	9.87·10 ⁻⁵	
SO ₄	5.27·10 ⁻³	5.27·10 ⁻³	
CI	5.54	5.54	
Br	3.20·10 ⁻²	3.20·10 ⁻²	
Li	1.48⋅10 ⁻³	1.48⋅10 ⁻³	
Sr	1.40·10 ⁻²	1.40·10 ⁻²	
F	2.00·10 ⁻⁵	2.00·10 ⁻⁵	
I	1.20·10 ⁻⁴	1.20·10 ⁻⁴	
В	1.65·10 ⁻²	1.65·10 ⁻²	
Si	1.62·10 ⁻⁴ 1.62·10 ⁻⁴		
Fe	1.31·10 ⁻¹ 1.31·10 ⁻¹		

The comparison of results obtained in Scenario 3 (Table 19, effect of both bentonite and C-Steel corrosion) with those obtained in Scenario 2 (Table 13, effect of steel corrosion only) indicate that in the concentrated groundwater studied, the bentonite effect results in a small pH decrease. The groundwater composition of the exchangeable cations (and related elements) is also affected.

3.4 SUMMARY

The groundwater composition under Scenario 1, Scenario 2 and Scenario 3 conditions has been assessed; Table 20 shows a summary of the groundwater compositions in the different scenarios. Those compositions will be used in the solubility assessment presented in the following section.

		SCENADIO 2	
	SCLIVARIO I	2 7 MPa (SC2 Base Case)	$27 \text{ MPa} (Case \Delta)$
Temperature		25°C	25°C
nH	55	7 82	23 0
ne	-3 30	-8 54	-7.88
Solutes (m)	-0.00	-0.04	-7.00
Na	2.51	2.51	2.63
K	0.25	0.25	0.08
Ca	1.17	1.17	1.10
Mg	0.34	0.34	0.37
HČO₃	3.00·10 ⁻⁴	2.46·10 ⁻⁵	9.09·10 ⁻⁵
SO ₄	3.10⋅10 ⁻³	3.10·10 ⁻³	5.27·10 ⁻³
CI	5.53	5.54	5.54
Br	3.20·10 ⁻²	3.20·10 ⁻²	3.20·10 ⁻²
Li	1.48⋅10 ⁻³	1.48·10 ⁻³	1.48·10 ⁻³
Sr	1.40·10 ⁻²	1.40·10 ⁻²	1.40·10 ⁻²
F	2.00·10 ⁻⁵	2.00·10 ⁻⁵	2.00·10 ⁻⁵
I	1.20·10 ⁻⁴	1.20.10-4	1.20·10 ⁻⁴
В	1.65·10 ⁻²	1.65·10 ⁻²	1.65·10 ⁻²
Si	2.30·10 ⁻⁵	2.30·10 ⁻⁵	1.62·10 ⁻⁴
Fe	1.00·10 ⁻⁴	6.66·10 ⁻³	1.31·10 ⁻¹

Table 20: Groundwater Compositions in Scenario 1, 2 and 3

4. RADIONUCLIDE SOLUBILITY CALCULATIONS

The approach followed to calculate radionuclides solubility is as follows:

- i. Selection of the solid phase most likely to precipitate in the studied system at each Scenario. In general, this selection is mainly based on 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.
- ii. The aqueous concentration of the element studied is given by equilibrium with the selected solid phase and the porewater composition. Thus, both the aqueous concentration of the element in equilibrium with the solid phase (solubility) and the corresponding aqueous speciation (concentration of all the individual species that summed up give the total aqueous concentration of the element of interest, i.e., the solubility) are calculated.

When the calculated total aqueous element concentration in equilibrium with the studied solid is higher than 10^{-2} m, we consider that the element is not solubility limited (n.s.l.).

Sulphide and phosphate concentrations in the reference water are below the detection limit and will not be considered in the base case calculations. However, an upper limit concentration of $1.6 \cdot 10^{-5}$ m (for sulphide) and $1 \cdot 10^{-6}$ m (for phosphate) will be used in sensitivity cases (Section 4.2) to assess the uncertainty related to the presence of these elements in solubility calculations.

PhreeqC/PhreeqCl Interactive version 3.6.2 (released on January 28, 2020) (Parkhurst and Appelo 2013) has been used to perform the solubility calculations. Some supporting calculations have also been performed with GibbsStudio version 3.1 (*https://gibbsstudio.io*) and Spana (Chemical Equilibrium Diagrams, *https://github.com/ignasi-p/eq-diagr*) program version 2020-Feb-05.

PhreeqC calculations are run in mol·kg_w⁻¹ (molality, m, mols of substance dissolved in the water solvent). Molality can be related to molarity (concentration, M, mols of substance dissolved in the solution volume) using density.

The main database used in the calculations is Phase2-TDB, as described in Section 2. Two additional databases are used for comparison purposes, THEREDA and the Modified ThermoChimie database (see Section 2).

Results of the solubility calculations are provided below. For each element, the following information is included:

- Information about the element that can be relevant for the solubility assessment, including main oxidation states, ligands mostly affecting its chemistry and availability of Pitzer parameters for aqueous species relevant under the studied conditions.
- The calculated solubility and associated speciation at each Scenario using Phase2-TDB, in the form of tables, and the associated discussion. If the element is not solubility

limited, the speciation has been calculated assuming a concentration of 10⁻⁶ m of the studied element in solution.

- In some cases, solubility and speciation calculated with additional databases are also
 presented to facilitate the discussion and indicate strengths and limitations of the
 approach used.
- A semi-quantitative analysis of the uncertainties affecting solubility calculations (for example, coprecipitation or lack of appropriate Pitzer parameters). For some relevant cases (i.e., tetravalent radionuclides), the discussion is reinforced with comparison with the results obtained with different databases, as described above.

4.1 SOLUBILITY CALCULATION RESULTS

4.1.1 Ag

Silver is a metallic element that under the conditions studied in the present work will only be in the oxidation state +I. It is expected that its aqueous chemistry will be mainly driven by complexation against soft ligands such as halides, carbonate or sulfate.

Complexation with chlorine will be of utmost importance in the saline groundwaters of interest in present work. Figure 24 shows AgCl(cr) solubility in a simplified NaCl solution. As seen in the figure, an increase of chloride concentration from 0.01 m to 10 m increases AgCl(cr) solubility of about six orders of magnitude; at chlorine concentration higher than 0.3 m, AgCl₄³⁻ dominates the aqueous silver chemistry.



Figure 24: AgCl(cr) Solubility (Solid Black Line) and Underlying Aqueous Ag Speciation (Dashed Lines) in NaCl Solution as a Function of Chloride Concentration, pH = 5.5. Vertical Dotted Line Indicates [Cl]_T = 5.5 m, as Expected in the Studied Porewater (Table 1)

4.1.1.1 Ag Solubility in Scenario 1

In Scenario 1 conditions, Ag is not solubility limited (n.s.l.). AgCl(cr) has a high solubility due to the formation of aqueous Ag chlorides in solution (Table 21). The aqueous chemistry of silver will be governed by chlorine complexation, $AgCl_4^{3-}$ being the only predominant species (Table 22).

Table 21: Silver Solid Phase and Concentration under Scenario 1 Conditions

	Scenario 1
Solid phase	Concentration (m)
AgCI(cr)	n.s.l.

Table 22: Silver Speciation under Scenario 1 Conditions

	Scena	ario 1
Solid phase	Speci	ation
AgCI(cr) (n.s.l.)	AgCl ₄ ³⁻	100%
Creation colordated	a a sumain as 10-6 ma of 1 a	

Speciation calculated assuming 10-6 m of Ag

4.1.1.2 Ag Solubility in Scenario 2

In Scenario 2 conditions, same as Scenario 1, AgCl(cr) has a high solubility due to the formation of aqueous Ag chlorides in solution and Ag is not solubility limited (Table 23). The aqueous chemistry of silver will be governed by chlorine complexation, being $AgCl_4^{3-}$ the predominant species (Table 24).

Table 23: Silver Solid Phase and Concentration under Scenario 2 Conditions

	Scenario 2
Solid phase	Concentration (m)
AgCl(cr)	n.s.l.

Table 24: Silver Speciation under Scenario 2 Conditions

	Scen	ario 1
Solid phase	Spec	iation
AgCI(cr) (n.s.l.)	AgCl ₄ ³⁻	100%
	1 100 54	

Speciation calculated assuming 10⁻⁶ m of Ag

4.1.1.3 Ag Solubility in Scenario 3

In Scenario 3 conditions, same as Scenario 1 and Scenario 2, AgCl(cr) has a high solubility due to the formation of aqueous Ag chlorides in solution and Ag is not solubility limited (Table 25).

The aqueous chemistry of silver will be governed by chlorine complexation being AgCl₄³⁻ the predominant species (Table 26).

Table 25: Silver Solid Phase and Concentration under Scenario 3 Conditions

	Scenario 3
Solid phase	Concentration (m)
AgCl(cr)	n.s.l.

Table 26: Silver Speciation under Scenario 3 Conditions

	Scena	ario 1
Solid phase	Speci	ation
AgCl(cr) (n.s.l.)	AgCl ₄ ³⁻	100%
Creation colordated	a a unain a 10-6 m of A a	

Speciation calculated assuming 10⁻⁶ m of Ag

4.1.1.4 Uncertainties

Ag solubility limits is directly related to the chloride concentration in the system; an increase in chloride groundwater concentration results in an increase in Ag solubility (see Figure 24).

An additional uncertainty for the solubility of silver is the content of sulphides in groundwater and the possible formation of Ag-sulphide solid phases. The formation of such phases will decrease the aqueous concentration of Ag in the system compared to the solubility control exerted by AgCl(cr) (see discussion in Section 4.2.1).

4.1.2 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 groundwater 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 or hydroxides, may exert a solubility control of Am. The solids considered in the present evaluation include $AmOHCO_3(s)$, $Am_2(CO_3)_3(s)$, $Am(OH)_3(s)$ and $Am(OH)_3(am)$; very crystalline solids or significantly soluble ones have not been evaluated.

4.1.2.1 Am Solubility in Scenario 1

The amorphous hydroxycarbonate phase $AmOHCO_3(s)$ seems to be the most likely solid to exert the solubility control of americium; calculated aqueous concentrations are shown in Table 27. The calculated speciation using Phase2-TDB is shown in Table 28. Am^{3+} is the main aqueous species.

Table 27: Americium Solid Phase and Concentration under	Scenario 1	Conditions

	Scenario 1	
Solid phase	Concentration (m)	
AmOHCO ₃ (s)	3.50·10 ⁻³	

Table 28: Americium Speciation under Scenario 1 Conditions

	Scena	rio 1
Solid phase	Specia	ntion
-	Am ³⁺	87%
AmOHCO ₃ (s)	Am(OH) ²⁺	5%
	AmCl ²⁺	3%
	Am(SO ₄)+	2%

The calculations obtained with Phase2-TDB have been compared with those obtained with THEREDA; both databases use the Pitzer approach and provide similar solubility and speciation results (Table 29).

AmOHCO₃(s) Scenario 1 Phase 2-TDB THEREDA (Pitzer) (Pitzer) Concentration (m) 3.50.10-3 7.62.10-3 Am³⁺⁻ Am³⁺⁻ 87% 82% Am(OH)2+ 5% Am(OH)2+ 8% AmCl²⁺ AmCl²⁺ Speciation 3% 4%

2%

1%

Am(SO₄)⁺

Am(CO₃)+

3%

3%

Am(SO₄)+

Am(CO₃)+

Table 29: Comparison of Calculated AmOHCO₃(s) Solubilities and Speciation with Different Databases under Scenario 1 Conditions

4.1.2.2 Am Solubility in Scenario 2

The pH of groundwater in Scenario 2 (pH = 7.82) is higher than that in Scenario 1 (pH = 5.5). Due to the pH increase, the hydroxycarbonate phase, $AmOHCO_3(s)$, or the hydroxide solid phases $Am(OH)_3(s)$ or $Am(OH)_3(am)$ may form. The more crystalline $Am(OH)_3(s)$ phase is likely to control the solubility of Am (in bold in Table 30); value for $AmOHCO_3(s)$ represents a more conservative approach.

As a result of the pH increase, Am hydrolysis species are predominant in Scenario 2 (Table 31) (more than in Scenario 1).

	Scenario 2
Solid phase	Concentration (m)
AmOHCO₃(s)	4.76.10-4
Am(OH)₃(s)	8.43·10 ⁻⁷
Am(OH)₃(am)	2.44·10 ⁻⁴

 Table 30: Americium Solid Phases and Concentrations under Scenario 2 Conditions.

 The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Table 31: Americium Speciation under Scenario 2 Conditions

	Scenari	o 2
Solid phase	Speciat	ion
$\Lambda m(OU)_{2}(a)$	Am(OH) ₂ +	96%
AIII(OH)3(S)	Am(OH) ²⁺	3%

4.1.2.3 Am Solubility in Scenario 3

The pH of groundwater in Scenario 3 (pH = 7.17) is slightly lower than that in Scenario 2 (pH = 7.82). Same as Scenario 2, assuming that the more crystalline $Am(OH)_3(s)$ phase (in bold in Table 32) is likely to control the solubility of Am represents a more realistic approach; results for $Am(OH)_3(am)$ are more conservative. Am hydrolysis species $Am(OH)_2^+$ and $Am(OH)^{2+}$ are expected to control aqueous speciation (Table 33).

Table 32: Americium Solid Phases and Concentrations under Scenario 3 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

	Scenario 3	
Solid phase	Concentration (m)	
AmOHCO ₃ (s)	1.19.10-4	
Am(OH)₃(s)	4.52·10 ⁻⁶	
Am(OH)₃(am)	1.30·10 ⁻³	

Table 33: Americium Speciati	on under Scenario	3 Conditions
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	Scena	ario 3
Solid phase	Speciation	
-	Am(OH) ₂ +	80%
Am(OH)₃(s)	Am(OH) ²⁺	13%
	Am ³⁺	5%
	AmF ²⁺	1%

4.1.2.4 Uncertainties

One of the main uncertainties affecting the americium solubility and speciation is the effect of the groundwater phosphate concentration and the possible formation of Am-phosphate solids; this is discussed in Section 4.2.2.

The second uncertainty is caused by the presence of boron in the groundwater. Boron may form complexes with trivalent lanthanides and actinides (e.g., Borkowski et al. 2010; Hinz et al. 2015). However, the stoichiometry of these complexes and their associated stability constants are uncertain and cannot be included in the Pitzer database.

Finally, the high ionic strength of the studied system introduces a certain degree of uncertainty. The free cation Am^{3+} has a relatively high charge, which will lead to significant interactions among Am^{3+} and anionic ligands such as Cl⁻ or SO₄²⁻. The impact of this uncertainty in the calculations is minimized using the Pitzer approach, for which the associated Pitzer parameters are available in Phase2-TDB database (see Section 2).

4.1.3 Bi

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

4.1.3.1 Bi Solubility in Scenario 1

In Scenario 1 conditions, $Bi_2O_3(s)$ has a high solubility (> 10^{-1} m) due to the formation of aqueous Bi chlorides in solution and Bi is not solubility limited (Table 34). The aqueous chemistry of bismuth will be governed by chlorine complexation, $BiCl_6^{3-}$ being the predominant species (Table 35).

Table 34: Bismuth Solid Phase and Concentration under Scenario 1 Conditions

	Scenario 1	
Solid phase	Concentration (m)	
$Bi_2O_3(s)$	n.s.l.	

Table 35: Bismuth Speciation under Scenario 1 Conditions

	Scena	ario 1
Solid phase	Speci	ation
Bi ₂ O ₃ (s) (n.s.l.)	BiCl ₆ ³⁻	100%
Speciation coloulated accuming 10 th m of Pi		

Speciation calculated assuming 10⁻⁶ m of Bi

4.1.3.2 Bi Solubility in Scenario 2

Under the studied conditions, bismuth is not affected by redox changes between Scenario 1 and Scenario 2. However, as a consequence of the pH increase, (pH = 5.5 in Scenario 1 and pH = 7.82 in Scenario 2), under Scenario 2 conditions, Bi₂O₃(s) solubility is lower (Table 36). The

aqueous chemistry of bismuth will be governed by chlorine complexation, $BiCl_6^{3-}$ being the main species in solution (Table 37).

Table 36: Bismuth Solid Phase and Concentration under Scenario 2 Conditions

	Scenario 2	
Solid phase	Concentration (m)	
Bi ₂ O ₃ (s)	1.62.10-4	

Table 37: Bismuth Speciation under Scenario 2 Conditions

	Scena	rio 2
Solid phase	Specia	ation
$\operatorname{Pi}_{-}(\mathbf{a})$	BiCl ₆ ³⁻	95%
DI2O3(5)	Bi(OH) ₃	5%

4.1.3.3 Bi Solubility in Scenario 3

Results calculated for Scenario 3 indicate that Bi solubility under those conditions is higher than 10^{-2} m (Table 38), BiCl₆³⁻ being the main species in solution (Table 39).

Table 38: Bismuth Solid Phase and Concentration under Scenario 3 Conditions

	Scenario 3
Solid phase	Concentration (m)
Bi ₂ O ₃ (s)	n.s.l.

Table 39: Bismuth Speciation under Scenario 3 Conditions

	Scen	ario 3
Solid phase	Spec	iation
Bi ₂ O ₃ (s) (n.s.l.)	BiCl ₆ ³⁻	100%
	1 100 5 5	

Speciation calculated assuming 10⁻⁶ m of Bi

4.1.3.4 Uncertainties

As discussed in Section 2, one of the biggest uncertainties related to Bi is the limited thermodynamic data available for this element.

The stability constants associated to $BiCl_5^{2-}$ and $BiCl_6^{3-}$ are only tentative (Lothenbach et al. 1999). Furthermore, BiOCI(s) may also form (Lothenbach et al. 1999) and could limit Bi solubility under the studied conditions. However, available thermodynamic data for this solid is uncertain and not consistent with the Bi-Cl aqueous speciation. This, and the lack of Pitzer parameters for the Bi-Cl system, are significant uncertainties affecting the results of the calculations at high chloride concentrations.

In addition, bismuth can 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 literature for bismuth sulphides. Consequently, the bismuth sulphide system is not included in Phase2-TDB (see Section 4.2.1).

4.1.4 C

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

4.1.4.1 C Solubility in Scenario 1

In Scenario 1, the carbon concentration is the same as in the SR-290-PW reference groundwater (see Table 20).

The original SR-290-PW composition (Table 1) was equilibrated with calcite $(CaCO_3(s))$ but using the Pitzer.dat database. When using Phase2-TDB, calcite is calculated to be slightly undersaturated, but still close to equilibrium. This agrees with the porewater characteristics described in Raven et al. (2011).

Carbon aqueous speciation is dominated by HCO_{3}^{-} , its complexation with Mg^{2+} (see Table 40) and the Pitzer interactions with Ca^{2+} .

	Scena	rio 1
Concentration (m)	Specia	ation
3.00.10-4	MgHCO₃⁺	83%
(Table 20)	HCO3 ⁻	11%
(Table 20)	CO ₂	5%

Table 40: Carbon Concentration and Speciation under Scenario 1 Conditions

4.1.4.2 C Solubility in Scenario 2

The carbon concentration in this Scenario is the one calculated for Scenario 2 conditions (see Table 20).

Groundwater interacts with the carbon-steel container prior to contacting the waste. The final carbon concentration of groundwater (Table 20) will be influenced by the pH increase (in comparison with Scenario 1) and with the possible precipitation of calcite or iron corrosion products such as siderite (FeCO₃(s)). Carbon aqueous speciation is dominated by interactions or complexation of HCO₃⁻ and CO₃²⁻ species with Mg²⁺ and Ca²⁺ (Table 41).

	Scer	nario 2
Concentration (m)	Spee	ciation
	MgHCO₃+	48%
	CaCO ₃	30%
2.46·10 ⁻⁵	MgCO ₃	7%
(Table 20)	HČO₃ ⁻	7%
	CO32-	7%
	FeCO ₃	1%

Table 41: Carbon Concentration and Speciation under Scenario 2 Conditions

4.1.4.3 C Solubility in Scenario 3

The carbon concentration in this scenario is the one calculated for Scenario 3 conditions (see Table 20).

C concentration and speciation is affected by the presence of bentonite (in comparison with Scenario 2), which causes changes in pH and changes in calcium aqueous concentration due to the effect of the bentonite exchanger. Carbon aqueous speciation is dominated by HCO_3^- and $CO_3^{2^-}$ species and its interactions or complexation with Mg^{2+} and Ca^{2+} (see Table 42).

Table 42: Carbon Concentration and Speciation under Scenario 3 Conditions

	Scenari	o 3
Concentration (m)	Speciat	ion
	MgHCO ₃ +	70%
	CaCO ₃	8%
9.09·10 ⁻⁵	HCO3 ⁻	8%
	FeCO ₃	7%
(Table 20)	CO32-	2%
	MgCO ₃	2%
	FeHCO ₃ -	2%

4.1.4.4 Uncertainties

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

4.1.5 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.

4.1.5.1 Ca Solubility in Scenario 1

In Scenario 1, the calcium concentration is the same as the concentration in the SR-290-PW reference groundwater (see Table 20).

The original SR-290-PW composition reported in Table 1 was equilibrated with calcite $(CaCO_3(s))$ and gypsum $(CaSO_4 \cdot 2H_2O(s))$ but using the Pitzer.dat database. When using Phase2-TDB, calcite and gypsum are calculated to be slightly undersaturated, but still very close to equilibrium (see Section 3.1). This agrees with the porewater characteristics described in Raven et al. (2011). Calcium aqueous speciation is dominated by the free Ca²⁺ ion (Table 43).

Table 43: Calcium Concentration and Speciation under Scenario 1 Conditions

	Scer	nario 1
Concentration (m)	Speciation	
1.17 (Table 20)	Ca ²⁺	100%

4.1.5.2 Ca Solubility in Scenario 2

In Scenario 2, groundwater interacts with the carbon-steel container prior to contacting the waste. Calcium is a non-redox sensitive element, so its concentration in Scenario 2 (Table 20) will not be influenced by Eh changes in groundwater produced by the steel canister corrosion. Taking into account the significant Ca concentration in the system, the influence of pH and carbonate concentration of the groundwater is also minor. Ca speciation is mainly driven by the free aqueous cation Ca²⁺ (Table 44).

Table 44: Calcium Concentration and Speciation under Scenario 2 Conditions

	Scer	nario 2
Concentration (m)	Speciation	
1.17 (Table 20)	Ca ²⁺	99%

4.1.5.3 Ca Solubility in Scenario 3

The calcium concentration in this Scenario is the one calculated for Scenario 3 conditions (see Table 20).

In Scenario 3, calcium concentration (Table 20) and speciation (Table 45) is slightly affected by the interaction with bentonite and the associated ion-exchange reactions. Ca speciation is mainly driven by the free aqueous cation Ca^{2+} (Table 45).

		Scenario 3
Concentration (m)		Speciation
1.10 (Table 20)	Ca ²⁺	99%

Table 45: Calcium Concentration and Speciation under Scenario 3 Conditions

4.1.5.4 Uncertainties

The calcium solubility and speciation behaviour in groundwaters will be affected by the pH of the groundwater and by the concentration of ligands produced from dissolution processes of main minerals, such as carbonate or sulphate.

4.1.6 Cd

Under environmental conditions cadmium will be found mainly as Cd(+II). The concentration of soft ligands such as halides, carbonate or sulphate will control the chemical behaviour of this element. The concentration of major cations (e.g., divalent elements) in groundwater may also influence on Cd chemistry due to ligand competition.

4.1.6.1 Cd Solubility in Scenario 1

In diluted groundwaters, $CdCO_3(s)$ is likely to control the Cd solubility (Colàs et al. 2021a). However, the solubility of this solid in the presence of high chloride concentrations will significantly increase (Figure 25). As a consequence, in the concentrated SR-290-PW groundwater under Scenario 1 conditions, Cd is expected to be not solubility limited (Table 46); the aqueous chemistry of cadmium will be governed by chlorine complexation, $CdCl_4^{2-}$ being the predominant species (Table 47).



Figure 25. Cd(CO₃)(s) Solubility (Solid Black Line) and Underlying Aqueous Cd Speciation (Dashed Lines) as a Function of Chloride Concentration under Scenario 1 Conditions. Vertical Dotted Line Indicates $[CI]_T = 5.5$ m, as Expected in the Porewater (Table 1)

Table 46: Cadmium Solid Phase and Concentration under Scenario 1 Conditions

	Scenario 1
Solid phase	Concentration (m)
CdCO ₃ (s)	n.s.l.

Scen	ario 1	
Speciation		
	99%	
	Scen Spec CdCl4 ²⁻	Scenario 1 Speciation CdCl4 ²⁻ 99%

Table 47: Cadmium Specia	tion under S	Scenario 1	Conditions
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Speciation calculated assuming 10⁻⁶ m of Cd

4.1.6.2 Cd Solubility in Scenario 2

Same as Scenario 1, under Scenario 2 conditions, cadmium is not solubility limited due to the formation of aqueous Cd chlorides (Table 48). Its aqueous chemistry will be governed by chlorine complexation with $CdCl_4^2$ being the predominant species (Table 49).
Table 48: Cadmium Solid Phase an	d Concentration under	Scenario 2 Conditions
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Scenario 2		
Solid phase Concentration (m)		
CdCO ₃ (s) n.s.l.		

Table 49: Cadmium Speciation under Scenario 2 Conditions

Scenario 2		
Solid phase		Speciation
$CdCO_{2}(a)$ $(a a b)$	CdCl ₄ ²⁻	99%
$Cucc_{3}(s)$ (ii.s.i.)	CdCl ₃ -	1%

Speciation calculated assuming 10⁻⁶ m of Cd

4.1.6.3 Cd Solubility in Scenario 3

As in the previous scenarios, under Scenario 3 conditions cadmium is not solubility limited (Table 50) and $CdCl_4^{2-}$ will be the predominant aqueous species (Table 51).

Table 50: Cadmium Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3		
Solid phase Concentration (m)		
CdCO ₃ (s) n.s.l.		

Table 51: Cadmium Speciation under Scenario 3 Conditions

Scenario 3		
Solid phase	Speci	iation
	CdCl ₄ ²⁻	99%
CaCO ₃ (s) (n.s.l.)	CdCl₃ ⁻	1%

Speciation calculated assuming 10⁻⁶ m of Cd

4.1.6.4 Uncertainties

Cd solubility limit is directly related to the chloride concentration in the system; as in the case of Ag (see Section 4.1.1), an increase in chloride groundwater concentration results in an increase in Cd solubility. The lack of Pitzer coefficients for aqueous cadmium species, and specially for the Cd-chloride complexes, is a limitation to obtain accurate results.

An additional uncertainty for cadmium is the content of sulphides in groundwater and the possible formation of Cd-sulphide solid phases. The formation of such phases will decrease the aqueous concentration of Cd in the system (see discussion in Section 4.2.1).

4.1.7 Cs

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

Cesium thermodynamic data selection in Phase2-TDB includes Cs^+ as the master species; Cs^+/Cl^- and Cs^+/SO_4^{2-} Pitzer coefficients are also included in the database.

4.1.7.1 Cs Solubility in Scenario 1

Cs is not solubility limited and no Cs solid is likely to be formed under the studied conditions (Table 52). The aqueous chemistry of caesium, calculated assuming a concentration of 10^{-6} m, will be governed by the free cation, Cs⁺ (Table 53).

Table 52: Cesium Solid Phase and Concentration under Scenario 1 Conditions

Scenario 1	
Solid phase Concentration (m)	
n.s.l. n.s.l.	

Table 53: Cesium Speciation under Scenario 1 Conditions

Scenario 1		
Solid phase	Speciation	
n.s.l.	Cs+	100%

Speciation calculated assuming 10⁻⁶ m of Cs

4.1.7.2 Cs Solubility in Scenario 2

As explained in Scenario 1, caesium is not expected to be solubility limited under Scenario 2 conditions (Table 54) and the free cation (Cs⁺) is the main species in groundwater solution (Table 55).

Table 54: Cesium Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2	
Solid phase Concentration (m)	
n.s.l.	n.s.l.

Table 55: Cesium Speciation under Scenario 2 Conditions

Scenario 2		
Solid phase	Spec	iation
n.s.l.	Cs⁺	100%
0	1 106 10	

Speciation calculated assuming 10⁻⁶ m of Cs

4.1.7.3 Cs Solubility in Scenario 3

Table 56 and Table 57 present the results of caesium solubility and speciation under Scenario 3 conditions. As in the case of Scenario 1 and Scenario 2, it is expected that Cs will not be solubility limited, Cs⁺ being the predominant aqueous species.

Table 56: Cesium Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3	
Solid phase Concentration (m)	
n.s.l.	n.s.l.

Table 57: Cesium Speciation under Scenario 3 Conditions

Scenario 3		
Solid phase	Spec	iation
n.s.l.	Cs+	100%
Speciation coloulated accuming 10-6 m of Co		

Speciation calculated assuming 10⁻⁶ m of Cs

4.1.7.4 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, in high ionic strength solutions, the presence of competing mono- and di-valent cations Na⁺, K⁺, Ca²⁺ or Mg²⁺ may affect Cs retention processes.

4.1.8 Cu

The current study assesses the solubility of copper, that is, the maximum concentration of copper in solution in case that it is limited by the formation of a solid phase under the conditions of interest. Therefore, it is not the intention of this work to assess the kinetic corrosion of copper, its passivation or other processes responsible for the copper loss in the media. For a complete discussion of the processes responsible for metal Cu corrosion under repository conditions, the reader is referred to Hall et al. (2021) and Keech et al. (2021).

4.1.8.1 Cu Solubility in Scenario 1

Scenario 1 assumes that groundwater contacts the waste with no previous interaction with the bentonite clay or steel container, which is extremely unlikely. Under these conditions, no solid phase able to limit the copper aqueous concentration below 10^{-2} m has been identified (Table 58). The aqueous chemistry of copper would be governed by Cu(I) chlorine complexation, CuCl₃²⁻ being the predominant species (Table 59).

Scenario 1	
Solid phase Concentration (m)	
Cu(cr)	n.s.l.

Table 58: Copper Solid Phase and Concentration under Scenario 1 Conditions

Table 59: Copper Speciation under	Scenario 1	Conditions
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Scenario 1			
Solid phase	Specia	ation	
Cu(ar)(n a l)	CuCl ₃ ²⁻	99%	
Cu(cr) (n.s.i.)	CuCl ₂ -	1%	

Speciation calculated assuming 10⁻⁶ m of Cu

4.1.8.2 Cu Solubility in Scenario 2

Copper is a redox sensitive element, so its solubility is affected by the change of the redox state of the system. Scenario 2 considers that groundwater has interacted with steel and, thereof, has been conditioned due to steel corrosion and formation of secondary corrosion products. This produces a decrease of the redox potential of groundwater and leads to a low solubility of copper, limited by equilibrium of Cu(cr) with the equilibrated groundwater (Table 60), CuCl₃²⁻ being the main aqueous species (Table 61). Figure 26 shows Cu(cr) solubility together with the underlying aqueous speciation under Scenario 2 conditions.



Figure 26: Cu(cr) Solubility (Solid Black Line) and Underlying Aqueous Cu Speciation (Dashed Lines) as a Function of Chloride Concentration at 25°C under Scenario 2 Conditions. Vertical Dotted Line indicates $[CI]_T = 5.5$ m, as expected in the Porewater (Table 20)

Table 60: Copper Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2			
Solid phase Concentration (m)			
Cu(cr)	1.88·10 ⁻⁸		

Table 61: Copper Speciation under Scenario 2 Conditions

	Scenario 2	
Solid phase	Spe	eciation
Cu(or)	CuCl ₃ ²⁻	99%
Cu(ci)	CuCl ₂ -	1%

4.1.8.3 Cu Solubility in Scenario 3

Similarly to what is observed in Scenario 2, the solubility of copper under Scenario 3 is limited by equilibration of the conditioned groundwater with Cu(cr) (Table 62), $CuCl_3^{2-}$ being the main aqueous species (Table 63).

Table 62: Copper Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3				
Solid phase Concentration (m)				
Cu(cr) 8.10.10 ⁻⁸				

Table 63: Copper Speciation under Scenario 3 Conditions

	Scenario 3	
Solid phase	Spe	eciation
Cu(or)	CuCl ₃ ²⁻	99%
Cu(cr)	CuCl ₂ -	1%

4.1.8.4 Uncertainties

In this study, we have assumed that sulphate to sulphide reduction does not occur as microbial activity is not considered. However, in the presence of sulphide, sulphide solid phases could be formed, modifying Cu solubility (see the discussion in Section 4.2.1).

Furthermore, phenomena such as passivation of metal, change in redox potential, kinetic effects for copper corrosion, etc. are not taken into account in the calculations.

4.1.9 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. Extensive details on how iron concentrations in the studied groundwaters are calculated can be found in Section 3.

4.1.9.1 Fe Solubility in Scenario 1

In Scenario 1, the iron concentration is the same as in concentration in the SR-290-PW reference groundwater (see Table 20). Iron phases as magnetite or siderite are calculated to be undersaturated under those conditions (Section 3.1 and Figure 27).



Figure 27. Eh vs pH Predominance Diagram for Iron Calculated Using Scenario 1 Groundwater Composition. Red Dot Represent pH/Eh Conditions for Scenario 1. Green Dashed Lines Stand for the Water Stability Field

Iron speciation is dominated by Fe(II) and, due to the high concentration of chlorides in the system, FeCl⁺ is expected to dominate aqueous iron chemistry (Table 64).

Table 64	: Iron	Concentration	and S	Speciation	under	Scenario 1	Conditions
		0011001101011		poolution	anaci		

	Scenario 1	
Concentration (m)	Sp	peciation
1.00.10-4	FeCl ⁺	93%
(Table 20)	Fe ²⁺	7%

4.1.9.2 Fe Solubility in Scenario 2

The iron concentration in this Scenario is the one calculated for Scenario 2 conditions (see Table 20). In Scenario 2, groundwater interacts with the carbon-steel container prior to contacting the waste. The C-steel corrosion (and therefore, Fe(0) corrosion) results in the formation of corrosion products (for example, magnetite, see Figure 28).



Figure 28. Eh vs pH Predominance Diagram for Iron Calculated Using Scenario 2 Groundwater Composition. Red Dot Represent pH/Eh Conditions for Scenario 2. Green Dashed Lines Stand for the Water Stability Field

Fe concentration in the groundwater increases from $[Fe]_{T}= 10^{-4}$ m in Scenario 1 to $[Fe]_{T}= 6.66 \cdot 10^{-3}$ m in Scenario 2 (see Table 20). Iron speciation is dominated by Fe(II) and, due to the high concentration of chlorides in the groundwater, FeCl⁺ is expected to dominate aqueous iron chemistry (Table 65).

	Scenario 2	
Concentration (m)	Spe	eciation
6.66·10 ⁻³	FeCl ⁺	93%
(Table 20)	Fe ²⁺	7%

Table 65: Iron	Concentration an	nd Speciation	under Scenario	2 Conditions

4.1.9.3 Fe Solubility in Scenario 3

The iron concentration in this scenario is the one calculated for Scenario 3 conditions (see Table 20).

In this Scenario, Fe concentration is significantly affected by the presence of both steel and bentonite (see Section 3.3) due to:

- the steel corrosion processes,
- the dissolution and precipitation of siderite present in the bentonite,
- the cation exchange processes of mono and divalent elements (including Fe²⁺) in bentonite.

The simultaneous occurrence of all those processes in a concentrated groundwater results in high calculated aqueous iron concentrations ($[Fe]_T = 1.31 \cdot 10^{-1}$ m, Table 20). Iron speciation is dominated by Fe(II) and FeCl⁺ is the main iron aqueous species (Table 66).

Table 66: Iron Concentration and Speciatior	n under Scenario 3 Conditions
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Scenario 3				
Concentration (m)	Spec	iation		
1.31·10 ⁻¹	FeCl ⁺	93%		
(Table 20)	Fe ²⁺	7%		

4.1.9.4 Uncertainties

Iron calculations under Scenario 3 conditions are subject to a significant uncertainty due to the simultaneous occurrence of complex, interdependent processes (carbon steel corrosion, mineral dissolution, cation exchange, etc.) in very concentrated media.

4.1.10 Hg

Hg is a chemical element with properties between a metal and a metalloid. It 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). In the environment, mercury has a strong tendency to form complexes with chlorine but also organo-metallic complexes such as the methylmercury, dimethylmercury, etc.

Figure 5 shows a predominance diagram for Hg in water. Taking into account the high chloride concentration in the studied system, we have considered the possible formation of the solid phase $Hg_2Cl_2(cr)$ in the calculations.



Figure 29. Eh vs pH Predominance Diagram for Mercury System in Water, Calculated Using the Thermodynamic Data Selected in the Present Work Phase 2-TDB. $[CI]_T = 5 \text{ m}$; $[Hg]_T = 10^{-6} \text{ m}$. Red Dots Indicates pH/Eh Conditions for Scenario 1, 2 and 3 Groundwaters. Green Dashed Lines Stand for the Water Stability Field

4.1.10.1 Hg Solubility in Scenario 1

In Scenario 1 conditions, the solid phase $Hg_2Cl_2(cr)$ may limit the solubility of mercury (Table 67); the formation of chloride species will increase the solubility of this solid (see Figure 30). The aqueous chemistry of mercury will be governed by chlorine complexation with $HgCl_4^{2-}$ being the only predominant species (Table 68).



Figure 30: $Hg_2CI_2(cr)$ Solubility (Solid Black Line) and Underlying Aqueous Hg Speciation (Dashed Lines) as a Function of Chloride Concentration, under Scenario 1 Conditions. Vertical Dotted Line Indicates $[CI]_T = 5.5$ m, As Expected in the Porewater (see Table 1)

Table 67: Mercury Solid Phases and Concentrations under Scenario 1 Conditions

Scenario 1
Concentration (m)
2.65·10 ⁻⁷

*See the discussion in Section 4.1.10.4

Table 68: Mercur	y Speciation	under Scenario 1	I Conditions
------------------	--------------	------------------	--------------

	Scena	ario 1
Solid phase	Speci	ation
Hg ₂ Cl ₂ (cr)	HgCl ₄ ²⁻	100%

4.1.10.2 Hg Solubility in Scenario 2

Mercury is a redox sensitive element. Its behaviour is affected by the change of the pe of the system; the decrease of pe of groundwater (from pe = -3.39 in Scenario 1 to pe = -8.54 in Scenario 2) due to canister corrosion leads to a significant decrease of the solubility of Hg in Scenario 2 in comparison with Scenario 1.

In Scenario 2 conditions, the solid phase $Hg_2Cl_2(cr)$ may limit the solubility of mercury (Table 69). The aqueous chemistry of mercury will be governed by chlorine complexation with $HgCl_4^{2-}$ being the only predominant species (Table 70 and Figure 31).



Figure 31: $Hg_2CI_2(cr)$ Solubility (Solid Black Line) and Underlying Aqueous Hg Speciation (Dashed Lines) as a Function of Chloride Concentration at 25°C under Scenario 2 Conditions. Vertical Dotted Line Indicates [CI]_T = 5.5 m, as Expected in the Porewater (Table 20)

Table 69: Mercury Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2		
Solid phase	Concentration (m)	
Hg ₂ Cl ₂ (cr)*	1.84·10 ⁻¹²	
*See the discussion in Section 4.1.10.4		

Table 70: Mercury Speciation under Scenario 2 Conditions

Scenario 2		
Solid phase	Speci	ation
Hg ₂ Cl ₂ (cr)	HgCl ₄ ²⁻	100%

4.1.10.3 Hg Solubility in Scenario 3

As in Scenario 2, under Scenario 3 conditions, the solid phase $Hg_2CI_2(cr)$ may limit the solubility of mercury (Table 71). The aqueous chemistry of mercury will be governed by chlorine complexation with $HgCI_4^{2^-}$ being the only predominant species (Table 72).

Table 71: Mercury Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3		
Solid phase	Concentration (m)	
Hg ₂ Cl ₂ (cr)*	8.76·10 ⁻¹²	
*See the discuss	ion in Section 4.1.10.4	

Table 72: Mercury Speciation under Scenario 3 Conditions

	Scenario 3	
Solid phase	Speci	ation
Hg ₂ Cl ₂ (cr)	HgCl ₄ 2-	100%

4.1.10.4 Uncertainties

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

We have assumed that solid $Hg_2Cl_2(cr)$ can be formed. Although this seems a reasonable hypothesis taking into account the reducing environment and the high chloride concentrations in groundwater, further experimental evidence of the formation of this solid under the studied conditions would be highly desirable.

Furthermore, the ability of Hg(I) to disproportionate (Eq. 4) is well known, being this process more feasible under alkaline conditions (Han et al. 2018).

 $Hg_2CI_2 + 2OH^- = Hg^0 + HgO + 2CI^- + H_2O$ Eq. 4

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 10⁻¹⁴ m in Scenario 1 and around 10⁻²⁴ m under the highly reducing conditions of Scenario 2 or 3. These mercury concentrations are very low comparing with some values measured in the environment and thus assuming that Hg(I) could exert a solubility control may not be realistic.

Another important uncertainty affecting the assessment of mercury refers to the presence of microbes and the reduction of sulphate to sulphide. The presence of sulphides could lead to the formation of the highly insoluble solid HgS(s) (see Section 4.2.1).

Finally, Hg is also well known to form strong complexes with organics (for example methylmercury species), although there is a general lack of thermodynamic data for Hg organic complexes. 4.1.11 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 and the calcium concentration.

Two different solids, $MoO_2(s)$ and $CaMoO_4(s)$ (Powellite) may be formed under the studied scenarios (see Figure 32).



Figure 32. Eh vs pH Predominance Diagram for Molybdenum Aqueous Species in Water, Calculated Using the Data Selection in the Present Work Phase 2-TDB. $[Ca]_T = 1.1 \text{ m}; [Mo]_T = 10^6 \text{ m}.$ Red Dots Indicates pH/Eh Conditions for Scenario 1, 2 and 3 Groundwater. Green Dashed Lines Stand for the Water Stability Field

4.1.11.1 Mo Solubility in Scenario 1

Two different solid phases may exert the solubility control of Mo under Scenario 1 conditions. If CaMoO₄(s) is the phase controlling Mo solubility, the concentration of molybdenum in groundwater would be about 10^{-7} m. If the oxide solid phase MoO₂(s) exerts the solubility control, the concentration of Mo is lower, around 10^{-13} m (Table 73).

Molybdate, $MoO_4^{2^-}$, would be the predominant aqueous species whether $CaMoO_4(s)$ or $MoO_2(s)$ is the solubility controlling phase (Table 74).

Scenario 1		
Solid phase	Concentration (m)	
CaMoO ₄ (s)	5.14·10 ⁻⁷	
MoO ₂ (s)	2.36-10 ⁻¹³	

 Table 73: Molybdenum Solid Phases and Concentrations under Scenario 1 Conditions.

 The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Table 74: Mol	ybdenum S	peciation	under	Scenario	1	Conditions

Scenario 1		
Solid phase	Speci	ation
CaMoO ₄ (s)	MoO ₄ ²⁻	100%
MoO ₂ (s)	MoO4 ²⁻	100%

4.1.11.2 Mo Solubility in Scenario 2

There is a significant lack of thermodynamic data for Mo(+IV) aqueous species and the aqueous chemistry of molybdenum is completely governed by the Mo(+VI) anion MoO₄²⁻. The MoO₂(s) dissolution reaction is then significantly affected by both the pe and the pH of the system (see Eq. 5). MoO₂(s) solubility decreases as the pe of the system decreases; but the solubility increases as the pH increases. On the contrary, CaMoO₄(s) (which is a Mo(+VI) solid) is not affected by the pe or the pH of the system (Eq. 6).

$MoO_2(s) + 2H_2O = MoO_4^{2-} + 2e^{-} + 4H^+$	Eq. 5
$CaMoO_4(s) + 2H_2O = Ca^{2+} + MoO_4^{2-}$	Eq. 6

The pe of Scenario 2 is lower than that of Scenario 1; however, the pH of Scenario 2 is higher than that of Scenario 1. Consequently, calculated $MoO_2(s)$ solubility in Scenario 2 conditions (Table 75) is similar to that calculated in Scenario 1. CaMoO₄(s) is not affected by the pe or the pH variations (Table 75).

Molybdate, MoO_4^{2-} , is the predominant aqueous species whether $MoO_2(s)$ or $CaMoO_4(s)$ is the solubility controlling phase (Table 76).

Table 75: Molybdenum Solid Phases and Concentrations under Scenario 2 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Scenario 2		
Solid phase	Concentration (m)	
CaMoO ₄ (s)	5.19·10 ⁻⁷	
MoO ₂ (s)	2.23-10 ⁻¹⁴	

Scenario 2			
Solid phase	Speci	ation	
CaMoO ₄ (s)	MoO ₄ ²⁻	100%	
MoO ₂ (s)	MoO ₄ ²⁻	100%	

Table 76: Molybdenum Speciation under Scenario 2 Conditions

4.1.11.3 Mo Solubility in Scenario 3

The pH of Scenario 3 (pH = 7.17) is lower than that of Scenario 2 (pH = 7.82). Therefore, calculated $MoO_2(s)$ solubility in Scenario 3 conditions (Table 77) is lower than that in Scenario 2. CaMoO₄(s) is not affected by the pH variations (Table 77). MoO_4^{2-} is the predominant aqueous species whether $MoO_2(s)$ or CaMoO₄(s) is the solubility controlling phase (Table 78).

Table 77: Molybdenum Solid Phases and Concentrations under Scenario 3 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Scenario 3		
Solid phase Concentration (m)		
CaMoO ₄ (s)	5.14·10 ⁻⁷	
MoO ₂ (s)	1.12·10 ⁻¹⁵	

Table 78: Molybdenum Speciation under Scenario 3 Conditions

Scenario 3				
Solid phase	Speci	ation		
CaMoO ₄ (s)	MoO ₄ ²⁻	100%		
MoO ₂ (s) MoO ₄ ²⁻ 100%				

4.1.11.4 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 (CaMoO₄(s) or MoO₂(s)) that can control Mo solubility under reducing 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 Scenario.

4.1.12 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.

4.1.12.1 Nb Solubility in Scenario 1

Niobium solubility is expected to be controlled by the solid phase Nb₂O₅(s) with an aqueous concentration in the groundwater about $\approx 10^{-9}$ m in Scenario 1 (Table 79). Nb aqueous speciation is governed by the hydroxide complexes, Nb(OH)₆⁻ being the predominant one (Table 80).

Table 79: Niobium Solid Phase and Concentration under Scenario 1 Conditions

Scenario 1		
Solid phase Concentration (m)		
Nb ₂ O ₅ (s)	8.57·10 ⁻⁹	

Table 80: Niobium Speciation under Scenario 1 Conditions

Scenario 1				
Solid phase	Speciation			
	Nb(OH)6 ⁻	88%		
Nb ₂ O ₅ (s)	Nb(OH)72-	7%		
	Nb(OH)₅(aq)	5%		

4.1.12.2 Nb Solubility in Scenario 2

Under Scenario 2 conditions, the aqueous concentration of niobium is likely to be limited by the solid phase Nb₂O₅(s) (Table 81). Nb solubilities in Scenario 2 are greater than in Scenario 1, mainly due to the effect of pH on Nb aqueous speciation (see Figure 33), which also results in an increase of the presence of Nb(OH) $_7^{2-}$ species in the Nb speciation scheme (Table 82).

Table 81: Niobium Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2		
Solid phase Concentration (m)		
Nb ₂ O ₅ (s)	2.84·10 ⁻⁵	

Table 82: Niobium Speciation under Scenario 2 Conditions

	Scenario 2	
Solid phase	Spe	eciation
$Nb_{2}O_{2}(c)$	Nb(OH)7 ²⁻	94%
ND2O5(S)	Nb(OH)6 ⁻	6%



Figure 33: Nb₂O₅(s) Solubility (Solid Black Line) and Underlying Aqueous Nb Speciation (Dashed Lines) as a Function of pH. Vertical Dotted Line Indicates pH = 7.82, as Expected in the Scenario 2 Porewater (Table 20)

4.1.12.3 Nb Solubility in Scenario 3

The pH of Scenario 3 (pH = 7.17) is lower than that of Scenario 2 (pH = 7.82). As a consequence, the calculated Nb₂O₅(s) solubility in Scenario 3 conditions (Table 83) is lower than in Scenario 2. Nb(OH)₇²⁻ and Nb(OH)₆⁻ are calculated to be the main aqueous Nb species (Table 84).

Table 83: Niobium Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3		
Solid phase Concentration (m)		
Nb ₂ O ₅ (s) 1.66·10 ⁻⁶		

	Scenario 3	
Solid phase	Speciation	
	Nb(OH)7 ²⁻	79%
ND2O5(5)	Nb(OH)6 ⁻	21%

4.1.12.4 Uncertainties

There is a general lack of thermodynamic data in the literature for niobium, which constitutes the most important drawback when studying the behaviour of this element.

Laboratory experiments (Talerico et al. 2004) indicate that calcium-niobiate 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.

4.1.13 Np

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

For different tetravalent actinide elements (including Np(IV)), An(CO₃)₅⁶⁻ may appear in calculations with highly concentrated groundwaters. Although the existence of these species is confirmed by spectroscopic measurements and their associated stability constants seem reliable, the evaluation of their predominance in a complex, highly concentrated media is challenging (see Section 2.30).

No reliable stability constants for Na⁺(or other counterion) complex formation with Np(CO₃)₅⁶⁻ are available, although this is probable to occur. Pitzer mixing terms θ (Np(CO₃)₅⁶⁻/Cl⁻) and Ψ (Np(CO₃)₅⁶⁻/Cl⁻/Na⁺) are not available, although they are required to properly predict Np(CO₃)₅⁶⁻ formation in high ionic strength media. Finally, the use of the SIT approach in these conditions would not be appropriate, since the SIT theory provides uncertain results for equilibria involving very high negative charges (Bruno et al. 1989).

In order to constrain a reasonable solubility range for this element, the calculations described in the sub-sections below have been performed using different thermodynamic databases.

4.1.13.1 Np Solubility in Scenario 1

Neptunium solubility is expected to be controlled by an amorphous Np(+IV) hydroxide solid under conditions for Scenario 1.

All the three databases described in Section 2 (Phase2-TDB, THEREDA and the modified ThermoChimie database) include this solid; their associated stability constants are very similar. Furthermore, in all these databases the stability constant associated to $Np(CO_3)_5^{6-}$ is identical. Thus, the main difference among them is the ionic strength approach (Pitzer or SIT) used to handle ionic strength corrections.

The different databases have been used to calculate the solubility and speciation of neptunium as shown in Table 85. As seen in the table, both Phase2-TDB and THEREDA (with Pitzer approach) provide very similar results, leading to high calculated Np solubilities (around 10^{-5} m) with the Np aqueous chemistry being dominated by the pentacarbonate complex Np(CO₃)₅⁶⁻. The predominance of this species is so high that Np(CO₃)₅⁶⁻ represents nearly 70% of the total carbonate in the system ([C]_T = $3 \cdot 10^{-4}$ m, see Table 20). This seems unrealistic, as calcium or

magnesium, which are present at very high concentrations, would probably compete with Np(+IV) for carbonate complexation.

On the contrary, the modified ThermoChimie database, which includes $Np(CO_3)_5^{6-}$ but uses SIT approach, predicts a much lower Np solubility and $Np(CO_3)_5^{6-}$ does not play a role in Np speciation (Table 85).

Table 85: Comparison of Calculated Np(OH)₄(am) Solubilities and Speciation with Different Databases under Scenario 1 Conditions

Np(OH)₄(am)	Scenario 1					
	Phase 2- (Pitze)	TDB r)	THERED (Pitzer)	Α	Modified Theri (SIT)	moChimie
Concentration (m)	4.12.10) ⁻⁵	5.82.10	5	2.26.10) ⁻⁹
Speciation	Np(CO ₃)5 ⁶⁻	100%	Np(CO ₃)5 ⁶⁻	100%	Np(OH)₃⁺ Np(OH)₄	55% 44%

In order to constrain a solubility range for Np, we have used Phase2-TDB with and without including Np(CO₃)₅⁶⁻ in the calculations. With this approach, we can obtain an upper-limit, very conservative value (defined by the formation of Np(CO₃)₅⁶⁻), and a more realistic value, similar to the one calculated with the SIT approach (without taking into account Np(CO₃)₅⁶⁻). The calculated solubility and the associated speciation are shown in Table 86 and Table 87 respectively.

Table 86: Neptunium Solid Phase and Concentrations under Scenario 1 Conditions

Scenario 1			
Solid phase	e Concentration (m)		
	Including Np(CO ₃)5 ⁶⁻	Without including Np(CO ₃)5 ⁶⁻	
Np(OH)₄(am)	4.12·10 ⁻⁵	1.87·10 ⁻⁹	

Table 87: Neptunium Speciation under Scenario 1 Conditions

Scenario 1					
Solid phase	Speciation				
	Including Np(CO ₃)5 ⁶⁻		Without including Np(CO ₃)5 ⁶⁻		
Np(OH)₄(am)	Np(CO ₃)5 ⁶⁻	100%	Np(OH)4	62%	
np(on)+(ani)			Np(OH)₃+	33%	
			Np ³⁺	5%	

4.1.13.2 Np Solubility in Scenario 2

Np solubility under the Scenario 2 conditions (Table 88) is similar to that under Scenario 1. Due to higher pH value of the groundwater in Scenario 2, a unique Np aqueous species $Np(OH)_4(aq)$ is expected (Table 89).

As in the previous Scenario, we have used Phase2-TDB with and without including Np(CO₃)₅⁶⁻ in the calculations in order to constrain a solubility range for Np.

Table 88: Neptunium Solid Phase and Concentrations under Scenario 2 Conditions

Scenario 2				
Solid phase	Concentration (m)			
	Including Np(CO ₃)5 ⁶⁻	Without including Np(CO ₃) ₅ ⁶⁻		
Np(OH)₄(am)	4.24·10 ⁻⁷	1.16·10 ⁻⁹		

Table 89: Neptunium Speciation under Scenario 2 Conditions

Scenario 2				
Solid phase	Speciation			
	Including N	p(CO ₃)5 ⁶⁻	Without includ	ng Np(CO₃)₅ ⁶⁻
Np(OH)4(am)	Np(CO ₃)5 ⁶⁻	100%	Np(OH)4	100%

4.1.13.3 Np Solubility in Scenario 3

Calculated solubility and speciation results for Scenario 3 (Table 90 and Table 91) are similar to those observed in Scenario 2. The minor differences observed are related to the fact that the pH of Scenario 3 (pH = 7.17) is lower than that of Scenario 2 (pH = 7.82).

Table 90: Neptunium Solid Phase and Concentrations under Scenario 3 Conditions

Scenario 3				
Solid phase	Concentration (m)			
-	Including Np(CO ₃) ₅ ⁶⁻ Without including Np(CO ₃) ₅			
Np(OH)₄(am)	9.94·10 ⁻⁶	1.17·10 ⁻⁹		

Table 91: Neptunium Speciation under Scenario 3 Conditions

		Sc	enario 3	
Solid phase		Sp	eciation	
-	Including Np(CO ₃) ₅ ⁶⁻ Without inclu			uding Np(CO ₃)5 ⁶⁻
Np(OH)₄(am)	Np(CO ₃) ₅ ⁶⁻	100%	Np(OH)4	99%
	,		Np(OH) ₃ +	1%

4.1.13.4 Uncertainties

The main uncertainty associated to Np solubility and speciation is the lack of the appropriate Pitzer ionic interaction parameters for $An(CO_3)_5^{6-}$, which introduces high uncertainties in the calculated results.

4.1.14 Pa

Protactinium mainly occurs in the oxidation states +IV and +V. 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.

4.1.14.1 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 92). Its aqueous chemistry, in equilibrium with this solid phase, is dominated by PaO_2^+ (Table 93).

Table 92: Protoactinium Solid Phase and Concentration under Scenario 1 Conditions

Scenario 1			
Solid phase Concentration (m)			
$Pa_2O_5(s)$	6.50·10 ⁻⁸		

Table 93: Protoactinium Speciation under Scenario 1 Conditions

	Scenario 1	
Solid phase	Spe	eciation
$D_{0} = O_{-}(0)$	PaO ₂ +	99%
Pa ₂ O ₅ (S)	PaO ₂ (OH)	1%

4.1.14.2 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 94. Its corresponding aqueous speciation in equilibrium with the selected solid is summarized in Table 95.

Table 94: Protoactinium Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2			
Solid phase Concentration (m)			
Pa ₂ O ₅ (s)	1.35·10 ⁻⁹		

Table 95: Protoactinium Speciation under Scenario 2 Conditions

Scenario 2				
Solid phase	Specia	tion		
-	PaO ₂ (OH)	65%		
Pa ₂ O ₅ (s)	PaO ₂ +	23%		
	PaO ₂ (OH) ₂ -	12%		

4.1.14.3 Pa Solubility in Scenario 3

As seen in Figure 34, Pa solubility and speciation in Scenario 2 and Scenario 3 are affected by the fact that pH values under Scenario 2 conditions (pH = 7.82) and Scenario 3 conditions (pH = 7.17) are higher than that of Scenario 1 (pH = 5.5).





Calculated solubility results for Scenario 3 (Table 96) are similar to those observed for Scenario 2. The differences in speciation between Scenario 3 (Table 97) and Scenario 2 are caused by the pH changes in the groundwaters.

Scenario 3			
Solid phase	Concentration (m)		
Pa ₂ O ₅ (s)	2.28·10 ⁻⁹		

Table 97: Protoactinium	Speciation under	Scenario 3	Conditions

	Scenario 3		
Solid phase	Speciat	ion	
	PaO ₂ +	60%	
Pa ₂ O ₅ (s)	PaO ₂ (OH)	38%	
	PaO ₂ (OH) ₂ -	2%	

4.1.14.4 Uncertainties

The assessment of Pa solubility is limited by the lack of reliable experimental thermodynamic data, as they are very scarce and controversial, even at low ionic strengths. Furthermore, its specific chemical characteristics makes it difficult to establish analogies with the chemistry of other actinides.

4.1.15 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 halides, sulphate, and carbonate in groundwater.

4.1.15.1 Pb Solubility in Scenario 1

In diluted, natural groundwaters, cerussite, $Pb(CO_3)(s)$ and hydrocerussite, $Pb_3(CO_3)_2(OH)_2(s)$, may limit Pb solubility. In high ionic strength media, paralaurionite, PbCI(OH), may also be a solubility-limiting solid. However, all these solids will increase its solubility due to the presence of chloride in the system and the formation of Pb-chloride complexes.

As discussed in Section 2.15, there is a high uncertainty about the stability of PbCl₄²⁻ species, and even about the existence of the species itself. Thus, the role of PbCl₄²⁻in the concentrated chloride systems under study may be overestimated. In order to constrain a solubility range for Pb, we have used Phase2-TDB with and without including this species in the calculations. With this approach, we can obtain an upper-limit, very conservative value (defined by the formation of PbCl₄²⁻), and a more realistic value. The calculated solubility and the associated speciation are shown in Table 98 and Table 99 respectively.

Scenario 1		
Solid phase	Con	centration (m)
	Including PbCl ₄ ²⁻	Without including PbCl ₄ ²⁻
PbCI(OH)	n.s.l. (~7.52⋅10 ⁻¹)	n.s.l. (~ 5.88⋅10 ⁻²)

Table 98: Lead Solid Phase and Concentration under Scenario 1 Conditions

Table 99: Lead Speciation under Scenario 1 Conditions

Scenario 1					
Solid phase	Speciation				
	Including	g PbCl₄²-	Without includ	ing PbCl₄²⁻	
PbCl(OH)	PbCl4 ²⁻ PbCl3 ⁻	98% 2%	PbCl₂(aq) PbCl⁺	99% 1%	

4.1.15.2 Pb Solubility in Scenario 2

In Scenario 2 conditions, lead solubility is high (Table 100), due to the formation of aqueous Pb chlorides. The aqueous chemistry of lead will be governed by chlorine complexation (Table 101).

As in the previous Scenario, we have used Phase2-TDB with and without including PbCl₄²⁻ in the calculations in order to constrain a solubility range for Pb.

Scenario 2		
Solid phase	Con	centration (m)
	Including PbCl ₄ ²⁻	Without including PbCl42-
PbCI(OH)	n.s.l. (~1.37⋅10 ⁻²)	2.81.10-4

Table 100: Lead Solid Phases and Concentrations under Scenario 2 Conditions

Table 101: Lead Speciation under Scenario 2 Conditions

Scenario 2					
Solid phase			Speciation		
-	Including	∣ PbCl₄²⁻	Without inclu	uding PbCl₄²⁻	
PbCl(OH)	PbCl ₄ ²⁻	98%	PbCl ₂ (aq)	99%	
	PbCl₃ ⁻	2%	PbCl ⁺	1%	

4.1.15.3 Pb Solubility in Scenario 3

Calculated solubility and speciation results for Scenario 3 Table 102 and Table 103) are similar to those observed in Scenario 2.

Table 102: Lead Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3			
Solid phase	Con	centration (m)	
	Including PbCl ₄ ²⁻	Without including PbCl4 ²⁻	
PbCI(OH)	n.s.l. (~5.61⋅10 ⁻²)	1.30·10 ⁻³	

Table 103: Lead Speciation under Scenario 3 Conditions

Scenario 3				
Solid phase			Speciation	
•	Including	PbCl ₄ ²⁻	Without includi	ng PbCl₄²⁻
PbCl(OH)	PbCl ₄ ²⁻	98%	PbCl ₂ (aq)	99%
	PbCl₃ ⁻	2%	PbCl+	1%

4.1.15.4 Uncertainties

The main uncertainty affecting the assessment of lead 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 (Section 4.2.1).

Furthermore, there is uncertainty about the thermodynamic data for the Pb-Cl system, specifically on the role of PbCl₄²⁻ in concentrated chloride groundwater.

4.1.16 Pd

Palladium can be found in several oxidation states in nature, being +II the most common in aqueous media. Its aqueous chemistry will be mainly driven by complexation against soft ligands such as halides, carbonate or sulphate, depending on the groundwater composition.

4.1.16.1 Pd Solubility in Scenario 1

Solid Pd hydroxides $(Pd(OH)_2(s))$ or solid Pd halides (as $PdCl_2(s)$) may control Pd solubility under the studied conditions. However, as seen for other elements, all these solids will increase its solubility due to the presence of chloride in the system and the formation of Pd-chloride complexes (Table 104 and Table 105).

Table 104: Palladium Solid Phase and Concentration under Scenario 1 Conditions

Scenario 1		
Solid phase Concentration (m)		
PdCl ₂ (s)	n.s.l.	

Table 105: Palladium Speciation under Scenario 1 Conditions

	Scenario 1	
Solid phase	Speci	ation
PdCl ₂ (s) (n.s.l.)	PdCl ₄ ²⁻	100%
Speciation calculated assuming 10 ⁻⁶ m of Pd		

4.1.16.2 Pd Solubility in Scenario 2

In Scenario 2 conditions, palladium is not limited by solubility due to the formation of aqueous Pd chlorides (Table 106). The aqueous chemistry of palladium will be governed by $PdCl_4^{2-}$ (Table 107).

Table 106: Palladium Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2		
Solid phase	Concentration (m)	
PdCl ₂ (s)	n.s.l.	

	Scenario 2		
Solid phase	Specia	tion	
$PdCl_{2}(s)$ (n s l)	PdCl ₄ ²⁻	99%	
Fuci2(3) (11.5.1.)	PdCl ₃ (OH) ²⁻	1%	

Table 107: Palladium Speciation under Scenario 2 Conditions

Speciation calculated assuming 10⁻⁶ m of Pd

4.1.16.3 Pd Solubility in Scenario 3

As in the previous scenarios, in Scenario 3 palladium is not solubility limited (Table 108) and its aqueous chemistry is dominated by $PdCl_4^{2-}$ (Table 109).

Table 108: Palladium Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3		
Solid phase Concentration (m)		
PdCl ₂ (s) n.s.l.		

Table 109: Palladium Speciation under Scenario 3 Conditions

tion
100%

Speciation calculated assuming 10⁻⁶ m of Pd

4.1.16.4 Uncertainties

The reduction of sulphate to sulphide is an uncertainty that may affect Pd solubility, as Pdsulphide solid phases such as PdS(s) may exert the solubility control of this element under reducing conditions (see Section 4.2.1).

Moreover, thermodynamic data selection including Pitzer coefficients has not been identified in open literature; this is a limitation for the accurate calculations for this element under saline conditions.

4.1.17 Pu

Plutonium is a redox sensitive element that presents strong interactions with some of the ligands in the groundwaters of interest, i.e., carbonate, sulfate.

In nature, this element could be found as +III, +IV, +V and +VI oxidation states; +III and +IV will be the most relevant ones under the conditions of interest in the present work. Although in the solid phase Pu will be found in the oxidation state +III or +IV, in the reducing conditions studied Pu(+III) species will dominate its aqueous chemistry. As a consequence, plutonium will be less

affected by the formation of the pentacarbonate species $An(IV)(CO_3)_5^{6-}$ than neptunium (see the discussion in Section 4.1.13).

4.1.17.1 Pu Solubility in Scenario 1

Under Scenario 1 conditions, $Pu(OH)_4(am)$ is the most likely Pu solubility limiting phase (Table 110). Although in the solid phase Pu is in the oxidation state +IV, in the aqueous phase Pu(+III) species dominate the aqueous chemistry (Table 111). $Pu(CO_3)_5^{6-}$ formation does not have a significant effect in the Pu solubility and speciation calculations.

Table 110: Plutonium Solid Phase and Concentration under Scenario 1 Conditions

Scenario 1	
Solid phase	Concentration (m)
Pu(OH)₄(am)	1.93·10 ⁻³

Table 111: Plutonium Speciation under Scenario 1 Conditions

	Scenario 1			
Solid phase	Redox state	Speciati	ion	_
		Pu ³⁺	87%	
		Pu(OH) ²⁺	5%	
		PuCl ²⁺	3%	
Pu(OH)₄(am)	Pu(+III)	Pu(SO ₄)+	3%	
		Pu(CO ₃)+	1%	
		Pu(OH) ₂ +	1%	
	Pu(+IV)	Pu(CO ₃)5 ⁶⁻	1%	

4.1.17.2 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. $Pu(OH)_4(am)$ (Pu(+IV) solid) or $Pu(OH)_3(s)$ (Pu(+III)solid) could control Pu solubility under those conditions (Table 112). $Pu(OH)_3(s)$ is only stable at very reducing conditions, and 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) solid. Thus, $Pu(OH)_4(am)$ seems to be the most likely solubility-limiting solid.

Speciation is still dominated by Pu(III) aqueous complexes, and $Pu(CO_3)_5^{6-}$ formation does not have a significant effect in the Pu solubility and speciation calculations (Table 113).

Table 112: Plutonium Solid Phase and Concentration under Scenario 2 Conditions.
The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

	Scenario 2
Solid phase	Concentration (m)
Pu(OH)₄(am)	4.36-10 ⁻⁵
Pu(OH)₃(s)	1.59·10 ⁻⁵

 Table 113: Plutonium Speciation under Scenario 2 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and Speciation

	Scenario 2		
Solid phase	Redox state	Specia	ation
Pu(OH)₄(am)	Pu(+III)	Pu(OH)₂ ⁺ Pu(OH)²+	96% 3%
Pu(OH)₃(s)	Pu(+III)	Pu(OH) ₂ + Pu(OH) ²⁺	96% 3%

4.1.17.3 Pu Solubility in Scenario 3

Similar to Scenario 2, under Scenario 3 conditions $Pu(OH)_4(am)$ or $Pu(OH)_3(s)$ could control Pu solubility (Table 114). Speciation is dominated by Pu(III) aqueous complexes, and $Pu(CO_3)_5^{6-1}$ formation does not have a significant effect in the Pu solubility and speciation calculations (Table 115).

Table 114: Plutonium Solid Phases and Concentrations under Scenario 3 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Scenario 3	
Solid phase	Concentration (m)
Pu(OH)₄(am)	2.31.10-4
Pu(OH) ₃ (s)	8.67·10 ⁻⁵

Table 115: Plutonium Speciation under Scenario 3 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and Speciation

	Sce	nario 3	
Solid phase	Redox state	Speciation	
Pu(OH)₄(am)	Pu(+III)	Pu(OH)₂⁺ Pu(OH)²⁺ Pu ³⁺ Pu(CO₃)⁺	80% 13% 5% 1%
	Pu(+IV)	Pu(CO ₃)5 ⁶⁻	2%
Pu(OH)₃(s)	Pu(+III)	Pu(OH) ₂ + Pu(OH) ²⁺ Pu ³⁺ Pu(CO ₃)+	79% 13% 5% 1%
	Pu(+IV)	Pu(CO ₃)5 ⁶⁻	3%

4.1.17.4 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, which leads to some uncertainties regarding Pu solubility and speciation behaviour.

Phosphates have been identified to form stable Pu(+III) solid phases that lead to lower Pu equilibrium concentrations (Section 4.2.2).

The sensitivity of Pu(+III) chemistry to pH, carbonate and sulfate in groundwater makes the solubility analysis very sensitive to variations in groundwater compositions, specially taking into account the high ionic strength of the studied system.

Finally, the high ionic strength of the studied system introduces a certain degree of uncertainty. The free cation Pu^{3+} has a relatively high charge, which will lead to significant interactions with anionic ligands such as Cl^{-} or $SO_4^{2^-}$. The impact of this uncertainty in the calculations is minimized using the Pitzer approach, for which the associated Pitzer parameters are available in Phase2-TDB database (see Section 2).

4.1.18 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.

4.1.18.1 Ra Solubility in Scenario 1

 $Ra(SO_4)(s)$ is the solubility limiting phase under the Scenario 1 conditions (Table 116). The main parameter expected to affect radium solubility and speciation is sulphate concentration in groundwater; $Ra(SO_4)(s)$ solubility decreases as sulphate concentration in solution increases (see Figure 35). Main radium aqueous species include Ra-chloride species and the free Ra^{2+} cation (Table 117).



Figure 35: Ra(SO₄)(s) Solubility (Solid Black Line) and Underlying Aqueous Ra Speciation (Dashed Lines) as a Function of Sulphate Concentration under Scenario 1 Conditions. Vertical Dotted Line Indicates $[SO_4]_T = 3.1 \cdot 10^{-3}$ m, as Expected in the Porewater (Table 1)

Scenario 1	
Solid phase	Concentration (m)
RaSO ₄ (s)	1.16.10-4

Table 116: Radium Solid Phase and Concentration under Scenario 1 Conditions

Table 117: Radium Speciation under Scenario 1 Conditions

	Scenario 1	
Solid phase	Sp	eciation
-	RaCl ₂	62%
RaSO ₄ (s)	RaCl ⁺	30%
	Ra ²⁺	8%

4.1.18.2 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 118 and Table 119) in comparison to those obtained in Scenario 1.

Table 118: Radium Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2	
Solid phase	Concentration (m)
RaSO ₄ (s)	1.15.10-4

Scenario 2				
Solid phase	S	peciation		
-	RaCl ₂	62%		
RaSO4(s)	RaCl+	30%		
	Ra ²⁺	8%		

4.1.18.3 Ra Solubility in Scenario 3

In Scenario 3, the presence of bentonite increases slightly the calculated sulphate concentration (from $3.10 \cdot 10^{-3}$ m in Scenario 2 to $5.27 \cdot 10^{-3}$ m in Scenario 3), which results in a small decrease of Ra solubility (see Table 120). The main aqueous species include Ra-chloride species and the free Ra²⁺ cation (Table 121).

Scenario 3		
Solid phase Concentration (m)		
RaSO ₄ (s)	6.61·10 ⁻⁵	

Table 120: Radium Solid Phase and Concentration under Scenario 3 Conditions

Table 121: Radium Speciation under Scenario 3 Conditions

Scenario 3				
Solid phase	S	peciation		
-	RaCl ₂	62%		
RaSO₄(s)	RaCl+	30%		
·	Ra ²⁺	8%		

4.1.18.4 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).

The formation of a Ra-Ba (radiobarite) solid solution is a more realistic case (Grivé et al. 2007; Grivé et al. 2010). The assumption of this solid solution as a solubility limiting solid will result in lower Ra concentrations in equilibrium, even as low 10⁻¹¹ m, this is, in the upper limit range of radium concentration in natural waters. Furthermore, the high NaCl concentration of the groundwaters is not expected to have a strong impact on the formation of the radiobarite (Brandt et al. 2018).

4.1.19 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}.

In the present work the approach by Schubert et al. (2012) has been followed (see Section 2.19); this approach allows to evaluate the water/air partition coefficient as a function of temperature and salinity. As seen in Figure 36, the $K_{w/air}$ is expected to decrease as salinity increases.



Figure 36: Dependence of the Partitioning Coefficient of Radon Gas between Water and Air ($K_{w/air}$) with Salinity

4.1.19.1 Rn Solubility in Scenarios 1, 2 and 3

Section 2.19 describes the equations (Eq. 1 and Eq. 2) and the parameters needed in order to calculate the $K_{w/air}$ for radon. Besides the six adjustable parameters described in Table 8, salinity is also needed in the calculations. Considering the sodium and chloride concentrations in the different Scenarios (Table 20), a salinity of \approx 323‰ has been used in all Scenarios.

Calculated $K_{w/air}$ for radon is shown in Table 122.

Table 122: Radon K_{w/air under} Scenario 1, Scenario 2 and Scenario 3 Conditions

Scenario	0 1, 2, 3
Radon K _{w/air}	0.05

4.1.19.2 Uncertainties

The dependence of the water/air partition coefficient of radon with salinity has not been extensively studied; this leads to a significant uncertainty in the solubility calculations for radon, especially in the highly saline groundwaters in the studied scenarios.

4.1.20 Ru

Ruthenium is a chemical element with a rather complex redox chemistry (see Section 2.20). Under the groundwater conditions studied, Ru will be found mainly in the redox states +III and

+II. Thermodynamic data available in the literature for this element is very scarce (inexistent at high ionic strengths) which limits the accuracy of the solubility analysis. All the calculations related with this element should be considered as tentative only.

4.1.20.1 Ru Solubility in Scenario 1

Under the Scenario 1 conditions, $Ru(OH)_3 \cdot H_2O(s)$ is the most likely phase to precipitate. However, the solubility of this solid in the presence of high chloride concentration will significantly increase (Figure 37).



Figure 37. Ru(OH)₃·H₂O(s) Solubility (Solid Black Line) and Underlying Aqueous Ru Speciation (Dashed Lines) as a Function of Chloride Concentration at 25°C under Scenario 1 Conditions, Calculated with Phase2-TDB. Vertical Dotted Line Indicates $[CI]_T = 5.5$ m, as Expected in the porewater (see Table 1)

Taking into account the complex chemistry of Ru and the fact that the associated Pitzer coefficients are inexistent, different databases described in Section 2 (Phase2-TDB, and the modified ThermoChimie database) have been used to calculate the solubility and speciation of Ru (Table 123).

As seen in Table 123, the Phase2-TDB (with Pitzer approach) and the modified ThermoChimie database (with SIT approach) predict a very different solubility under Scenario 1 conditions. The SIT approach is not most adequate for the high ionic strength condition system; however, the large difference of calculated solubility and speciation using SIT and Pitzer approaches indicates that the lack of Pitzer coefficients of Ru in Phase2-TDB is a limiting issue when simulating the chemistry of this element.

Ru(OH) ₃ ·H ₂ O(s)	Scenario 1			
Concentration (m)	Phase (Pitz n.s	2-TDB zer) s.l.	Modified The (SIT 4.01،	rmoChimie ſ) 10 ⁻⁵
Speciation	RuCl ₆ ³⁻	100%	RuCl₀ ³⁻ RuCl₅ ²⁻ Ru ²⁺ RuCl⁺	94% 2% 3% 1%

Table 123: Comparison of Calculated Ru(OH)₃·H₂O Solubilities and Speciation with Different Databases under Scenario 1 Conditions

4.1.20.2 Ru Solubility in Scenario 2

Ruthenium is a redox sensitive element and thus changes in the pH/Eh values of groundwater induced by the steel canister corrosion will strongly affect its solubility and speciation.

In Scenario 2, $Ru(OH)_3 H_2O(s)$ may limit Ru solubility with Ru(+II) species dominating its aqueous chemistry (Table 124). However, this calculation result is subject to a high uncertainty. The aqueous Ru species expected to be formed in solution when using Phase2-TDB are highly charged ($Ru(SO_4)_3^{4-}$) and no Pitzer coefficients are available. This leads to a situation similar to that described for Np (see Section 4.1.13), where the formation of highly charged species and the unavailability of the adequate ionic strength corrections largely overestimates the solubility. This may also explain the significant difference between the Pitzer and the SIT calculations (Table 124).

Table 124: Comparison of Calculated Ru(OH)₃·H₂O Solubility and Speciation with Different Databases under Scenario 2 Conditions

Ru(OH) ₃ ·H ₂ O(s)	Scenario 2		
Concentration (m)	Phase 2-TDB (Pitzer) 2.77·10 ⁻⁴	Modified ThermoChimie (SIT) 2.79·10 ⁻⁸	
Speciation	Ru(SO ₄) ₃ 4- 100%	Ru ²⁺ RuCl ⁺ RuCl ₂ Ru(OH) ₂ Ru(OH) ₂ + RuCl ₄ ²⁻ RuCl ₃ -	57% 14% 13% 6% 5% 2% 2% 2% 2%

4.1.20.3 Ru Solubility in Scenario 3

In Scenario 3, $Ru(OH)_3 \cdot H_2O(s)$ may limit Ru solubility with Ru(+II) species dominating its aqueous chemistry (Table 125). As in Scenario 2, the formation of highly charged species and the unavailability of the adequate ionic strength corrections makes the calculations inaccurate.

Ru(OH) ₃ ·H ₂ O(s)	Scenario 3		
Concentration (m)	Phase 2-TDB (Pitzer) 1.32·10 ⁻³	Modified ThermoChimie (SIT) 4.28·10 ⁻⁷	
Speciation	Ru(SO ₄)3 ⁴⁻ 98% RuCl ₆ ³⁻ 2%	Ru ²⁺ 69% RuCl ⁺ 6% RuCl ₂ 6% RuOH ⁺ 3% RuCl ₄ ²⁻ 2%	

Table 125: Comparison of Calculated Ru(OH)₃·H₂O Solubility and Speciation with Different Databases under Scenario 3 Conditions

4.1.20.4 Uncertainties

The assessment of Ru solubility and speciation behaviour is highly uncertain due to the very limited reliable thermodynamic data, especially for Ru(+III) aqueous species (Rard 1985, 1987). Furthermore, no information is available for the chemical and thermodynamic behaviour of Ru under high ionic strength conditions. As mentioned above, all the solubility and speciation calculations related with Ru should be considered as tentative only.

4.1.21 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.

4.1.21.1 S Solubility in Scenario 1

In Scenario 1, the sulphate concentration is the same as in the SR-290-PW reference groundwater (see Table 20).

The original SR-290-PW composition reported in Table 1 was equilibrated with gypsum $(CaSO_4 \cdot 2H_2O(s))$ but using the Pitzer.dat database. When using Phase2-TDB, gypsum is calculated to be slightly undersaturated, but still very close to equilibrium (see Section 3.1). This agrees with the porewater characteristics described in Raven et al. (2011). Sulphate aqueous speciation is shown in Table 126.

Table 126: Sulphate Concentration and Speciation under Scenario 1 Conditions

	Scenario 1	
Concentration (m)	S	peciation
3.10·10 ⁻³	CaSO ₄ (aq)	56%
(Table 20)	SO4 ²⁻	44%

4.1.21.2 S Solubility in Scenario 2

The sulphate concentration in this Scenario is the one calculated for Scenario 2 conditions (see Table 20).

As the microbiologically mediated reduction of sulphate to sulphide is not considered in this work, redox changes from Scenario 1 to Scenario 2 do not affect sulphate chemistry. Sulphate aqueous speciation in Scenario 2 is shown in Table 127.

Table 127: Sulphate Concentration and	Speciation under Sc	enario 2 Conditions
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	Scenario 2	
Concentration (m)	Sp	eciation
3.10·10 ⁻³	CaSO ₄ (aq)	55%
(Table 20)	SO4 ²⁻	45%

4.1.21.3 S Solubility in Scenario 3

The sulphate concentration in this Scenario is the one calculated for Scenario 3 conditions (see Table 20).

The presence of bentonite increases slightly the calculated sulphate concentration (from $3.10 \cdot 10^{-3}$ m in Scenario 2 to $5.27 \cdot 10^{-3}$ m in Scenario 3). Sulphate aqueous speciation is shown in Table 128.

Table 128: Sulphate Concentrat	tion and Speciation und	ler Scenario 3 Conditions
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	Scenario 3	
Concentration (m)	Speci	ation
5.27·10 ⁻³	CaSO ₄ (aq)	55%
(Table 20)	SO4 ²⁻	45%

4.1.21.4 Uncertainties

Sulphate reduction to sulphide has not been considered in the calculations, as microbial activity is not considered. Sulphide concentration in the reference water is below the detection limit and has not been taken into account in the base case calculations above; however, an upper limit concentration of 1.6 · 10⁻⁵ m will be used in sensitivity cases (Section 4.2.1) to assess the uncertainty related to the presence of this element in solubility calculations.

4.1.22 Sb

Antimony is a metalloid; its chemical properties are rather similar to non-metallic elements such as arsenic but also similar to metals like silver.
4.1.22.1 Sb Solubility in Scenario 1

Under Scenario 1 conditions, the oxide solid phase Sb_2O_3 (Valentinite) is expected to limit the solubility of antimony (Table 129). $Sb(OH)_3(aq)$ will be the predominant aqueous species (Table 130).

Table 129: Antimony	Solid Phase and Concentration (under Scenario 1 Conditions
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Scenario 1		
Solid phase Concentration (m)		
Sb ₂ O ₃ (Valentinite)	3.86.10-5	

Table 130: Antimony Speciation under Scenario 1 Conditions

Scenario 1		
Solid phase Speciation		tion
Sb ₂ O ₃ (Valentinite)	Sb(OH)₃(aq)	100%

4.1.22.2 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 131 and Table 132) are almost equal to those obtained in Scenario 1.

Table 131: Antimony Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2		
Solid phase Concentration (m)		
Sb ₂ O ₃ (Valentinite)	3.87.10-5	

Table 132: Antimony Speciation under Scenario 2 Conditions

Scenario 2		
Solid phase Speciation		
Sb ₂ O ₃ (Valentinite)	Sb(OH)₃(aq)	100%

4.1.22.3 Sb Solubility in Scenario 3

Under Scenario 3 conditions, the oxide solid phase Sb_2O_3 (Valentinite) is expected to limit the solubility of antimony (Table 133) with $Sb(OH)_3(aq)$ being the predominant aqueous species (Table 134). The influence of bentonite buffer material on the groundwater (Scenario 3) is not affecting the antimony chemistry.

Table 133: Antimony Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3		
Solid phase Concentration (m)		
Sb ₂ O ₃ (Valentinite)	3.86·10 ⁻⁵	

Table 134: Antimony Speciation under Scenario 3 Conditions

Scenario 3		
Solid phase	Solid phase Speciation	
Sb ₂ O ₃ (Valentinite)	Sb(OH)₃(aq)	100%

4.1.22.4 Uncertainties

Under repository conditions, it is expected that sulphide may have an effect on antimony chemistry by the formation of aqueous species or solid phases such as stibnite $(Sb_2S_3(s))$ (see the discussion in Section 4.2.1).

4.1.23 Se

Selenium is an oxoanionic element predominantly existing in the redox states -II, +IV and +VI. HSe⁻ prevails under reducing conditions, whereas $SeO_3^{2^-}$ (or $HSeO_3^{-}$) and $SeO_4^{2^-}$ dominate under oxidant conditions.

The parameters mostly affecting the selenium chemistry are the Eh and the iron concentration of the system. 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.

4.1.23.1 Se Solubility in Scenario 1

Se solubility assuming ferroselite (FeSe₂(s)), Fe_{1.04}Se(s) or Se(s) as solubility limiting phases, is shown in Table 135. Under Scenario 1 conditions, ferroselite (FeSe₂(s), in bold in Table 135) seems to be the most likely Se solubility limiting phase; selecting Se(s) would represent a more conservative approach.

HSe⁻ is the predominant aqueous species independently of the solid considered.

Table 135: Selenium Solid Phases and Concentrations under Scenario 1 Conc	litions.
The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solu	bility

Scenario 1			
Solid phase	Concentration (m)		
Fe _{1.04} Se(s)	5.03.10-4		
FeSe ₂ (s) (Ferroselite)	4.56-10 ⁻⁸		
Se(s)	4.30·10 ⁻⁶		

	Scenario 1	
Solid phase	Spe	ciation
FeSe ₂ (s) (Ferroselite)	HSe-	100%

Table 136: Selenium Speciation under Scenario 1 Conditions

4.1.23.2 Se Solubility in Scenario 2

In Scenario 2, due to the steel canister corrosion, Fe concentration in solution increases and the Eh of the groundwater decreases. Under those conditions, $Fe_{1.04}Se(s)$ (in bold in Table 137) seems to be the most likely Se solubility limiting phase; ferroselite would represent a more conservative approach. HSe⁻ species is the predominant aqueous Se species (Table 138).

Table 137: Selenium Solid Phases and Concentrations under Scenario 2 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Scenario 2		
Solid phase Concentration (m		
Fe _{1.04} Se(s)	1.18-10 ⁻⁸	
FeSe ₂ (s) (Ferroselite)	3.76·10 ⁻⁶	

Table 138: Selenium Speciation under Scenario 2 Conditions

Scenario 2		
Solid phase	Speciation	
Fe1.04Se(s)	HSe-	100%

4.1.23.3 Se Solubility in Scenario 3

In Scenario 3, Fe concentration is significantly affected by the presence of both steel and bentonite (see Section 4.1.9.3), which results in an increase of calculated aqueous iron concentrations (Table 20). As a consequence, Se solubility in Scenario 3 (Table 139) decreases in comparison with Scenario 2. HSe⁻ species is the predominant Se species (Table 140).

 Table 139: Selenium Solid Phases and Concentrations under Scenario 3 Conditions.

 The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Scenario 3		
Solid phase	Concentration (m)	
Fe _{1.04} Se(s)	2.66-10 ⁻⁹	
FeSe ₂ (s) (Ferroselite)	8.21·10 ⁻⁷	

Scenario 3		
Solid phase	Speciation	
Fe104Se(s)	HSe-	100%

Table 140: Selenium Speciation under Scenario 3 Conditions

4.1.23.4 Uncertainties

The selenium chemistry is highly dependent on the iron chemistry and, consequently, the uncertainty on the iron concentration in solution represents a source of uncertainty for the behaviour of selenium.

The reduction of sulphate to sulphide 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; Colàs et al. 2021b).

4.1.24 Sn

Tin is a pseudo-metallic, easily hydrolysable element normally existing in +II and +IV redox states. The main parameters affecting the chemistry of this element are the pH and Eh of the system. Under the low Eh conditions driving the redox of the three different studied scenarios, $SnO_2(am)$ or $CaSn(OH)_6(s)$ may control the tin solubility (Figure 38).



Figure 38. Eh vs pH Predominance Diagram for Tin Calculated Using Phase2-TDB. [Ca]_T = 1.1 m; [Cl] = 5.5 m; [Sn]_T = 10^{-6} m. Red Dots Indicates pH/Eh Conditions for Scenario 1, 2 and 3 Groundwaters at 25°C. Green Dashed Lines Stand for the Water Stability Field

4.1.24.1 Sn Solubility in Scenario 1

Under Scenario 1 conditions, the amorphous phase $SnO_2(am)$ is the more likely solubility limiting solid. The solid phase $CaSn(OH)_6(s)$ would be formed at more alkaline conditions (see Figure 38).

The Sn solubility and speciation, assuming $SnO_2(am)$ as the solubility limiting phase, are shown in Table 141 and Table 142 respectively.

 Table 141: Tin Solid Phases and Concentrations under Scenario 1 Conditions. The

 Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Scenario 1		
Solid phase	Concentration (m)	
SnO₂(am)	3.56·10 ⁻⁸	
CaSn(OH) ₆ (s)	2.64·10 ⁻⁵	

	Scenario 1	
Solid phase	Speciation	
SnO ₂ (am)	Sn(OH)4	97%
	SnCl ₄ ²⁻	3%

4.1.24.2 Sn Solubility in Scenario 2

In Scenario 2, the groundwater pH is more alkaline than in Scenario 1; in this case, $CaSn(OH)_6(s)$ may limit Sn solubility (Table 143).

The calculated aqueous speciation is shown in Table 144. The fact that no Pitzer coefficients are available in the calculation limits the accuracy of the speciation analysis.

Table 143: Tin Solid Phases and Concentrations under Scenario 2 Conditions. The Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Scenario 2		
Solid phase	Concentration (m)	
SnO ₂ (am)	1.47·10 ⁻⁷	
CaSn(OH)₀(s)	2.53-10 ⁻⁹	

Table 144: Tin Speciation under Scenario 2 Conditions

Scenario 2		
Solid phase	Spe	eciation
	Sn(OH)62-	31%
CaSn(OH) ₆ (s)	Sn(OH)₅⁻	28%
	Sn(OH)₄	24%
	SnCl ₄ 2-	6%
	Sn(OH) ₂	6%
	Sn(OH)́₃⁻	5%

4.1.24.3 Sn Solubility in Scenario 3

Calculated Sn solubility in Scenario 3 is similar to that in Scenario 2, $CaSn(OH)_6(s)$ being the most likely solubility limiting solid phase (Table 145). However, under these conditions the predominant aqueous species is $SnCl_4^{2-}$ (Table 146). As in the previous case, the fact that no Pitzer coefficients are available limits the accuracy of the speciation analysis.

 Table 145: Tin Solid Phases and Concentrations under Scenario 3 Conditions. The

 Bold Corresponds to the Most Likely Solubility Controlling Solid and Solubility

Scenario 3		
Solid phase	Concentration (m)	
SnO ₂ (am)	2.14·10 ⁻⁷	
CaSn(OH) ₆ (s)	7.68-10 ⁻⁸	

Scenario 3		
Solid phase	Speciation	
	SnCl ₄ ²⁻	73%
CaSn(OH) ₆ (s)	Sn(OH)₄	16%
	Sn(OH)₅⁻	4%
	Sn(OH) ₂	4%
	Sn(OH)62-	1%
	Sn(OH)₃⁻	1%

Table 146: Tin Speciation under Scenario 3 Conditions

4.1.24.4 Uncertainties

The absence of Pitzer coefficients for Sn species in the database limits the accuracy of the speciation analysis.

In addition, in the presence of sulphide, tin may precipitate as tin sulphides, which would affect its aqueous concentration (see Section 4.2.1).

4.1.25 Sr

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

4.1.25.1 Sr Solubility in Scenario 1

In Scenario 1, the strontium concentration is the same as the concentration in the SR-290-PW reference groundwater (see Table 20).

When using Phase2-TDB, strontianite (SrCO₃(s)) and celestite (SrSO₄(s)), which are relevant Sr solid phases, are slightly undersaturated. This agrees with the porewater characteristics described in Raven et al. (2011). Strontium aqueous speciation is dominated by the free Sr²⁺ ion (Table 147).

Table 147: Strontium concentration and S	peciation under Scenario 1 Conditions
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Scenario 1		
Concentration (m)	Spec	ciation
1.40·10 ⁻²	Sr2+	100%
(Table 20)	51-1	100 %

4.1.25.2 Sr Solubility in Scenario 2

The strontium concentration in this Scenario is the one calculated for Scenario 2 conditions (see Table 20).

Strontium aqueous speciation is dominated by the free Sr²⁺ ion (Table 148). The effect of steel canister corrosion on Sr chemistry is negligible, as neither Eh/pH nor the iron content is affecting Sr solubility or speciation.

Scenario 2		
Concentration (m)	Spe	eciation
1.40·10 ⁻² (Table 20)	Sr ²⁺	100%

Table 148: Strontium Concentration and Speciation under Scenario 2 Conditions

4.1.25.3 Sr Solubility in Scenario 3

The strontium concentration in this Scenario is the one calculated for Scenario 3 conditions (see Table 20). No relevant differences are observed in Scenario 3 results in comparison with Scenario 1 or Scenario 2 (Table 149).

Table 149: Strontium Concentration and Speciation under Scenario 3 Conditions

	Scenario 3	
Concentration (m)	Speci	ation
1.40·10 ⁻²	Cr 2+	100%
(Table 20)	31-1	100%

4.1.25.4 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 $CaCO_3(s)$.

4.1.26 Tc

Technetium is a redox sensitive element which may appear in several redox states (+II to +VII), although the most stable redox states are Tc(+IV) under reducing conditions and Tc(+VII) under oxidizing conditions.

The formation of technetium aqueous species and solid phases depends on the master variables Eh and pH of groundwater. Under the reducing conditions of the selected groundwaters, the main aqueous species for technetium is the hydroxocomplex TcO(OH)₂(aq). Concerning the solid phases, the amorphous hydrous oxide TcO₂·1.6H₂O(s) has been selected as the solid phase limiting the technetium solubility.

4.1.26.1 Tc Solubility in Scenario 1

Tc solubility and speciation for Scenario 1 are shown in Table 150 and Table 151. The most likely solid phase limiting the Tc solubility is $TcO_2 \cdot 1.6H_2O(s)$, $TcO(OH)_2(aq)$ being the main aqueous species in solution.

Table 150: Technetium Solid Phase and Concentration under Scenario 1 Conditions

Scenario 1			
Solid phase Concentration (m)			
TcO ₂ 1.63H ₂ O(s)	4.82·10 ⁻⁹		

Table 151: Technetium Speciation under Scenario 1 Conditions

Scenario 1				
Solid phase	Spec	iation		
	TcO(OH) ₂	98%		
TCO2: 1.03H2O(S)	Tc(OH) ₂ CO ₃	2%		

4.1.26.2 Tc Solubility in Scenario 2

Similar 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, Tc solubility and speciation calculated in Scenario 2 (Table 152 and Table 153) are similar to the ones obtained under Scenario 1 conditions.

Table 152: Technetium Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2			
Solid phase	Concentration (m)		
TcO2 1.63H2O(s)	4.74·10 ⁻⁹		

Table 153: Technetium Speciation under Scenario 2 Conditions

Scenario 2				
Solid phase	Speciation			
	TcO(OH) ₂	99%		
1002-1.03H2O(S)	TcO(OH)₃ ⁻	1%		

4.1.26.3 Tc Solubility in Scenario 3

Assuming $TcO_2 \cdot 1.6H_2O(s)$ as the Tc solubility limiting phase, Tc solubility and speciation results in Scenario 3 (Table 154 and Table 155) are almost identical to those of Scenario 1 and Scenario 2.

Table 154: Technetium Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3			
Solid phase Concentration (m)			
TcO ₂ .1.63H ₂ O(s)	4.72·10 ⁻⁹		

Table 155: Technetium Speciation under Scenario 3 Conditions

Scenario 3			
Solid phase	Specia	ation	
TcO ₂ .1.63H ₂ O(s)	TcO(OH) ₂	100%	

4.1.26.4 Uncertainties

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 very reduced Tc(III) species, and the consequent omission of these species from the thermodynamic database, may also introduce some uncertainty in the calculations.

4.1.27 Th

Thorium is a non-redox tetravalent actinide. 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.

Carbonate can control the aqueous speciation of thorium in groundwater at neutral pH values, while hydrolyzed species will become more relevant under acidic or alkaline pH and lower carbonate concentration conditions. An extensive discussion on thermodynamic data selection for this element is provided in Section 2.

4.1.27.1 Th Solubility in Scenario 1

Thorium solubility is expected to be controlled by an amorphous Th hydroxide solid $(Th(OH)_4(am))$ under Scenario 1 conditions (see Table 156). The aqueous speciation is dominated by Th aqueous hydroxides (Table 157).

Table 156: Thorium Solid Phase and Concentration under Scenario 1 Conditions

Scenario 1		
Solid phase Concentration (m)		
Th(OH)₄(am)	5.49·10 ⁻⁵	

Scenario 1				
Solid phase	Spe	ciation		
Th(OH)₄(am)	ThOH ³⁺ Th(OH) ₂ ²⁺	98% 2%		

Table 157: Thorium Sp	peciation under	Scenario 1	Conditions
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The Th solubility and speciation were calculated and compared using 3 different thermodynamic databases (Phase2-TDB, THEREDA and the modified ThermoChimie database).

As seen in Table 158, both Phase2-TDB and THEREDA (with Pitzer approach) provide very similar solubilities, leading to Th concentrations in solution around 10^{-5} m. However, the calculated speciation is very different; THEREDA predicts that Th(CO₃)₅⁶⁻ dominates aqueous Th chemistry (see the discussion about the formation of pentacarbonate species in Section 4.1.13). Thorium hydrolysis species (ThOH³⁺, Th(OH)₂²⁺ and Th(OH)₃⁺) are not included in THEREDA; as a consequence, the aqueous speciation calculated with this database at acidic pH values is unrealistic.

The modified ThermoChimie database, which uses SIT approach, predicts a lower Th solubility. Its speciation is dominated by thorium fluorides; those aqueous species are not included neither in Phase2-TDB nor in THEREDA.

Finally, it should be mentioned that Phase2-TDB does not have Pitzer coefficients for ThOH³⁺, Th(OH)₂²⁺ and Th(OH)₃⁺. This increases the uncertainty of the calculations in this Scenario, especially for the species with higher charge (ThOH³⁺).

Table 158: Comparison of Calculated Th(OH)₄(am) Solubilities and Speciation with Different Databases under Scenario 1 Conditions

Th(OH)₄(am)	Scenario 1					
Concentration (m)	Phase 2-TDB (Pitzer) 5.49⋅10 ⁻⁵		THEREDA (Pitzer) 2.41⋅10 ⁻⁵		Modified ThermoChimie (SIT) 3.44·10 ⁻⁸	
Speciation	ThOH ³⁺ Th(OH)2 ²⁺	98% 2%	Th(CO₃)₅ ⁶⁻	99%	ThF ³⁺ Th(OH) ₃ + ThF2 ²⁺ Th(OH)2 ²⁺ ThOH ³⁺	43% 21% 16% 14% 3%

Figure 39 shows the solubility of hydrous Th(IV) oxide in 3 m NaCl solution reported by Felmy et al. (1991) and the corresponding solubility and speciation calculated using Phase2-TDB (Figure 39 left) and modified ThermoChimie (Figure 39 right). Notice that Felmy et al. (1991) indicates that the experimental data at pH > 7 is not reliable because the Th concentrations are too close to the analytical detection limit. At the pH of interest for Scenario 1 (pH = 5.5), Phase2-TDB overestimates the experimental data, and modified ThermoChimie underestimates the experimental data, in agreement with the analysis shown above (Table 158). The main difference in speciation is the predominance of the ThOH³⁺ species predicted by Phase2-TDB, for which no Pitzer coefficients are available. Finally, the thorium hydroxide solid in modified

ThermoChimie database is more crystalline; thorium hydroxide solubility is in fact very sensitive to the ageing effects and particle size variation of the solid.



Figure 39. Solubility of Hydrous Th(IV) Oxide in 3 m NaCl Solution and Underlying Calculated Speciation. Symbols: Experimental Data from Felmy et al. (1991). Lines: Calculated using Phase2-TDB (Left) or Modified ThermoChimie (Right)

The comparison allows to identify the uncertainties associated to this calculation and point out that, although the Phase2-TDB provides reasonable results, the Th solubility may be slightly overestimated in Scenario 1.

4.1.27.2 Th Solubility in Scenario 2

The Th solubility and speciation for Scenario 2 calculated using Phase2-TDB are shown in Table 159 and Table 160, respectively. As Th is a non-redox sensitive element, the impact of Eh variation between Scenario 2 and Scenario 1 is negligible; on the contrary, the pH increase (pH = 7.82 in Scenario 2, pH = 5.5 in Scenario 1) has an impact on both calculated solubility and speciation.

Pitzer mixing terms θ (Th(CO₃)₅⁶⁻/Cl⁻) and Ψ (Th(CO₃)₅⁶⁻/Cl⁻/Na⁺) are included in the database Phase2-TDB (see discussion in Section 4.1.13) and the pentacarbonate species Th(CO₃)₅⁶⁻ does not have an impact in the calculated solubilities.

Table 159: Thorium Solid Phase and	d Concentration under	Scenario 2 Conditions
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Scenario 2		
Solid phase Concentration (m)		
Th(OH)₄(am)	7.00·10 ⁻⁹	

Scenario 2				
Solid phase	Speci	ation		
-	Th(OH)4	52%		
Th(OH)₄(am)	Th(OH) ₃ (CO ₃) ⁻	42%		
	Th(OH)₃⁺	6%		

Table 160: Thorium Speciation under Scenario 2 Conditions

4.1.27.3 Th Solubility in Scenario 3

Calculated solubility and speciation results for Scenario 3 by Phase2-TDB are shown in Table 161 and Table 162. Differences observed between Scenario 2 and Scenario 3 are related to the higher carbonate concentration and the lower pH value in Scenario 3 (Table 20).

Table 161: Thorium Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3				
Solid phase Concentration (m)				
Th(OH) ₄ (am) 2.03·10 ⁻⁸				

Table 162: Thorium Speciation under Scenario 3 Conditions

	Scenario 3		
Solid phase	Speci	ation	
	Th(OH)₃(CO₃)⁻	68%	
Th(OH)₄(am)	Th(OH)₄	18%	
-	Th(OH)₃⁺	9%	

4.1.27.4 Uncertainties

The main uncertainty is related to the lack of Pitzer parameters for Th hydrolysis species in the Phase2-TDB database, especially in the Scenario 1 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.

4.1.28 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. An extensive discussion on thermodynamic data selection for this element is provided in Section 2.

For tetravalent actinide elements, $An(CO_3)_5^{6-}$ may appear in high ionic strength solutions (see the discussion in the Np case, Section 4.1.13). Three different databases described in Section 2 (Phase2-TDB, THEREDA and the modified ThermoChimie database) have been used to evaluate the accuracy of calculations involving this species.

4.1.28.1 U Solubility in Scenario 1

Under the conditions of Scenario 1, following the Ostwald's principle, the amorphous hydroxide $U(OH)_4(am)$ was selected instead of the crystalline oxide as the most likely U solubility limiting phase.

All the three different databases (Phase2-TDB, THEREDA and the modified ThermoChimie database) include this solid; in all cases their associated stability constants are nearly identical. The stability constant associated to $U(CO_3)_5^{6-}$ is similar in all databases (see Eq. 7). The main difference among the databases is the approach used to handle ionic strength corrections (Pitzer or SIT).

$$U^{4+} + 5CO_3^{2-} = U(CO_3)_5^{6-}$$
 log K°=32.35 (Phase2-TDB)
log K°=32.35 (THEREDA) Eq. 7
log K°=34.00 (Modified ThermoChimie)

The solubility and speciation of U calculated using different databases are shown in Table 163. U shows similar behaviour as that of neptunium. Both Phase2-TDB and THEREDA (with Pitzer approach) provide very similar results, leading to calculated U solubilities around 10^{-5} m, with the U aqueous chemistry being dominated by the pentacarbonate complex U(CO₃)₅⁶⁻. Pitzer mixing terms θ (U(CO₃)₅⁶⁻/Cl⁻) and Ψ (U(CO₃)₅⁶⁻/Cl⁻/Na⁺) are not available, although they are required to properly predict the U(CO₃)₅⁶⁻ formation in high ionic strength media.

On the contrary, the modified ThermoChimie database, which includes $U(CO_3)_5^{6-}$ but uses SIT approach, predicts a much lower U solubility. The speciation is predicted to be dominated by U(+IV) and U(+VI) hydrolysis species, $U(CO_3)_5^{6-}$ does not play a role in U speciation (Table 163).

Table 163: Comparison of Calculated U(OH)₄(am) Solubilities and Speciation with Different Databases under Scenario 1 Conditions

U(OH)₄(am)		Scenario 1		
	Phase 2-TDB (Pitzer)	THEREDA (Pitzer)	Modified ThermoChimie (SIT)	
Concentration (m)	3.11·10 ⁻⁵	5.71·10 ⁻⁵	5.86·10 ⁻⁹	
Speciation	U(CO ₃)5 ⁶⁻ 100%	U(CO ₃)5 ⁶⁻ 100%	U(OH) ₄ 42% UO ₂ (OH) ₂ 38% U(OH) ₃ + 18%	

In order to constrain a solubility range for U, we have used Phase2-TDB with and without including $U(CO_3)_5^{6-}$ in the calculations. With this approach, we can obtain an upper-limit, very conservative value (defined by the formation of $U(CO_3)_5^{6-}$), and a more realistic value, similar to

the one calculated with the SIT approach (without taking into account $U(CO_3)_5^{6-}$). The calculated solubility and the associated speciation are shown in Table 164 and Table 165 respectively.

Table 164: Uranium Solid Phase and	Concentration under	Scenario 1 Conditions

Scenario 1					
Solid phase Concentration (m)					
-	Including $U(CO_3)_5^{6-}$ Without including $U(CO_3)_5^{6-}$				
U(OH) ₄ (am) 3.11·10 ⁻⁵ 8.74·10 ⁻⁹					

Table 165: Uranium Speciation under Scenario 1 Conditions

Scenario 1				
Solid phase	olid phase Speciation			
-	Including U	J(CO ₃)5 ⁶⁻	Without inclu	ding U(CO ₃) ₅ 6-
U(OH)₄(am)	U(CO ₃)5 ⁶⁻	100%	U(OH)4	42%
			UO ₂ (OH) ₂	38%
			U(OH) ₃ +	18%

4.1.28.2 U Solubility in Scenario 2

The U solubility and speciation for Scenario 2 are shown in Table 166 and Table 167, respectively. The groundwater Eh decrease and pH increase in Scenario 2 (in comparison with Scenario 1) has an impact on both calculated solubility and speciation; U(+VI) species are not expected to be formed in the aqueous phase under Scenario 2 conditions.

As in the previous Scenario 1, we have used Phase2-TDB with and without including $U(CO_3)_5^{6-1}$ in the calculations to constrain a range for U solubility.

Table 166: Uranium Solid Phase and Concentration under Scenario 2 Conditions

Scenario 2					
Solid phase	blid phase Concentration (m)				
	Including U(CO ₃) ₅ ⁶⁻ Without including U(CO ₃) ₅ ⁶⁻				
U(OH)4(am)	5.82·10 ⁻⁸	3.66·10 ⁻⁹			

Table 167: Uranium Speciation under Scenario 2 Conditions

Scenario 2				
Solid phase Speciation				
	Including U(CO ₃) ₅ ⁶⁻ Without including U(CO ₃) ₅ ⁶⁻			
U(OH)₄(am)	U(CO ₃) ₅ ⁶⁻	94%	U(OH)4	100%
	U(OH) ₄	6%	. ,	

4.1.28.3 U Solubility in Scenario 3

Uranium solubility and speciation under Scenario 3 conditions (Table 168 and Table 169) is similar to that calculated in Scenario 2.

Table 168: Uranium Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3					
Solid phase Concentration (m)					
-	Including U(CO ₃) ₅ ⁶⁻ Without including U(CO ₃) ₅ ⁶⁻				
U(OH)4(am)	6.03·10 ⁻⁶	3.69·10 ⁻⁹			

Table 169: Uranium Speciation under Scenario 3 Conditions

Scenario 3				
Solid phase Speciation				
-	Including	U(CO ₃)5 ⁶⁻	Without includ	ing U(CO₃)₅ ⁶⁻
U(OH)₄(am)	U(CO ₃) ₅ ⁶⁻	100%	U(OH) ₄	99%
			U(OH) ₃ +	1%

4.1.28.4 Uncertainties

As in the case of Np, the main uncertainty associated to U is the lack of the appropriate Pitzer parameters for $An(CO_3)_5^{6-}$, which introduces high uncertainties in the calculated results.

4.1.29 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.

4.1.29.1 Zr Solubility in Scenario 1

In Scenario 1 conditions, the hydroxide solid phase $Zr(OH)_4$ (am, aged) is expected to limit the solubility of zirconium (Table 170), $Zr(OH)_4$ (aq) being the predominant aqueous species (Table 171).

Although Zr is a tetravalent element, $Zr(CO_3)_5^{6-}$ is not included in thermodynamic databases; thus, the evaluation of its chemistry is different from that of Np(+IV) or U(+IV). However, it should be noticed that another highly-charged carbonate species, $Zr(CO_3)_4^{4-}$, appears in the speciation calculations.

Table 170: Zirconium Solid Phase and Concentration under Scenario 1 Conditions

Scenario 1				
Solid phase Concentration (m)				
Zr(OH)4 (am, aged)	1.97·10 ⁻⁸			

Table 171: Zirconium Speciation under Scenario 1 Conditions

Scenario 1				
Solid phase	Specia	tion		
Zr(OH) (am agod)	Zr(OH)₄(aq)	93%		
ZI(OH)4 (alli, ageu)	Zr(CO ₃) ₄ ⁴⁻	7%		

4.1.29.2 Zr Solubility in Scenario 2

Zr is a non-redox sensitive element, thus the redox decrease in Scenario 2 (in comparison with Scenario 1) will not affect its chemistry.

In Scenario 2 conditions, the oxide solid phase $Zr(OH)_4$ (am, aged) is expected to limit the solubility of zirconium (Table 172), $Zr(OH)_4$ (aq) being the predominant aqueous species (Table 173).

Table 172: Zirconium Solid Phase and Concentration under Scenario 2 Conditions

	Scenario 2			
Solid phase	Concentration (m)			
Zr(OH)4 (am, aged)	1.82·10 ⁻⁸			

Table 173: Zirconium Speciation under Scenario 2 Conditions

Scenario 2			
Solid phase	Specia	tion	
Zr(OH)4 (am, aged)	Zr(OH)₄(aq)	100%	

4.1.29.3 Zr Solubility in Scenario 3

Zr solubility and speciation results for Scenario 3 (Table 174 and Table 175) are identical to those of Scenario 2, as Zr is not affected by the pH decrease.

Table 174: Zirconium Solid Phase and Concentration under Scenario 3 Conditions

Scenario 3				
Solid phase Concentration (m)				
Zr(OH)4 (am, aged)	1.82·10 ⁻⁸			

Scenario 3			
Solid phase Speciation			
Zr(OH)₄ (am, aged)	Zr(OH)₄(aq)	100%	

4.1.29.4 Uncertainties

The main uncertainties in the evaluation of Zr solubility is the formation of polynuclear species. The solubility calculations have been performed excluding the polynuclear species $(Zr_3(OH)_4^{8+}, Zr_4(OH)_{15}^+ \text{ and } Zr_4(OH)_{16})$ from the database.

4.2 SENSITIVITY ANALYSIS: SULPHIDE OR PHOSPHATE EFFECT

4.2.1 Effect of sulphide

According to the NWMO, sulphide concentrations in the reference groundwater SR-290-PW were below detection limit. As such, $1.6 \cdot 10^{-5}$ m was defined by NWMO as an upper bound (maximum) for its use in model parameterizations. The presence of sulphide has not been taken into account in the previous calculations; however, a sensitivity analysis is performed in the present sub-section to assess the uncertainty related to the presence of this element in Scenario 1 solubility and speciation calculations.

Additional sulphate to sulphide reduction has not been taken into account, as sulphate reduction is normally microbiologically mediated, and the microbial activity has not been considered in this study.

If sulphide concentrations of 1.6·10⁻⁵ m are included in Scenario 1 calculations, the formation of sulphide solids could significantly decrease the solubility of elements Ag, Bi, Cd, Cu, Hg, Mo, Pb, Pd, Sb and Sn (see Table 176), although the formation of such insoluble phases could be limited by kinetic constrains.

Bi, Mo, Sb and Sn can form strong complexes with sulphide; however, the lack of thermodynamic data prevents a quantitative evaluation.

In the case of Hg, the equilibrium with HgS(s) results in very low calculated solubilities ($\sim 10^{-12}$ m). Further evidence of the formation of this solid under the studied conditions would be desirable.

Finally, the equilibration with PdS(s) in the calculations results in extremely low aqueous palladium concentrations ($\sim 10^{-29}$ m), as the thermodynamic data used for PdS(s) corresponds to that of visotskite, a very crystalline phase studied under high temperature experiments.

Element	Scen Base	ario 1 case	Scenario 1 Sensitivity case: Sulphide *			
	Solid phase*	Solubility (m)	Solid phase	Solubility (m)	Speciati	on
Ag	n.s.l.	-	Ag₂S (Acanthite)	1.00·10 ⁻³	AgCl ₄ ³⁻	100%
Bi	n.s.l.	-	Lack of thermoo	dynamic data for B	Bi-sulphide systen	n
Cd	n.s.l.	-	CdS(s)	1.67·10 ⁻⁷	CdCl42-	99%
Cu	n.s.l.	-	CuS(s)	2.84·10 ⁻⁶	CuCl ₃ ²⁻	99%
Hg	See Section 4.1	.10.4	HgS(s)	1.61·10 ⁻¹²	HgS(HS) ⁻ HgS HgS ₂ -²	43% 37% 11%
Мо	MoO ₂ (s)	2.36·10 ⁻¹³	Lack of thermo	dynamic data for N	1o-sulphide syste	т
Pb	n.s.l.	-	PbS(s) (Galena)	1.51·10 ⁻¹⁰	PbCl₂(aq) Pb(HS)₂(aq) PbCl⁺	98% 1% 1%
Pd	n.s.l.	-	Lack of thermo	dynamic data for F	Pd-sulphide solid	
Sb	Sb ₂ O ₃ (Valentinite)	3.86.10 ⁻⁵	Lack of thermodynamic data for Sb-sulphide system			m
Sn	SnO ₂ (am)	3.56·10 ⁻⁸	Lack of thermoo	dynamic data for S	Sn-sulphide syste	m

Table 176: Comparison of Solubility Results in the Absence (Base Case) and Presence(Sensitivity Case) of Sulphide for Scenario 1

* Calculated using sulphide concentrations of 1.6.10⁵ m, see text

4.2.2 Effect of phosphate

Phosphate concentration in the reference groundwater SR-290-PW was below detection limit. As such, $1 \cdot 10^{-6}$ m phosphate was defined by NWMO as an upper bound (maximum) for use in model parameterizations. The presence of phosphate has not been taken into account in the previous calculations; however, a sensitivity analysis is performed in the present sub-section to assess the uncertainty related to the presence of this element in Scenario 1 solubility and speciation calculations.

If phosphate concentration is taken into account, formation of phosphate solids may affect the solubility of Am and Pu (see Table 177). Phosphate may also have an effect on Th solubility; the lack of thermodynamic data for those systems does not allow to evaluate its influence under the studied conditions.

Table 177: Comparison of Solubility Results in the Absence (Base Case) and Presence(Sensitivity Case) of Phosphate

Flowert	0	Base case		Sensitivity case: Phosphate ^a		
Element	Scenario	Solid phase	Solubility (m)	Solid phase	Solubility (m)	
	Scenario 1	AmOHCO3(s)	3.50·10 ⁻³	AmPO ₄ (am)	2.05·10 ⁻⁹	
Am	Scenario 2	Am(OH)₃(s)	8.43·10 ⁻⁷	AmPO₄(am)	2.16·10 ⁻⁹	
	Scenario 3	Am(OH)₃(s)	4.52·10 ⁻⁶	AmPO ₄ (am)	4.73·10 ⁻¹⁰	
	Scenario 1	Pu(OH)₄(am)	1.93·10 ⁻³		b	
	Scenario 2	Pu(OH)₄(am)	4.36·10 ⁻⁵		0 50 40 10	
Pu		Pu(OH)₃(s)	1.59·10 ⁻⁵	PuPO ₄ (s)	2.53.10-10	
	o	Pu(OH)₄(am)	2.31.10-4		5.50·10 ⁻¹¹	
	Scenario 3	Pu(OH)₃(s)	8.67·10 ⁻⁵	PuPO ₄ (s)		

^a Calculated using phosphate concentrations of 1.10⁻⁶ m, see text for details ^b Pu(III)- phosphate solid is not expected to form in Scenario 1

5. CONCLUSIONS

The project: "NWMO Radionuclides Solubility Calculation (Phase 2)" aims at calculating the solubility limits for several chemical elements in a Canadian sedimentary reference groundwater (SR-290-PW). The work within this project 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.

The reference groundwater is highly saline, and the Pitzer model is preferred for ion activity correction in the calculations. Although the Pitzer model approach is used in some thermodynamic databases, none is complete enough to fulfill the needs of the extensive element list to be studied. Therefore, a specific thermodynamic database has been developed for its specific use in the calculations. The YMP dataset data0.ypf.R2 has been modified with additional information from the THEREDA database and the available Pitzer data from the literature. In several cases, additional data from ThermoChimie database has also been required to cover all the elements of interest. To minimize inconsistencies due to the mixture of sources, complete data sets (rather than individual species) are added to the database. Furthermore, preliminary speciation and solubility calculations have been performed to evaluate the accuracy of the database and identify the main uncertainties and data gaps.

The resulting dataset is named Phase2-TDB. Three different groups of elements have been identified in the database (Figure 40):

- Elements for which the amount of thermodynamic data (stability constants and associated Pitzer parameters) is enough to calculate the solubility under the conditions of interest in the present work with a reasonable degree of confidence. This includes most of the major elements (C, Ca, Fe, S, Sr) and some radionuclides and toxic elements (Ag, Am, Cs, Cu, Np, Pb, Pu, Ra, Th, U). Those elements are highlighted in green in Figure 40.
- Elements for which reliable Pitzer data are lacking (Bi, Cd, Pd, Se, Sn, Zr), highlighted in yellow in Figure 40.
- Elements for which the lack of thermodynamic information is a handicap, even for calculations at low ionic strengths. Those elements (Hg, Mo, Nb, Pa, Ru, Sb, Tc) are highlighted in red in Figure 40.



Figure 40: Periodic Table Showing the Elements of Interest in Present Work (in Colour). Green: Elements for which a Reasonable Amount of Thermodynamic Data are Available. Yellow: Elements for Which Relevant Pitzer Data are Lacking. Red: Elements for which the Lack of Thermodynamic Data is a Handicap

The composition of the groundwater can be affected by its interaction with the components of the repository near field. Three different scenarios are studied:

- Scenario 1 (SC1). Groundwater enters the canister without interacting with the bentonite buffer or the canister materials (SR-290-PW groundwater).
- Scenario 2 (SC2). Groundwater interacts with the carbon-steel container prior to contacting the waste. 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. This corrosion process will have an influence in the groundwater composition, increasing the alkalinity and the reducing character of the groundwater.
- Scenario 3 (SC3). Groundwater interacts with both bentonite buffer and the C-steel container prior to contacting the waste. Besides corrosion processes, bentonite chemical properties and cation exchange process will also influence the groundwater composition.

Different sensitivity cases have been considered in Scenario 2 and Scenario 3, in order to deal with uncertainties related to parameters such as corrosion rates, bentonite porosity and density, or maximum hydrogen fugacity. The results of the calculations have shown that the impact of those parameters in the final calculated groundwater compositions is small.

The thermodynamic database Phase2-TDB and the calculated groundwater compositions are then used in the solubility assessment, calculating the solubility limits for the elements of interest under the three different scenarios. The solid phase most likely to precipitate in the studied system at each Scenario is selected; in agreement with the Ostwald's rule, less crystalline phases are favoured in the selection. The aqueous concentration of the element studied is then given by equilibrium with the selected solid phase and the porewater composition. The corresponding aqueous speciation is also calculated. A semi-quantitative description of the main associated uncertainties in solubility and speciation calculations are also provided.

A summary of the calculated solubility results for the different scenarios is shown in (Table 178). When the calculated total aqueous element concentration in equilibrium with the studied solid is higher than 10⁻² m, the element has been considered to be non solubility limited (n.s.l.). The differences in the element solubility and speciation between Scenario 1 and Scenario 2 are mainly related 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. The differences in the element solubility and speciation between Scenario 2 and Scenario 3 are smaller. Sulphide and phosphate concentrations in the reference water are below the detection limit, and upper limit concentrations have been used in a specific sensitivity analysis.

Element	Scenario	Solid phase	Solubility 25°C (m)	Main sensitive parameters	Main uncertainties
	Scenario 1	n.s.l.*	-		
Ag	Scenario 2	n.s.l.*	-	Chloride	Formation of sulphides
	Scenario 3	n.s.l.*	-		
	Scenario 1	AmOHCO ₃ (s)	3.50·10 ⁻³		Pitzer effect on highly-
Am	Scenario 2	Am(OH) ₃ (s)	8.43·10 ⁻⁷	pH Carbonate	charged species Effect of phosphate
	Scenario 3	Am(OH)₃(s)	4.52·10 ⁻⁶		Effect of boron
	Scenario 1	n.s.l.*	-		Formation of sulphides Scarcity of thermodynamic data Lack of Pitzer parameters
Ві	Scenario 2	Bi ₂ O ₃ (s)	1.62·10 ⁻⁴		
	Scenario 3	n.s.l.*	-	-	
	Scenario 1	b	3.00·10 ⁻⁴		Formation of C(-IV)
с	Scenario 2	b	2.46·10 ⁻⁵	pH Calcium	
	Scenario 3	b	9.09·10 ⁻⁵		
	Scenario 1	b	1.17	рН	
Ca	Scenario 2	b	1.17	Carbonate Sulphate	Variations in carbonate and sulphate concentration
	Scenario 3	b	1.10	lon-exchange	
	Scenario 1	n.s.l.*	-		
Cd	Scenario 2	n.s.l.*	-	Chloride	Formation of sulphides Lack of Pitzer parameters
	Scenario 3	n.s.l.*	-		

Table 178: Main Results and Conceptual Uncertainties of the Solubility Calculations

Element	Scenario	Solid phase	Solubility 25°C (m)	Main sensitive parameters	Main uncertainties
	Scenario 1	n.s.l.*	-		
Cs	Scenario 2	n.s.l.*	-		Cation exchange
	Scenario 3	n.s.l.*	-		
	Scenario 1	n.s.l.*	-		
Cu	Scenario 2	Cu(cr)	1.88·10 ⁻⁸	Lh Chloride	Formation of sulphides
	Scenario 3	Cu(cr)	8.10·10 ⁻⁸		
	Scenario 1	b	1.00.10-4		
Fe	Scenario 2	b	6.66·10 ⁻³	Eh	Formation of sulphides
	Scenario 3	b	1.31·10 ⁻¹		
	Scenario 1	Hg ₂ Cl ₂ (cr)	2.65·10 ⁻⁷		Scarcity of thermodynamic data
Hg ^a	Scenario 2	Hg ₂ Cl ₂ (cr)	1.84·10 ⁻¹²	Eh Chloride	Lack of information for solid
	Scenario 3	Hg ₂ Cl ₂ (cr)	8.76·10 ⁻¹²		Formation of sulphides
	Scenario 1	MoO ₂ (s)	2.36·10 ⁻¹³		Coordity of thermodynamic
Мо	Scenario 2	MoO ₂ (s)	2.23·10 ⁻¹⁴	pH	Scarcity of thermodynamic data Formation of sulphides
	Scenario 3	MoO ₂ (s)	1.12·10 ⁻¹⁵	Calcium	
	Scenario 1	Nb ₂ O ₅ (s)	8.57·10 ⁻⁹	pH	Scarcity of thermodynamic data Formation of Ca-Nb phases
Nb	Scenario 2	Nb ₂ O ₅ (s)	2.84·10 ⁻⁵		
	Scenario 3	Nb ₂ O ₅ (s)	1.66·10 ⁻⁶	Calcium	
	Scenario 1	NpO ₂ ·2H ₂ O(am)	1.87·10 ⁻⁹		Lack of Pitzer parameters
Np	Scenario 2	NpO ₂ ·2H ₂ O(am)	1.16·10 ⁻⁹		
	Scenario 3	NpO ₂ ·2H ₂ O(am)	1.17·10 ⁻⁹		
	Scenario 1	Pa ₂ O ₅ (s)	6.50·10 ⁻⁸		
Ра	Scenario 2	Pa₂O₅(s)	1.35·10 ⁻⁹	рН	Scarcity of thermodynamic data
	Scenario 3	Pa₂O₅(s)	2.28·10 ⁻⁹		
	Scenario 1	n.s.l.*	-		Formation of sulphides
Pb	Scenario 2	PbCl(OH)	2.81.10-4	Chloride Carbonate	Uncertainty in
	Scenario 3	PbCl(OH)	1.30·10 ⁻³		thermodynamic data
	Scenario 1	n.s.l.*	-		
Pd	Scenario 2	n.s.l.*	-		Lack of Pitzer parameters Formation of sulphides
	Scenario 3	n.s.l.*	-		•
	Scenario 1	Pu(OH)4(am)	1.93·10 ⁻³	Eb.	Pitzer effect on highly-
Pu	Scenario 2	Pu(OH)4(am)	4.36·10 ⁻⁵	Carbonate	
	Scenario 3	Pu(OH)₄(am)	2.31.10-4	Sulphate	Effect of phosphate
Pa	Scenario 1	Ra(SO ₄)(s)	1.16.10-4	Sulphoto	Formation of colid colutions
Ra	Scenario 2	Ra(SO ₄)(s)	1.15.10-4	Sulphate	Formation of Solid-Solutions

Element	Scenario	Solid phase	Solubility 25°C (m)	Main sensitive parameters	Main uncertainties
	Scenario 3	Ra(SO ₄)(s)	6.61·10 ⁻⁵		
Rn	water/air partition coefficient			Ionic strength	Lack of information in high saline media
Ru ª	Scenario 1	n.s.l.*	-	Eh	Scarcity of thermodynamic
	Scenario 2	Ru(OH)₃·H₂O(s)	2.77·10 ⁻⁴	Chlorides	data Pitzer effect on highly-
	Scenario 3	Ru(OH)₃·H₂O(s)	1.32·10 ⁻³	Sulphates	charged species
	Scenario 1	b	3.10·10 ⁻³		
S	Scenario 2	b	3.10·10 ⁻³	Calcium	Formation of sulphides
	Scenario 3	b	5.27·10 ⁻³		
	Scenario 1	Sb ₂ O ₃ (Valentinite)	3.86·10 ⁻⁵		Scarcity of thermodynamic
Sb	Scenario 2	Sb ₂ O ₃ (Valentinite)	3.87·10 ⁻⁵		data
	Scenario 3	Sb ₂ O ₃ (Valentinite)	3.86·10 ⁻⁵		Formation of sulphides
	Scenario 1	FeSe ₂ (Ferroselite)	4.56·10 ⁻⁸		Dependency on iron
Se	Scenario 2	Fe _{1.04} Se(s)	1.18·10 ⁻⁸	Eh Iron	Lack of Pitzer parameters
	Scenario 3	Fe _{1.04} Se(s)	2.66·10 ⁻⁹		species
	Scenario 1	SnO ₂ (am)	3.56·10 ⁻⁸	Eh pH	Lack of Pitzer parameters Formation of sulphides
Sn	Scenario 2	CaSn(OH)6(s)	2.53·10 ⁻⁹		
	Scenario 3	CaSn(OH) ₆ (s)	7.68·10 ⁻⁸		
	Scenario 1	b	1.40·10 ⁻²		
Sr	Scenario 2	b	1.40·10 ⁻²	Sulphate Carbonate	Co-precipitation with other maior solids
	Scenario 3	b	1.40·10 ⁻²		
	Scenario 1	TcO ₂ ·1.63H ₂ O(s)	4.82·10 ⁻⁹		Scarcity of thermodynamic
Тс	Scenario 2	TcO ₂ .1.63H ₂ O(s)	4.74·10 ⁻⁹	Eh	data Formation of Tc(cr)
	Scenario 3	TcO ₂ ·1.63H ₂ O(s)	4.72·10 ⁻⁹		Formation of Tc(III) species
	Scenario 1	ThO ₂ (am, aged)	5.49·10 ⁻⁵		Pitzer effect on highly-
Th	Scenario 2	ThO2(am, aged)	7.00·10 ⁻⁹	Carbonate	charged species
	Scenario 3	ThO ₂ (am, aged)	2.03·10 ⁻⁸		Phosphate
	Scenario 1	U(OH)₄(am)	8.74·10 ⁻⁹	Eh	Lask of Ditage
U	Scenario 2	U(OH)₄(am)	3.66·10 ⁻⁹	pH	for highly-charged species
	Scenario 3	U(OH)₄(am)	3.69·10 ⁻⁹	Carbonale	·····
	Scenario 1	Zr(OH)₄(am, aged)	1.97·10 ⁻⁸		
Zr	Scenario 2	Zr(OH)4(am, aged)	1.82·10 ⁻⁸		Formation of polynuclear species
	Scenario 3	Zr(OH)4(am, aged)	1.82·10 ⁻⁸		

* n.s.l. – Not solubility limited. ^a Calculations for this element are tentative only ^b The solubility for this element is the element concentration in the groundwater for the three different scenarios

For major elements C, Ca, Fe, S and Sr (in brown in Figure 41), the concentration is those calculated for the groundwater at each Scenario.

The groundwaters studied are highly saline, with a significant concentration of chloride, sodium, and calcium. The chemistry of several elements of interest (Ag, Bi, Cd, Cu, Pb and Pd, in blue in Figure 41) is highly influenced by the complexation with chloride, and its solubility significantly increases due to the formation of metal-chloride complexes.

Even if the Phase2-TDB database utilizes the Pitzer approach for ionic strength corrections, uncertainties related to the lack of the appropriate set of Pitzer parameters are still significant. The species $An(+IV)(CO_3)_5^{6-}$ is a very specific example; the high charge of this species requires not only accurate log K° values, but also the inclusion of Pitzer mixing terms in the database in order to avoid unrealistic speciation results.

As a rule of thumb, the lack of Pitzer data affects more on those elements whose aqueous chemistry is dominated by species with charge 3 or higher. The comparison with other databases (especially with those using the SIT approach for ionic strength correction) can be a useful tool in order to identify the uncertainties associated to this data gap.

Besides the lack of Pitzer data, for some elements the thermodynamic data are scarce even for diluted systems. 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, thermodynamic data is scarce for Hg, Mo, Nb, Pa and Tc (in red in Figure 41). Ru is the most extreme case, and the calculations for this element are tentative only.

Finally, the aqueous concentration of some elements is expected to be limited by the formation of solid solutions or co-precipitation; this is especially relevant in the case of Ra, considering a pure phase as the solubility-limiting solid overestimates its concentration in solution.



Figure 41: Periodic Table Showing the Elements of Interest in Present Work (in Colour). Brown: Elements for which the Concentration is that Calculated for the Groundwater at Each Scenario. Blue: Elements for which Chloride Complexation Dominates the Aqueous Chemistry. Green: Elements for which the Formation of $An(CO_3)_5^{6-}$ Species has been Discussed. Red: Elements for which the Lack of Thermodynamic Data is a Handicap. Grey: Other Elements

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APPENDIX A: Pu(IV) Thermodynamic Data

Table A1 summarizes Pu(IV) species and its associated Log K° values included in Phase2-TDB.

Table A1: Pu(IV) Aqueous Species and Solid Compounds Included in Phase2-TDB for
which Original Data Source is THEREDA

Reaction	Log K°
$H_2O + Pu^{4+} = Pu(OH)^{3+} + H^+$	0.60
$2H_2O + Pu^{4+} = Pu(OH)_2^{2+} + 2H^+$	0.60
$3H_2O + Pu^{4+} = Pu(OH)_3^+ + 3H^+$	-2.30
$4H_2O + Pu^{4+} = Pu(OH)_4 + 4H^+$	-8.50
$CI^{-} + Pu^{4+} = PuCI^{3+}$	1.80
$SO_4^{2-} + Pu^{4+} = Pu(SO_4)^{2+}$	6.87
$2SO_4^{2-} + Pu^{4+} = Pu(SO_4)_2$	11.11
$4CO_3^{2-} + Pu^{4+} = Pu(CO_3)_4^{4-}$	37.00
$5CO_3^{2-} + Pu^{4+} = Pu(CO_3)_5^{6-}$	35.65
$2CO_3^{2-} + 2H_2O + Pu^{4+} = Pu(OH)_2(CO_3)_2^{2-} + 2H^+$	18.24
$4Ca^{2+} + 8H_2O + Pu^{4+} = Ca_4Pu(OH)_8^{4+} + 8H^{+}$	-57.00
$Pu(OH)_4(am) = 4OH^- + Pu^{4+}$	-58.33
APPENDIX B: Th(IV) Thermodynamic Data

Table B1 compares Th(IV) hydroxide, carbonate and hydroxycarbonate aqueous species and its associated Log K° values included in different databases.

Table B1: Th(IV) Hydroxide, Carbonate and Hydroxycarbonate Aqueous Species in YMP data0_ypf_R2, THEREDA and ThermoChimie version 10a. Last Column Shows Data Included in Phase2-TDB

Species	Log K° YMP	Log K THEREDA	Log K ThermoChimie	Log K Phase2-TDB
Th(OH) ³⁺	-2.2		-2.5	-2.2
Th(OH) ₂ ²⁺	-6		-6.2	-6
Th(OH)₃⁺	-11		-11	-11
Th(OH)₄(aq)	-17.5	-17.4	-17.4	-17.5
$Th_2(OH)_2^{6+}$	-5.7		-5.9	-5.7
Th ₂ (OH) ₃ ⁵⁺			-6.8	
Th ₄ (OH) ₈ ⁸⁺	-20.4		-20.4	-20.4
Th ₄ (OH) ₁₂ ⁴⁺	-26.6		-26.6	-26.6
Th ₆ (OH) ₁₄ ¹⁰⁺			-36.8	
Th ₆ (OH) ₁₅ 9+	-33.9		-36.8	-33.9
Th(CO₃)₅ ⁶⁻	32.33 ^(*)	29.1	31	29.1
Th(OH)(CO ₃) ₄ ⁵⁻			21.6	
Th(OH) ₂ (CO ₃)			2.5	
$Th(OH)_2(CO_3)_2^{2-1}$			8.8	
Th(OH) ₃ (CO ₃) ⁻		-1.72	-3.7	-1.72
Th(OH) ₄ (CO ₃) ⁻²			-15.6	

(*) The original Log K° = -19.314 in YMP database data0_ypf_R2 corresponds to a reaction written in terms of HCO_3^- . It has been rewritten in terms of $CO_3^{2^-}$ to allow comparison with other databases