R-10-50

Determination and assessment of the concentration limits to be used in SR-Can

Supplement to TR-06-32

Mireia Grivé, Cristina Domènech, Vanessa Montoya, David García, Lara Duro

Amphos 21

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SKB

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Abstract

This document complements and updates the report TR-06-32, *Determination and assessment of the concentration limits to be used in SR-Can* /Duro et al. 2006a/, in which the solubility limits of different radionuclides in the near field system and under the different scenarios selected by SKB were assessed.

Since 2006, several important changes in different fields affecting solubility assessment calculations have been reported. These changes basically concern some of the thermodynamic data used in the calculations and the groundwater compositions for scenarios of interest defined by SKB.

In this document we update the thermodynamic data corresponding to Ni, Zr, Th and U and we describe the thermodynamic database selected for Pb.

This document also reports the update of the assessment of the concentration limits to be used in SR-Can, which has been done considering the recent thermodynamic database updates and the new groundwater compositions of interest supplied by SKB.

Finally, we also present the Simple Functions spreadsheet tool, born from the need of having a confident and easy-to-handle tool to calculate solubility limits of some radionuclides under determined conditions in an agile and relatively fast manner.

Sammanfattning

Det här dokumentet kompletterar och uppdaterar rapporten TR-06-32 *Determination and assessment of the concentration limits to be used in SR-Can* /Duro m fl 2006a/, i vilken återfinns en utvärdering av löslighetsgränser för olika radionuklider i närfältet i de av SKB utvalda scenarierna.

Sedan 2006 har ett flertal olika viktiga förändringar rapporterats vad gäller beräkningar av uppskattade lösligheter. Dessa förändringar gäller i huvudsak några av de termodynamiska data som använts i beräkningarna, samt grundvattensammansättning i de olika scenarierna som analyseras av SKB.

I det här dokumentet uppdaterar vi termodynamiska data för Ni, Zr, Th, och U och vi beskriver den termodynamiska databasen som används för Pb.

Det här dokumentet uppdaterar också för Sr-Site den bedömning av koncentrationsgränser som användes i SR-Can. Denna uppdatering har gjorts med tanke på uppdateringarna av de termo-dynamiska databaserna och grundvattensammansättningarna som används i SR-Site.

Slutligen presenterar vi också verktyget Simple Functions vilket togs fram på grund av behovet av ett säkert och lätthanterligt verktyg för att snabbt och smidigt beräkna löslighetsgränser för vissa radionuklider under bestämda förhållanden.

Contents

1   Introduction

Within the frame of the SR-Can project, Amphos 21 (formerly Enviros Spain) assessed the solubility limits of different radionuclides in the near field system and under the different scenarios selected by SKB. This assessment was fully documented in the report TR-06-32, *Determination and assessment of the concentration limits to be used in SR-Can* /Duro et al. 2006a/.

In the calculations /Duro et al. 2006a/ used the thermodynamic database reported in the Technical Report TR-06-17 /Duro et al. 2006b/. /Duro et al. 2006b/ revised, modified, completed and/or updated the radionuclide dataset of NAGRA/PSI Chemical Thermodynamic Data base 01/01 /Hummel et al. 2002/ but not the major elements dataset (including oxides, halides, sulphur, nitrogen, phosphate, carbon, aluminium, calcium, iron, sodium, magnesium and silica).

Several updates and new sets of thermodynamic data have appeared since 2006. It is important to consider these changes because they may affect radionuclide solubility calculations and consequently, the assessment of their concentration limits (or solubility limits).

The assessment of solubility limits reported in /Duro et al. 2006a/ was based in 4 different groundwater compositions and 2 different scenarios: one in which the groundwater was supposed to interact with the fuel without interacting either with the buffer or the canister and another in which groundwater interacted with the fuel after being affected by the canister. Since 2006, SKB has modified the scenarios of interest and is currently considering a new set of groundwater compositions (listed in Table A-1, Appendix A) that may affect the radionuclide solubility limit calculations.

Calculations needed for a complete solubility assessment, such as that of /Duro et al. 2006a/, are done with complex geochemical tools and are, in general, time consuming. During these last years, the necessity of having a confident and easy-to-handle tool to calculate solubility limits in an agile and relatively fast manner has been revealed. Amphos 21 has created and developed a tool called Simple Functions spreadsheet especially designed for Performance Assessment exercises /Grivé et al. 2010/, which determines the solubility limits and the solid phases likely to exert the solubility control of some radionuclides under specific conditions.

The aim of this supplement is therefore three-fold:

*   Summarising the changes introduced in the thermodynamic database used to do the solubility calculations since 2006.
*   Summarising the changes in the solubility assessment due to changes of both the thermodynamic database and/or groundwater compositions.
*   Presenting the Simple Functions spreadsheet tool.

2 Update of the SKB thermodynamic database

The update of the SKB thermodynamic database has consisted in the inclusion of new thermodynamic data for Ni, Se, Zr and Th according to thermodynamic reviews conducted by NEA /Brown et al. 2005, Gamsjäger et al. 2005, Olin et al. 2005, Rand et al. 2009/ and in the selection of a set of thermodynamic data for Pb. These modifications are briefly summarised below.

Since 2006, some updates of thermodynamic data concerning Sulphur species /Grivé et al. 2008/ and Fe system /Arcos and Piqué 2009/ have also been considered although, as these changes do not directly affect calculations of Simple Functions spreadsheet tool they are not described here.

2.1 Nickel Thermodynamic data

Ni thermodynamic data come from the NEA review of /Gamsjäger et al. 2005/. In addition to their selection, we selected thermodynamic data for $Ni(OH)_2(aq)$ while the NEA selection omitted them. The reason that the NEA team gives for this omission is that available experimental values /Gayer and Garrett 1949, Tremaine and LeBlanc 1980, Ziemniak et al. 1989/ can be satisfactorily explained with $Ni(OH)_3^-$ as the only aqueous species in alkaline solutions. The NEA review also states that the constant of $Ni(OH)_3^-$ is the only hydrolysis constant that can be determined with reasonable certainty. Nevertheless, they do not deny the existence of this species /Gamsjäger et al. 2005/, and even an upper limit value is suggested for this complex. From a chemical point of view, each step in the formation of the hydrolysis behaviour occurs by the loss of successive protons and we preferred to give a complete hydrolysis scheme. Given that this species seems not strictly necessary to explain the available experimental data, we included the selection in the database for the second hydrolysis as an upper value, following the reasoning of the NEA team.
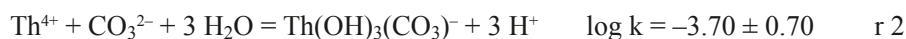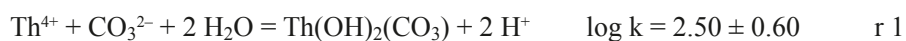
2.2 Zirconium Thermodynamic data

Zirconium data have been mainly selected from the Zirconium book of the NEA chemical Thermodynamics Series /Brown et al. 2005/.

Concerning the solid oxides and hydroxides, the NEA team has selected data corresponding to monoclinic $ZrO_2(cr)$ and to $Zr(OH)_4$ (am, fresh) solid phases. Two different groups of solubility data can be found in the literature at circumneutral pH values: a first group presenting Zr concentrations around 10^{-4} M, and a second one in the range $10^{-7}–10^{-10}$ M. Explaining zirconium solubilities of 10^{-7} M requires to consider the existence of an "aged" hydroxide with lower solubility. Therefore, we have selected the solid phase $Zr(OH)_4$(am, aged) with a log K^0_s value of -5.55 ± 0.20 (recalculated in /Brown et al. 2005/ from /Ekberg et al. 2004/).

2.3 Thorium Thermodynamic data

Thorium data have been mainly selected from the Thorium book of the NEA chemical Thermodynamics Series /Rand et al. 2009/.

Special attention has been paid to the formation of ternary hydroxide-carbonate complexes. Three mixed hydroxide-carbonate thorium species are selected in the NEA review: $Th(OH)(CO_3)_4^{5-}$, $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)_4(CO_3)^{2-}$. In addition, the complexes $Th(OH)_2(CO_3)(aq)$ and $Th(OH)_3(CO_3)^-$ have been found to be relevant at low carbonate concentrations in the near neutral pH range /Rand et al. 2009/. Although these two last species are not selected by the NEA team, /Rand et al. 2009/ recognise that they are relevant only at low carbonate concentrations in the near neutral range and recommend as guidance the use of the following stability constants to conduct thermodynamic calculations: (r 1 and r 2).

$$Th^{4+} + CO_3^{2-} + 2\ H_2O = Th(OH)_2(CO_3) + 2\ H^+ \qquad \log k = 2.50 \pm 0.60 \qquad r\ 1$$

$$Th^{4+} + CO_3^{2-} + 3\ H_2O = Th(OH)_3(CO_3)^- + 3\ H^+ \qquad \log k = -3.70 \pm 0.70 \qquad r\ 2$$
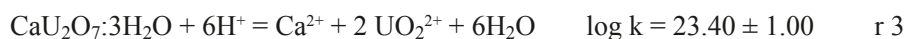
2.4 Uranium Thermodynamic data

Uranium data included in the database come from the NEA reviews /Guillaumont et al. 2003/ and /Grenthe et al. 1992/.

Uranates have been reported to precipitate under alkaline conditions /Brownsword et al. 1990/ giving solubilities between 2.5×10^{-8} to 3×10^{-6} mol/dm^3. Solubility calculations assuming the limiting solid phase $CaUO_4(cr)$ selected in the SKB thermodynamic database /Duro et al. 2006b/ gave unrealistic and very low concentrations of U. /Altmaier et al. 2005/ provided solubility constants for Ca-uranates ($CaU_2O_7 \cdot 3H_2O$ (s)) that seemed to be more realistic when performing solubility calculations under cementitious conditions.

Although the stability constant determined in /Altmaier et al. 2005/ is the only available thermodynamic data for this solid phase, it has been included in the Thermodynamic database (r 3). This is based on published experimental evidences on the existence of this solid under cementitious conditions (see for instance /Tits et al. 2008/ and /Meca et al. 2008/).

$$CaU_2O_7{:}3H_2O + 6H^+ = Ca^{2+} + 2\ UO_2^{2+} + 6H_2O \qquad \log k = 23.40 \pm 1.00 \qquad r\ 3$$

2.5 Lead thermodynamic data

The NAGRA/PSI Chemical Thermodynamic Data base 01/01 /Hummel et al. 2002/ does not include thermodynamic data for Pb.

This section includes the selection of the thermodynamic data for Pb aqueous species and solid phases. A good set of thermodynamic data for Pb is contained in /Blanc et al. 2006/ and this allowed the assessment of the solubility of this element. Some changes to the /Blanc et al. 2006/ selection have been conducted on the basis of different experimental criteria which are discussed later.

Thermodynamic data of the solubility limiting solids of Pb under the groundwater compositions of interest for SKB, and data on the aqueous species accounting for more than a 10% of the dissolved Pb are shown in Table 2-1 and Table 2-2.

The basic species of lead is Pb^{2+} and their thermodynamic data have been selected from the NEA selection of /Grenthe et al. 1992/.

Pb^{2+} is the main oxidation state of lead, although Pb^{4+} might appear at oxidizing redox potentials. Indeed, the stability field for $PbO_2(s)$ and $Pb_3O_4(s)$ is at Eh higher than +400 mV (Figure 2-1), which is out of the conditions of interest for SKB (Table A1). We have not selected these solids.

/Lothenbach et al. 1999/ presented an exhaustive review of the data in the literature and calculated the constants for mononuclear Pb(II) hydroxo complexes. According to /Lothenbach et al. 1999/, the species $Pb(OH)_4^{2-}$ only appeared at pH higher than 14. Some years later, /Perera et al. 2001/ measured the concentrations of Pb(II) hydroxo complexes by spectroscopy and demonstrated the existence of the species $Pb(OH)_4^{2-}$ at pH < 14. /Blanc et al. 2006/ compared the speciation schemes of both authors and proposed a mixed model in which log K values for $Pb(OH)^+$ and $Pb(OH)_2(aq)$ were selected from /Lothenbach et al. 1999/ and log K values for $Pb(OH)_3^-$ and $Pb(OH)_4^{2-}$ from /Perera et al. 2001/. We have adopted this selection. /Lothenbach et al. 1999/ do not provide uncertainties. We have assigned an uncertainty to the values coming from these authors which cover the range of equilibrium constants reported.

We have not selected any polymeric species given that they have been shown only to be important for Pb concentrations higher than 10^{-1} M /Lothenbach et al. 1999/. These high Pb concentrations are not expected to occur under the conditions of interest of SKB.

Figure 2-2 shows the distribution of hydroxide aqueous species as a function of pH with the speciation scheme proposed in this work.

Table 2-1 . Selected Pb aqueous species and their corresponding log K_{eq} values.

Aqueous species	Reaction	Log K_{eq}	Reference
$PbOH^+$	$Pb^{2+} + H_2O = PbOH^+ + H^+$	$-7.51 \pm 0.50^*$	/Blanc et al. 2006/ (from /Lothenbach et al. 1999/)
$Pb(OH)_2$ (aq)	$Pb^{2+} + 2 H_2O = Pb(OH)_2 + 2 H^+$	$-16.95 \pm 0.20^*$	/Blanc et al. 2006/ (from /Lothenbach et al. 1999/)
$Pb(OH)_3^-$	$Pb^{2+} + 3 H_2O = Pb(OH)_3^- + 3 H^+$	-27.20 ± 0.70	/Blanc et al. 2006/ (from /Perera et al. 2001/)
$Pb(OH)_4^{2-}$	$Pb^{2+} + 4 H_2O = Pb(OH)_4^{2-} + 4 H^+$	-38.90 ± 0.80	/Blanc et al. 2006/ (from /Perera et al. 2001/)
$PbCO_3$ (aq)	$Pb^{2+} + CO_3^{2-} = PbCO_3$	7.00 ± 0.50	/Blanc et al. 2006/
$Pb(CO_3)_2^{2-}$	$Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-}$	$10.13 \pm 0.50^*$	/Blanc et al. 2006/ (from /Lothenbach et al. 1999/)
$PbHPO_4$ (aq)	$Pb^{2+} + H_2PO_4^- = PbHPO_4 + H^+$	-4.11	/Nriagu 1974/
$PbH_2PO_4^+$	$Pb^{2+} + H_2PO_4^- = PbH_2PO_4^+$	1.50	/Nriagu 1974/
$PbSO_4$ (aq)	$Pb^{2+} + SO_4^{2-} = PbSO_4$	$2.82 \pm 0.20^*$	/Blanc et al. 2006/ (from /Lothenbach et al. 1999/)
$Pb(SO_4)_2^{2-}$	$Pb^{2+} + 2 SO_4^{2-} = Pb(SO_4)_2^{2-}$	$3.47 \pm 1.10^*$	/Blanc et al. 2006/ (from /Martell and Smith 1997/)
$PbCl^+$	$Pb^{2+} + Cl^- = PbCl^+$	$1.55 \pm 0.25^\#$	/Lothenbach et al. 1999/
$PbCl_2$ (aq)	$Pb^{2+} + 2 Cl^- = PbCl_2$	$2.00 \pm 0.30^\#$	/Lothenbach et al. 1999/
$PbCl_3^-$	$Pb^{2+} + 3 Cl^- = PbCl_3^-$	$2.01 \pm 0.50^\#$	/Lothenbach et al. 1999/
$PbCl_4^{2-}$	$Pb^{2+} + 4 Cl^- = PbCl_4^{2-}$	$1.35 \pm 0.25^\#$	/Lothenbach et al. 1999/

*Uncertainty assigned in this work. See text for explanations. # Uncertainty from /Blanc et al. 2006/

Table 2-2. Selected Pb solid phases and their corresponding log K_{eq} values.

Solid phases	Reaction	Log Keq	Reference
Pb (cr)	$Pb^{2+} + 2e^- = Pb(cr)$	-4.25 ± 0.07	/Lemire et al. 2001/
Litharge	$Pb^{2+} + H_2O = PbO + 2 H^+$	$-12.63 \pm 0.35^*$	/Blanc et al. 2006/ (from /Chase 1998/)
Massicot	$Pb^{2+} + H_2O = PbO + 2 H^+$	$-12.74 \pm 0.35^*$	/Blanc et al. 2006/ (from /Chase 1998/)
$Pb(OH)_2(s)$	$Pb^{2+} + 2 H_2O = Pb(OH)_2 + 2 H^+$	$-13.05 \pm 0.60^*$	/Lothenbach et al. 1999/
Cerussite	$Pb^{2+} + CO_3^{2-} = PbCO_3$	13.29 ± 0.69	/Blanc et al. 2006/ (from /Taylor and Lopata 1984/)
Hydrocerussite	$3 Pb^{2+} + 2 CO_3^{2-} + 2 H_2O = Pb_3(CO_3)_2(OH)_2 + 2 H^+$	17.91 ± 1.94	/Blanc et al. 2006/ (from /Taylor and Lopata 1984/)
Alamosite	$Pb^{2+} + Si(OH)_4 = PbSiO_3 + H_2O + 2 H^+$	-6.17 ± 0.74	/Blanc et al. 2006/ (from /Chase 1998/)
$PbSiO_3$ (am, s)	$Pb^{2+} + Si(OH)_4 = PbSiO_3 + H_2O + 2 H^+$	-6.60	/Blanc et al. 2006/ (from /Naumov et al. 1974/)
Pb_2SiO_4 (s)	$2 Pb^{2+} + Si(OH)_4 = Pb_2SiO_4 + 4 H^+$	-15.89 ± 2.56	/Blanc et al. 2006/ (from /Chase 1998/)
Phosgenite	$2 Pb^{2+} + CO_3^{2-} + 2Cl^- = Pb_2(CO)_3Cl_2$	-19.90	/Naumov et al. 1974/
$PbHPO_4$ (s)	$Pb^{2+} + H_2PO_4^- = PbHPO_4 + H^+$	4.25	/Nriagu 1974/
$Pb(H_2PO_4)_2(s)$	$Pb^{2+} + 2 H_2PO_4^- = Pb(H_2PO_4)_2$	9.84	/Nriagu 1974/
Hydroxipyromorphite	$5 Pb^{2+} + 3 H_2PO_4^- + H_2O = Pb_5(PO_4)_3OH + 7 H^+$	4.15	/Nriagu 1974/
Pyromorphite	$5 Pb^{2+} + 3 H_2PO_4^- + Cl^- = Pb_5(PO_4)_3Cl + 6 H^+$	25.75	/Nriagu 1974/
Pyromorphite–F	$5 Pb^{2+} + 3 H_2PO_4^- + F^- = Pb_5(PO_4)_3F + 6 H^+$	13.10	/Nriagu 1974/
Pyromorphite–Br	$5 Pb^{2+} + 3 H_2PO_4^- + Br^- = Pb_5(PO_4)_3Br + 6 H^+$	19.45	/Nriagu 1974/
$Pb_3(PO_4)_2(s)$	$3 Pb^{2+} + 2 H_2PO_4^- = Pb_3(PO_4)_2 + 4 H^+$	5.26 ± 0.20	/Nriagu 1974/
Anglesite	$Pb^{2+} + SO_4^{2-} = PbSO_4$	7.85 ± 0.13	/Lemire et al. 2001/
PbClOH(s)	$Pb^{2+} + Cl^- + H_2O = PbClOH + H^+$	-0.62	/Lothenbach et al. 1999/
Cotunnite	$Pb^{2+} + 2 Cl^- = PbCl_2$	4.81 ± 0.19	/Blanc et al. 2006/ (from /Chase 1998/)

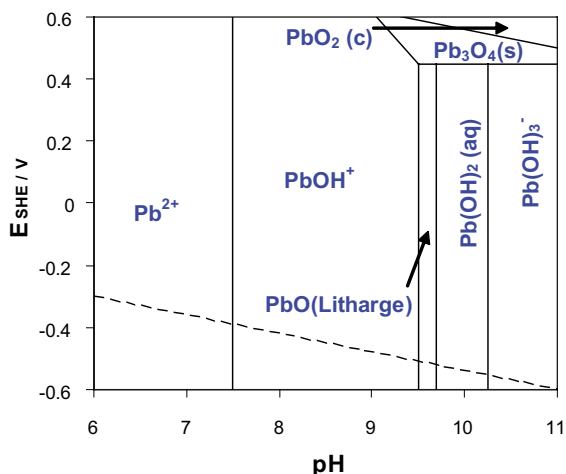*Uncertainty assigned in this work. See text for explanations.

Figure 2-1. *Predominance diagram (Eh vs pH) of the Pb system in which the stability fields of the Pb(IV) oxides are shown.* $[Pb]_{tot} = 10^{-4}$ *M.*
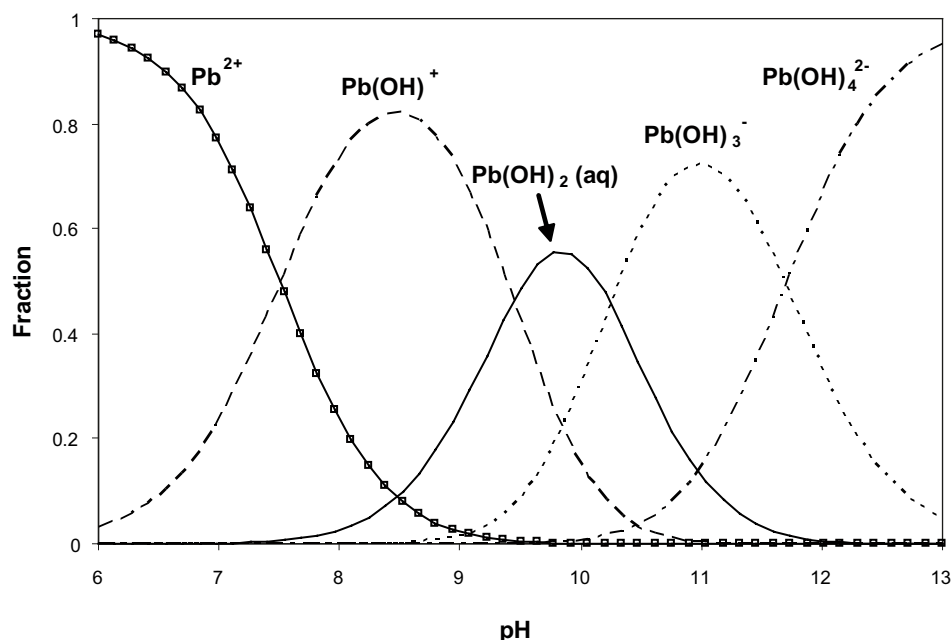

Figure 2-2. *Diagram showing the aqueous hydroxide species distribution as a function of pH (Eh = −0.25V; $[Pb]_{tot} = 10^{-6}$ M).*

We have selected two different Pb(II) solid oxides: litharge and massicot (PbO) with tetragonal and orthorhombic structures, respectively. Massicot is metastable at 25ºC /Blanc et al. 2006/. Stability constants for these two minerals have been taken from /Blanc et al. 2006/ (which come from calorimetric data of /Chase 1998/), and we have assigned an uncertainty covering the stability ranges reported in other works (/Wagman et al. 1982, Lothenbach et al. 1999/).

Since crystalline $Pb(OH)_2(c)$ is only stable at high temperatures (~300ºC) (/Marani et al. 1995, Lothenbach et al. 1999/), only stability data for amorphous $Pb(OH)_2(s, am)$ have been selected. /Cromières 1997/ selected the largest solubility value reported in literature ($logK_s^0 = −13.6$, from different sources) to be conservative in the assessment of the solubility limits. /Lothenbach et al. 1999/ suggested a value of −13.05 based upon the solubility data obtained by /Schock 1980/ and, /Blanc et al. 2006/ calculated a value from data reported in /Latimer 1952/ equal to −13.51. Given the resemblance between these three values we have kept the value provided by /Lothenbach et al. 1999/ and we have assigned an uncertainty of 0.6.

There are two solid carbonate phases that can exert the control of Pb solubility under the conditions of interest for SKB. They are cerussite ($PbCO_3(s)$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$). There are different sources of stability data for these solid phases, but in this selection we have kept the solubility constants of /Blanc et al. 2006/ which are consistent with the other values reported in literature (/Lothenbach et al. 1999, Cromières 1997/) and include uncertainties covering the range of the stability constants reported in the literature. /Blanc et al. 2006/ based their selection on the thermodynamic data of /Taylor and Lopata 1984/, who determined equilibrium conditions for each reaction in the solid interconversion sequence $PbO \leftrightarrow Pb_{10}O(OH)_6(CO_3)_6$ (Plumbonacrite) $\leftrightarrow Pb_3(OH)_2(CO_3)$ (Hydrocerussite) $\leftrightarrow PbCO_3$ (cerussite), in aqueous carbonate solutions near 25°C (changing I, pCO_2 and pH) and extrapolated their results to I = 0m. /Lothenbach et al. 1999/ derived the stability constant of cerussite and hydrocerussite by extrapolating to I = 0 m different stability constants obtained by other authors in solubility experiments (I≤0.3 m) and proposed a log K = 13.23 for cerussite and a log K = 17.64 for hydrocerussite. /Cromières 1997/ selected a stability constant for cerussite equal to log K = 12.80 ± 0.50 compiled from data in literature and pointed out the role of hydrocerussite as Pb solubility limiting mineral in natural groundwaters selecting a log K = 17.8 ± 2.50 for its stability, from NEA calculations and in concordance with the experimental results of /Schock and Gardels 1983/.

The aqueous carbonate speciation scheme also comes from /Blanc et al. 2006/. These authors selected the aqueous species $PbCO_3(aq)$ and $Pb(CO_3)_2{}^{2-}$ and proposed a log K = 7.00 ± 0.30 for the first aqueous carbonato complex, slightly lower than that proposed by /Lothenbach et al. 1999/, (log K = 7.30) and a log K = 10.13 for $Pb(CO_3)_2{}^{2-}$ (originally from /Lothenbach et al. 1999/). Values of /Lothenbach et al. 1999/ are derived from extrapolation to I = 0 m of experimental measurements reported in literature. We have assigned an uncertainty of 0.50 to the stability constant of $Pb(CO_3)_2{}^{2-}$ to cover the range of values reported in literature.

Figure 2-3 and Figure 2-4 show the distribution of Pb carbonato species and solid phases as a function of pH and carbonate concentration.
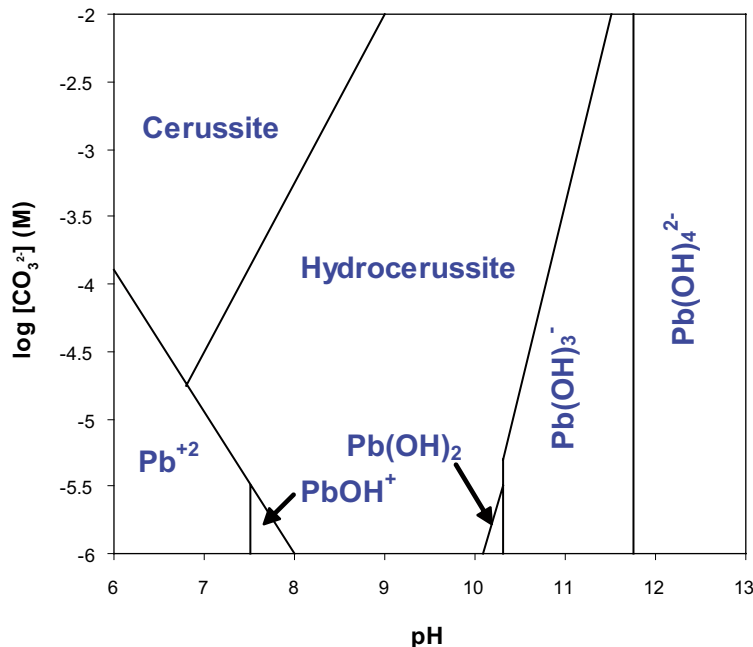

Figure 2-3. *Predominance diagram showing the stability field of Pb-carbonate solid phases as a function of pH and $[CO_3{}^{2-}]_{tot}$ (Eh = −0.25 V; $[Pb^{2+}]_{tot}$ = 10^{-5} M).*
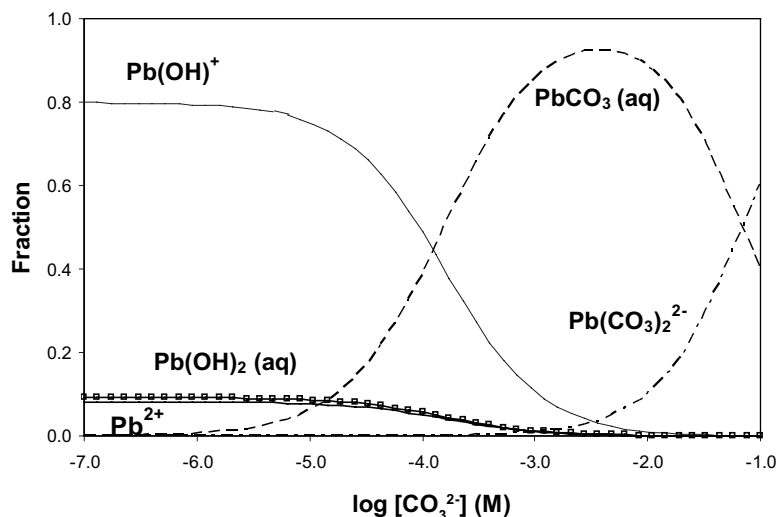
Figure 2-4. *Diagram showing the stability of carbonato species as a function of CO_3^{2-} concentration (Eh = –0.25V; pH=8.5; $[Pb^{2+}]_{tot} = 10^{-6} M$).*

We have not included in the selection the solids $PbCO_3.PbO(s)$ and $2 PbCO_3.PbO(s)$, mainly because these solids form from the decarbonation of cerussite at high temperatures and high $CO_2(g)$ pressures.

Concerning lead silicates, three different solids have been identified in the open literature: $PbSiO_3(am)$, alamosite ($PbSiO_3$) and $Pb_2SiO_4(s)$. We have kept the selection from /Blanc et al. 2006/, who suggested stabilities of, –6.60, –6.17 ± 0.74 and 15.89 ± 2.56, respectively, calculated from thermodynamic values of /Chase 1998/ and /Naumov et al. 1974/.

Pb nitrate aqueous complexes are weak complexes and as reported elsewhere /Cromières 1997/ the affinity of nitrate ions for Pb^{2+} is poor. Nitrate aqueous species only account for less than 1.5% of the total Pb aqueous concentration for NO_3^- concentrations equal to 10^{-3} M. For this reason we have not selected Pb-nitrate data.

Lead forms stable aqueous complexes with phosphate and there are different solid phases bearing Pb and phosphate.

The log K values for the different Pb phosphate aqueous complexes mainly come from the work of /Nriagu 1972, 1973ab, 1974/. Both /Lothenbach et al. 1999/ and /Blanc et al. 2006/ selected these data. Concerning data for the solid phases both data compilations select thermodynamic data published by /Nriagu 1972, 1973ab, 1974/. We have adopted this selection.

 /Lothenbach et al. 1999/ conducted extrapolations to zero ionic strength of different data in the literature to select the stability constants for Pb sulphate complexes. The log K for the formation reaction of $PbSO_4(aq)$ was obtained from 7 determinations in the literature at different ionic strength (log K = 2.82). For the stability of the second complex, $Pb(SO_4)_2^{2-}$, /Lothenbach et al. 1999/ used two independent determinations at I = 3 m and I = 0.7 m, and obtained a log K = 2.37, very similar to the one of the first complex.

/Blanc et al. 2006/ adopted the suggested data from /Lothenbach et al. 1999/ for the stability constant of $PbSO_4(aq)$, which came from the extrapolation of different stability constants reported in literature to I = 0 m. /Cromières 1997/ selected a stability constant for $PbSO_4(aq)$ equal to log K = 2.75 ± 0.30 compiled from data in literature. /Blanc et al. 2006/ added an uncertainty of 0.2 to cover this range of stability constants. We have kept this selection.

As stated in /Blanc et al. 2006/, there is a poor agreement on the stability of the second sulphate species, with stability constants ranging from 2.37 /Lothenbach et al. 1999/ to 3.75 /Cromières 1997/. We have adopted the value suggested by /Blanc et al. 2006/ (log K = 3.47) coming from /Martell and Smith 1997/ but we widen the uncertainty value to include the range of experimental variability.

For Anglesite (PbSO$_4$(s)) we have included the value reported in the NEA selection /Lemire et al. 2001/.

The most important source of lead in nature is Galena, PbS(s). /Lothenbach et al. 1999/ preferred the solubility data at room temperature of /Uhler and Helz 1984/ to the calculations based on thermodynamic properties at high temperatures to calculate the solubility constant of galena. They obtained a stability value of log K = 12.17 for r 4. The experimental data of /Hemley 1953/ were used together with the solubility value of galena to calculate the equilibrium constants of Pb(HS)$_2$(aq) and Pb(HS)$_3^-$. /Lothenbach et al. 1999/ proposed thus, a stability value of log K = 12.34 for r 5 and log K = 13.59 for r 6.

$$Pb^{2+} + HS^- = PbS + H^+ \qquad r\ 4$$

$$Pb^{2+} + 2\ HS^- = Pb(HS)_2(aq) \qquad r\ 5$$

$$Pb^{2+} + 3\ HS^- = Pb(HS)_3^- \qquad r\ 6$$
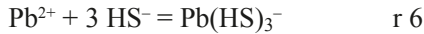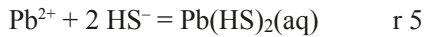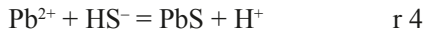
/Blanc et al. 2006/ calculated the solubility of galena from thermodynamic data from /Chase 1998/ and obtained a value of log K = –14.84. They preferred this value to the one proposed by /Lothenbach et al. 1999/ because the data /Uhler and Helz 1984/ did not considered the complexation of lead with chloride. /Blanc et al. 2006/ relied on the experimental results of /Barret and Anderson 1988/ which studied galena solubility at different ionic strengths (from 1 to 5 M) and at temperatures ranging from 25 to 300ºC. These authors suggested a solubility constant of log K = –14.95 at 25ºC and I = 0.

As did /Lothenbach et al. 1999, Blanc et al. 2006/ used the data of /Hemley 1953/ to obtain the equilibrium constants of Pb(HS)$_2$(aq) and Pb(HS)$_3^-$, but as they selected a different solubility constant for galena, they obtained a value of log K = 15.01 for r 5 and log K = 16.26 for r 6.

Figure 2-5 and Figure 2-6 compare the behaviour of the Pb-HS$^-$ system with both sets of thermodynamic data. The thermodynamic set of /Lothenbach et al. 1999/ enhances the solubility of galena at low [HS$^-$] concentrations.

At this stage, we would recommend a deeper study of galena solubility in order to widen the knowledge on this field and make a more accurate decision. However, bearing in mind that the objective of this selection is the inclusion of Pb in the Simple functions spreadsheet /Grivé et al. 2010/ and reminding that Simple Functions spreadsheet does not include sulphide in the input sheet, we have not selected a final value for this set of reactions.
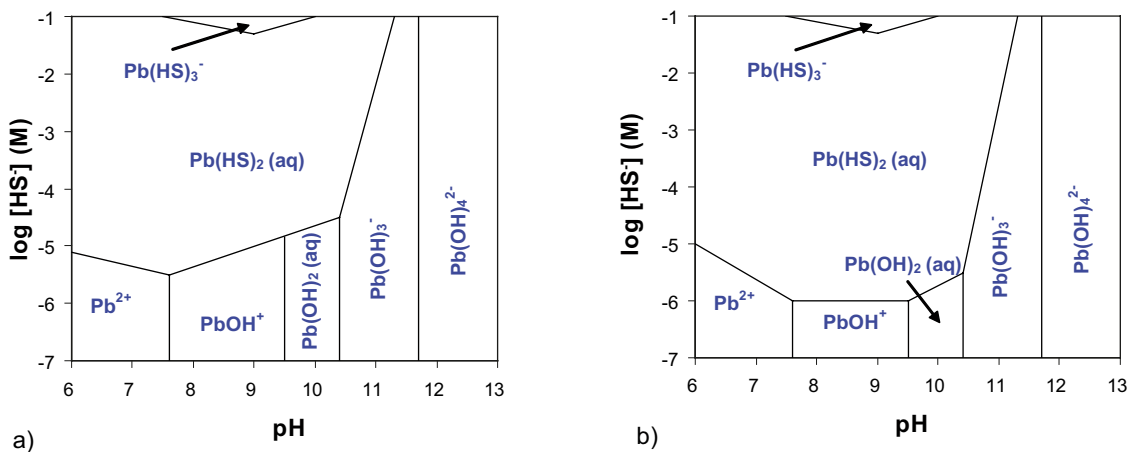
Figure 2-5. *Predominance diagrams showing the speciation of Pb as a function of pH and [HS$^-$]$_{tot}$, using the constants from a) /Lothenbach et al. 1999/ and b) /Blanc et al. 2006/ (Eh = –0.25V; [Pb^{2+}]$_{tot}$ = 10^{-6} M).*
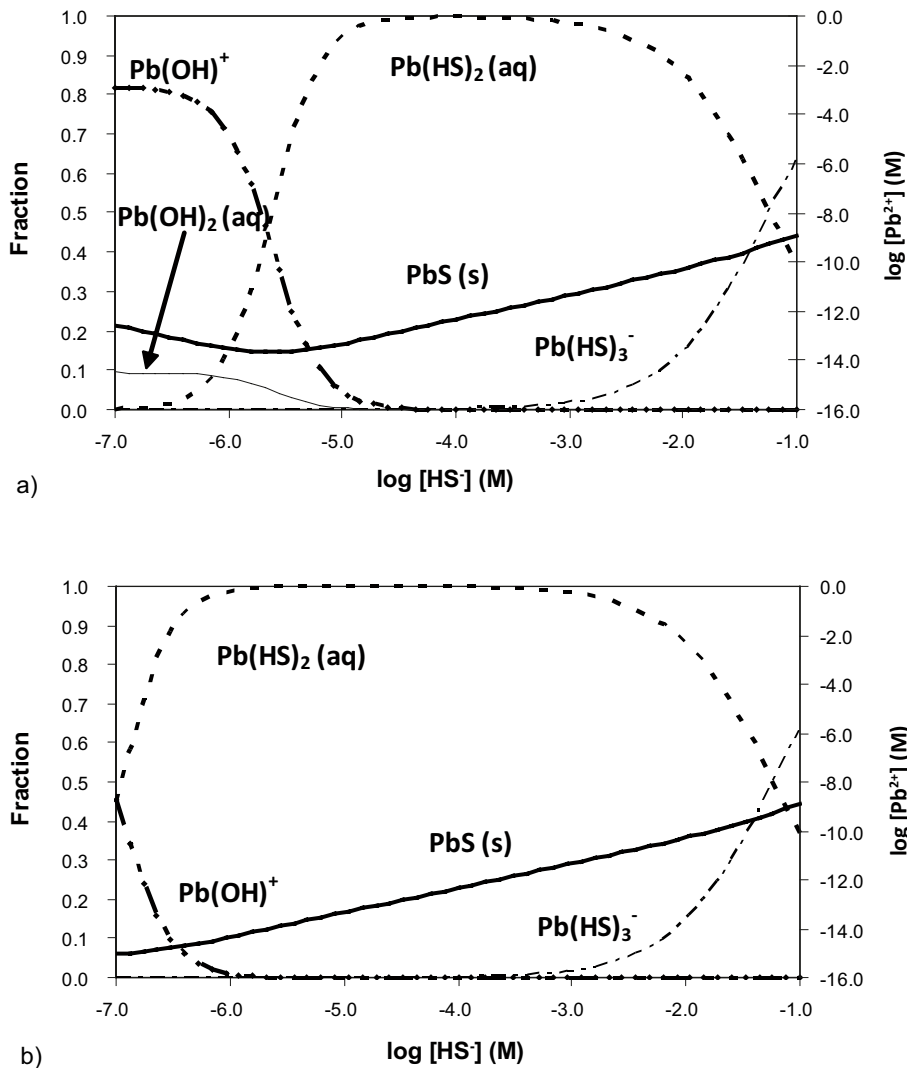
Figure 2-6. *Diagrams showing the solubility of galena and the aqueous speciation in equilibrium with as a function of log $[HS^-]_{tot}$, calculated using the constants from a) /Lothenbach et al. 1999/ and b) /Blanc et al. 2006/ (Eh = –0.25V; pH = 8.5).*

Lead forms stable aqueous complexes with halides. /Lothenbach et al. 1999/ extrapolated experimental data obtained in chloride and perchlorate media to I = 0 M to obtain the stability constants for $PbCl^+$, $PbCl_2^0$, $PbCl_3^-$ and $PbCl_4^{2-}$. /Blanc et al. 2006/ calculated these constants from the thermodynamic data of /Sverjensky et al. 1997/. Both set of data are equivalent considering the uncertainties. We have preferred the set of constants reported by /Lothenbach et al. 1999/ because they come from experimental sources.

Cotunnite ($PbCl_2(s)$) is a solid phase frequently found in oxidised Pb deposits as a result of the galena alteration in marine environments. It is a typical mineral covering the old Pb objects immersed in the sea. No differences are observed in the stability constant of this mineral. In this case, we have selected the data of /Blanc et al. 2006/, coming from /Chase 1998/ because they gave also a value for the uncertainty. This value agrees with the value selected by /Lothenbach et al. 1999/ (log K = 4.81).

Laurionite and paralaurionite are two dimorphs of PbClOH. They normally precipitate because of the influence of saline water on Pb wastes. There are few thermodynamic data concerning these minerals and frequently they do not indicate to which dimorph they refer. /Lothenbach et al. 1999/ extrapolated the experimental results of /Nasanen and Lindell 1976/ to zero ionic strength and pro-posed a value for the solubility constant equal to log K = 0.62. /Blanc et al. 2006/ adopted also this selection. We have selected this value and assigned it to the solid PbClOH(s), without distinguishing between both phases.

Phosgenite ($Pb_2(CO)_3Cl_2$) is another Cl^- bearing mineral found in the oxidised zone of Pb ores when there is a clear Cl^- source, such as saline water. There is only one value from Naumov et al. (1974).

In the absence of carbonates in solution, the stability field of PbClOH (s) is shown in Figure 2-7.

We consider the final set of selected data listed in Table 2-1 and Table 2-2, a qualified set of data.

Figure 2-7. *Predominance diagram showing the stability field of Pb-Cl-solid phases as a function of $[Cl^-]_{tot}$ and $[Pb^{2+}]_{tot.}$. (Eh = –0.25 V; pH = 8.5).*

3 Update of the solubility assessment

Changes in both the thermodynamic database and the groundwater compositions cause changes in the solubility assessment of radionuclides.

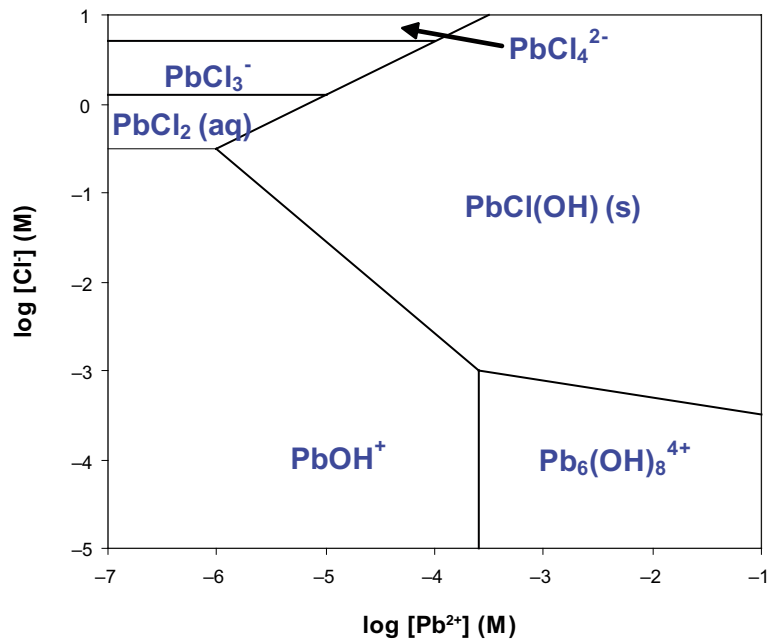In this section we present in detail the solubility assessment of lead under the conditions of interest of SKB (Table A-1, Appendix A) because of the recent inclusion of this element in the Thermodynamic database.

We also present an update of the radionuclide solubility limiting phases by considering the new set of groundwater compositions as they are in Table A-1 (Appendix A) for:

Ag, Am, Cm, Ho, Nb, Ni, Np, Pa, Pb, Pd, Pu, Ra, Se, Sm, Sn, Sr, Tc, Th, U, Zr.

3.1 Lead solubility assessment

3.1.1 Lead in nature and in natural analogues

Lead has many isotopes but only four of them are stable ([204]Pb, [206]Pb, [207]Pb and [208]Pb).

The abundance range of Pb in igneous, sedimentary and soils are 0.3–24, 5–25 and 15–65 ppm respectively /Maynard 1983, Adriano 1992/. In some cases, pollution can cause an increase of the Pb content, e.g. 5,000 ppm in northern Kosovo around the Zvečan Pb-Zn smelter /Borgna et al. 2009/ or 189 ppm in soils from Asia /Adriano 1992/.

The range of Pb content in natural waters goes from 3×10^{-5} ppm (1.5×10^{-10} mol/dm^3) in seawater to 80 ppm (4×10^{-4} mol/dm^3) in brines /Maynard 1983/. In polluted surface waters, contents can increase up to 3.6 ppm (1.7×10^{-5} mol/dm^3) /Adriano, 1992/.

Concentrations of Pb in El Berrocal are below the analytical detection limit, 2.5×10^{-7} mol/dm^3, in Poços de Caldas are in the range 10^{-9} to 10^{-7} mol/dm^3, in Cigar Lake waters around 10^{-8} mol/dm^3, in the clayey groundwater of Oklo around 4×10^{-9} mol/dm^3 and in the hyperalkaline waters of Maqarin around 10^{-9} mol/dm^3 /Bruno et al. 2001/.

/Ochs et al. 1997/ indicated solubilities of PbO (litharge) in cementititous conditions in the order of 10^{-3} M, being the solubilities very high and very pH-dependant.

/Caboi et al. 1999/ reported Pb contents in waters from wells of the west area of Montevecchio mine of 326 ppb Pb (1.6×10^{-6} mol/dm^3).

Lead is found in ores with zinc, silver and copper. The main lead mineral is galena (PbS) but anglesite (PbSO$_4$) and cerussite (PbCO$_3$) are also common minerals. Pb is also observed to sorb onto goethite forming tightly bound inner-sphere complexes /Krauskopf and Bird 1995/. /McLean and Bledsoe 1992/ observed that at pH values above 6, lead was either adsorbed onto clay surfaces or formed lead carbonate minerals. /Bruno et al. 2001/ pointed out the good correlation of Pb and P$_2$O$_5$ in Morro de Ferro natural analogue and indicated the possibility of Pb-phosphates controlling its solubility, although the lack of phosphates measurements prevented testing this hypothesis. /Martínez et al. 2004/ indicated that due to their relatively low solubility, lead-phosphate minerals may control Pb solution levels at a low value in natural environments.

Pb contents and occurrences in nature and in Natural Analogues have been obtained from data published in open literature, agencies and scientific books; all of them outside the SKB framework of data qualification. This set of data is used for clarifying the relationships of Pb with the host rock, and it is especially considered in the expert judgement of the solubility assessment, as it gives information on the processes that may occur in the KBS-3 repository. Despite the selected reports and papers are outside the SKB framework of data qualification, the original sources and references therein give relevant information on both data quality and the methodology used to obtain them. Moreover, the selected reports and papers give information on both the variability and representativity of published data. This set of data is considered Qualified Data.

3.1.2 Conceptual and representativity uncertainties of Pb solubility assessment

The assessment of Pb solubility under the groundwater of interest for SKB, listed in Table A1, is subjected to conceptual and representativity uncertainties.

Sulphate reduction to sulphide will have an immediate effect on lead solubility because of the precipitation of galena. A similar effect may have the reduction of carbonate to methane, because the loss of aqueous carbonate will sensibly modify the aqueous speciation of lead and also the solubility of cerussite and hydrocerussite.

The representativity of the lead solubility data is also affected by the lack of data on phosphate concentration of groundwaters as phosphate can form stable Pb aqueous complexes or solid phases. Table 3-1 summarises these two uncertainties.

3.1.3 Pb solubility assessment in the groundwaters of interest for SKB

In this section we present the solubility assessment of Pb in the groundwaters of interest for SKB (Table A-1). Calculations have been done with the PHREEQC code /Parkhurst and Appelo 2001/.

From calculations we have seen that the main geochemical parameters affecting the behaviour of lead are pH, CO_3^{2-} and Cl^-. The results of the calculations of the solubility assessment are shown in Table 3-2.

We have grouped the groundwaters of interest for SKB (Table A1) in four categories to explain the results obtained in the solubility assessment. These categories are:

* Chloride-rich groundwaters (Most saline groundwater at Olkiluoto, Most saline groundwater at Laxemar and Maximum salinity from glacial upcoming).
* Carbonate-rich groundwaters (Baltic seawater, Finnsjon, and Laxemar groundwaters).
* Intermediate groundwaters (Forsmark, Äspö, Ocean groundwaters; Gidea and Grimsel groundwaters).
* Cementitious pore water.

The speciation of lead in the chloride-rich groundwaters is dominated by the species $PbCl^+$, $PbCl_2$ and $PbCl_3^-$. The solubility of Pb in these waters is controlled by the solid phase $PbClOH(s)$, which gives a concentration of Pb between $7–9 \times 10^{-6}$ M.

The carbonate-rich groundwaters Pb speciation is dominated by the species $PbCO_3(aq)$. In these waters we have studied the solubility of two Pb carbonate bearing solid phases: cerussite and hydrocerussite. The lowest solubility value is provided by cerussite and varies from 5×10^{-7} to 6.5×10^{-7} M. Equilibrium with hydrocerussite phase gives values of Pb concentration around 10^{-6} M, higher than with cerussite.

Although the carbonate content of Forsmark water is similar to that of the carbonated groundwaters group, its Cl^- concentration is higher. Because of this, the speciation of this water is governed by the species $PbCO_3$ (46%), $PbCl^-$ (26%) and Pb^{2+} (16%). The solubility of Pb in this water is controlled by cerussite phase ($[Pb] \sim 10^{-6}$ M). We have also tested hydrocerussite as Pb solubility limiting phase, obtaining a value of 3×10^{-6} M, close to cerussite solubility. Pb speciation in ocean water and Äspö groundwater is dominated by carbonate and Cl^- complexes ($PbCO_3$, $PbCl^+$, $PbCl_2$, Pb^{2+}). Pb solubility in Äspö water is governed by hydrocerussite, with a Pb concentration around 3.5×10^{-6} M. This value is very similar to the value given by cerussite which is 3.8×10^{-6} M. In the case of Ocean water, cerussite solid phase gives a Pb solubility of 8×10^{-7} M. Pb concentration given by hydrocerussite (1.2×10^{-6} M) is higher than the value given by cerussite. Waters with low Cl^- concentration (Gidea and Grimsel) have a speciation dominated by hydroxo and carbonate complexes ($PbCO_3$, $PbOH^+$ and $Pb(OH)_2$). In these waters Pb solubility is controlled by hydrocerussite phase ($3–2.8 \times 10^{-7}$ M).

Table 3-1. Uncertainties identified for Pb.

Element	Conceptual uncertainty
Pb	SO_4^{2-} to HS^- reduction

Element	Representativity uncertainty
Pb	Effect of phosphates in water

Table 3-2. Lead solubility-controlling phases, concentrations (in mol/dm³) and underlying speciation for the groundwaters of interest for SKB (Compositions in Table A1).

		Forsmark	Laxemar	Äspö	Finnsjon	Gideå	Grimsel: interacted glacial meltwater	"Most Saline" groundwater at Laxemar	"Most Saline" groundwater at Olkiluoto	Cement pore water	Baltic seawater	Ocean water	Maximun salinity from glacial upconing
Concentration	**Cerussite** $PbCO_3$ (s)	1.08×10^{-6}	5.62×10^{-7}	3.82×10^{-6}	5.48×10^{-7}	8.94×10^{-7}	8.41×10^{-7}	8.85×10^{-5}	4.49×10^{-4}	n.s.l.	6.47×10^{-7}	8.04×10^{-7}	–
	Hydrocerussite $Pb_3(CO_3)(OH)_2$ (s)	3.54×10^{-6}	1.31×10^{-6}	3.53×10^{-6}	1.49×10^{-6}	3.01×10^{-7}	2.81×10^{-7}	4.39×10^{-5}	5.09×10^{-4}	n.s.l.	1.18×10^{-6}	1.18×10^{-6}	–
	$PbClOH$ (s)	4.84×10^{-5}	–	1.05×10^{-5}	–	–	–	9.28×10^{-6}	7.13×10^{-5}	n.s.l.	–	8.86×10^{-6}	7.36×10^{-6}
Speciation		$PbCO_3$ (46%) $PbCl^+$ (26%) Pb^{2+} (16%)	$PbCO_3$ (90%)	$PbCl^+$ (38%) Pb^{2+} (21%) $PbCO_3$ (13%) $PbOH^+$ (13%) $PbCl_2$ (10%)	$PbCO_3$ (93%)	$PbCO_3$ (57%), $PbOH^+$ (23%), $Pb(OH)_2$ (15%)	$PbCO_3$ (61%), $Pb(OH)_2$ (17%), $PbOH^+$ (12%)	$PbCl_3^-$ (38%) $PbCl_2$ (30%), $PbCl^+$ (21%)	$PbCl_3^-$ (39%) $PbCl_2$ (31%) $PbCl^+$ (22%)	$Pb(OH)_4^{2-}$ (95%)	$PbCO_3$ (77%)	$PbCO_3$ (55%) $PbCl^-$ (16%) $PbCl_2$ (10%)	$PbCl^+$ (32%), $PbCl_2$ (29%), $PbCl-$ (24%)

Pb is found as $Pb(OH)_4^{2-}$ in cement porewater. Concentration of lead is not solubility limited.

Pb concentrations calculated in this report are higher than values measured in natural analogues of granitic environments (Figure 3-1) showing that maybe solid phases controlling Pb solubility in natural waters are not well established. Phosphate complexation, reduction of sulphates and Pb sorption onto Fe-oxyhidroxides could be other important processes governing Pb concentration. Solubilities calculated in this study fall in the range of solubilities calculated for Pb in other performance assessments /ENRESA 1997/.

Values measured in clay and cement natural analogues and calculated in performance assessments in these conditions /ENRESA 1999, Giffaut et al. 2000, Berner 2002/ are also plotted in Figure 3-1 for sake of comparison.

Details of the performance assessments used in Figure 3-1 are listed in Table 3-3.

Table 3-3. Lead solubility-controlling phases and concentrations reported in other Performance Assessments.

PA	Medium	Solid phase	$[Pb]_{tot}$ (M) Proposed	$[Pb]_{tot}$ (M) Cons.	Ref.
Fran	Clay	$PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$	3×10^{-6}	10^{-5}	/Giffaut et al. 2000/
Swi	Clay	$PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$	1.9×10^{-6}		/Berner 2002/
Spa	Clay	$PbCO_3$ and PbS	10^{-7}	10^{-5}	/Enresa 1999/
Spa	Granite	$PbCO_3$, PbS, $PbSO_4$, PbO and Pb_3O_4	8×10^{-4}–5×10^{-13}	10^{-3}–10^{-9}	/Enresa 1997/
Fran	Cement	PbO	5×10^{-3}	10^{-2}	/Giffaut et al. 2000/

	Main conditions under study
France	pH = 7–8.5, Eh < –200mV, $pCO_2(g) = 10^{-4}$–10^{-2} atm
Switzerland	Eh = –193.6mV, pH = 7.25, $pCO_2 = 10^{-2.2}$, T = 25ºC
Spain–clay	Eh = –260mV, 7 < pH< 9, T = 25ºC.
Spain–granite	–400 < Eh < –260 mV, 7 < pH< 11, T = 75ºC

These values have been obtained outside the SKB framework of data qualification, but their quality is ensured by the information given in the corresponding reports. This set of data is also considered as Qualified.
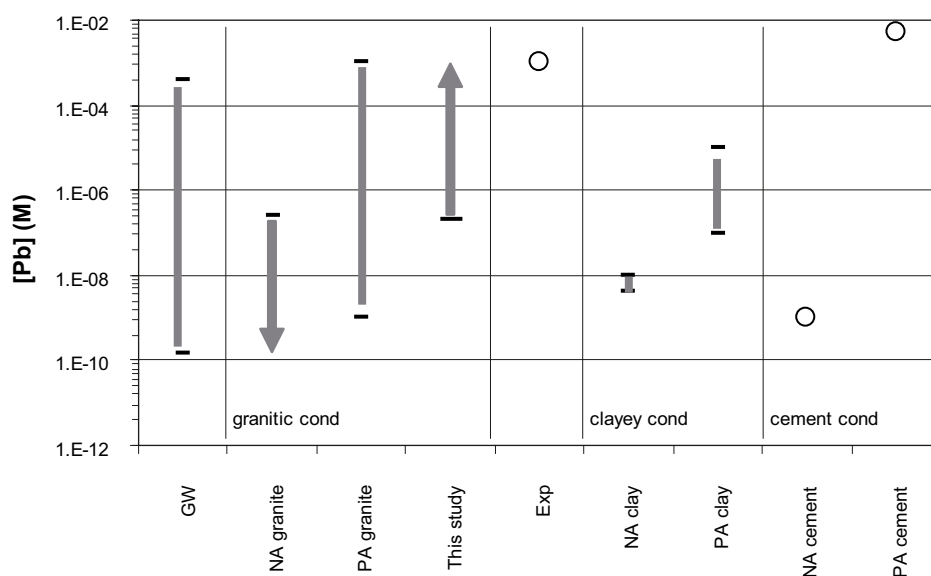
Figure 3-1. *Comparison of the solubility values calculated in this study with Pb concentration ranges measured in natural groundwaters (GW) and with Pb concentrations experimentally measured. Values measured in Natural Analogues of granite rocks and calculated in performance assessments in granite environments are also shown for comparison. Values measured in clayey environments (NA clay) or cement environments (NA-cement) and in other performance assessments (PA Clay and PA cement) are also listed for sake of comparison.*

3.2 Updated solubility calculations

In Table 3-4, we list the solubility controlling solid phases for each of the radionuclides of interest obtained considering the updated thermodynamic database and the new set of groundwater compositions of interest for SKB (Table A-1, Appendix A).

Calculations are presented for the scenario in which groundwater is supposed to interact with the fuel without interacting either with the buffer or the canister.

Table 3-4. Results of the solubility calculations obtained in this work considering the updated thermodynamic database and the groundwater compositions of interest for SKB (Table A-1, Appendix A).

log [ ] (mol dm^{-3})	Forsmark	Laxemar	Äspö (red.)	Finnsjön (red.)	Gideå (red.)	Grimsel
Ag	AgCl	AgCl	AgCl	AgCl	AgCl	AgCl
	−5.11	−5.77	−5.01	−6.06	−6.27	−5.79
Am	$Am(CO_3)_2$ $Na·5H_2O(s)$	$Am(CO_3)_2$ $Na·5H_2O(s)$	$Am_2(CO_3)_3(s)$	$AmCO_3OH(am)$	$Am(OH)_3(s)$	$Am(OH)_3(s)$
	−5.57	−6.05	−5.43	−5.88	−7.11	−7.16
Cm	$Cm_2(CO_3)_3(s)$	$Cm_2(CO_3)_3(s)$	$CmCO_3OH(am)$	$Cm_2(CO_3)_3(s)$	$Cm(OH)_3(s)$	$Cm(OH)_3(s)$
	−5.46	−5.85	−5.43	−5.88	−7.11	−7.16
Ho	$Ho_2(CO_3)_3(s)$	$Ho_2(CO_3)_3(s)$	$Ho_2(CO_3)_3(s)$	$Ho_2(CO_3)_3(s)$	$Ho(OH)_3(am)$	$Ho(OH)_3(am)$
	−5.64	−5.84	−5.17	−5.83	−5.86	−5.66
Nb	Nb_2O_5	Nb_2O_5	Nb_2O_5	Nb_2O_5	Nb_2O_5	Nb_2O_5
	−4.51	−4.09	−4.2	−4.11	−2.83	−2.54
Ni	$Ni(OH)_2(beta)$	$Ni(OH)_2(beta)$	$Ni(OH)_2(beta)$	$Ni(OH)_2(beta)$	$Ni(OH)_2(beta)$	$Ni(OH)_2(beta)$
	−2.81	−4.36	−3.79	−4.44	−6.77	−6.87
Np	$NpO_2:2H_2O$	$NpO_2:2H_2O$	$NpO_2:2H_2O$	$NpO_2:2H_2O$	$NpO_2:2H_2O$	$NpO_2:2H_2O$
	−8.96	−8.93	−9.02	−8.89	−9	−8.99
Pa	$Pa_2O_5(s)$	$Pa_2O_5(s)$	$Pa_2O_5(s)$	$Pa_2O_5(s)$	$Pa_2O_5(s)$	$Pa_2O_5(s)$
	−6.52	−6.51	−6.52	−6.5	−6.5	−6.5
Pb	cerussite	cerussite	Hydrocerussite	Cerussite	Hydrocerussite	Hydrocerussite
	−5.97	−6.25	−5.45	−6.05	−6.52	−6.55
Pd	$Pd(OH)_2(s)$	$Pd(OH)_2(s)$	$Pd(OH)_2(s)$	$Pd(OH)_2(s)$	$Pd(OH)_2(s)$	$Pd(OH)_2(s)$
	−5.46	−5.41	−5.42	−5.4	−5.4	−5.4
Pu	$Pu(OH)_4(am)$	$Pu(OH)_4(am)$	$Pu(OH)_4(am)$	$Pu(OH)_4(am)$	$Pu(OH)_4(am)$	$Pu(OH)_4(am)$
	−7.57	−6.99	−6.92	−7.24	−9.3	−9.3
Ra	$RaSO_4(cr)$	$RaSO_4(cr)$	$RaSO_4(cr)$	$RaSO_4(cr)$	$RaSO_4(cr)$	$RaSO_4(cr)$
	−6.62	−6.51	−6.6	−6.31	−3.91	−5.82
Se	$FeSe_2(s)$	$FeSe_2(s)$	$FeSe_2(s)$	$FeSe_2(s)$	$FeSe_2(s)$	Se(s)
	−10.74	−8.82	−7.94	−9.65	−11.12	−10.42
Sm	$SmOHCO_3(s)$	$SmOHCO_3(s)$	$SmOHCO_3(s)$	$SmOHCO_3(s)$	$SmOHCO_3(s)$	$SmOHCO_3(s)$
	−6.84	−7.44	−7.11	−7.36	−8.7	−8.59
Sn	$SnO_2(am)$	$SnO_2(am)$	$SnO_2(am)$	$SnO_2(am)$	$SnO_2(am)$	$SnO_2(am)$
	−7.23	−6.99	−7.08	−7	−5.87	−5.57
Sr	Celestite	Strontianite	Celestite	Strontianite	Strontianite	Strontianite
	−3.01	−3.82	−2.98	−4.11	−4.32	−4.95
Tc	$TcO_2:1.6H_2O$	$TcO_2:1.6H_2O$	$TcO_2:1.6H_2O$	$TcO_2:1.6H_2O$	$TcO_2:1.6H_2O$	$TcO_2:1.6H_2O$
	−8.37	−8.38	−8.4	−8.37	−8.39	−8.35
Th	ThO_2 (am,aged)	ThO_2 (am,aged)	ThO_2 (am,aged)	ThO_2 (am,aged)	ThO_2 (am,aged)	ThO_2 (am,aged)
	−8.05	−7.82	−8.8	−7.61	−8.73	−8.62
U	UO_2 (am,aged)	UO_2 (am,aged)	UO_2 (am,aged)	UO_2 (am,aged)	Becquerelite	Becquerelite
	−6.38	−8.37	−8.52	−7.6	−8.00	−7.22
Zr	$Zr(OH)_4$ (am,aged)	$Zr(OH)_4$ (am,aged)	$Zr(OH)_4$ (am,aged)	$Zr(OH)_4$ (am,aged)	$Zr(OH)_4$ (am,aged)	$Zr(OH)_4$ (am,aged)
	−7.76	−7.75	−7.76	−7.74	−7.74	−7.74

Table 3-4. Continuation.

log [ ] (mol dm^{-3})	Saline Laxemar	Saline Olkiluoto	Cement porewater	Baltic seawater	Ocean water	Maximum salinity from glacial upconing
Ag	AgCl −4.08	AgCl −4.1	Ag(OH)$_3$ −4.98	AgCl −5.33	AgCl −4.18	AgCl −4.04
Am	AmCO$_3$OH(am) −5.53	AmCO$_3$OH(am) −4.6	Am(OH)$_3$(s) −9.28	Am(CO$_3$)$_2$ Na·5H$_2$O(s) −6.07	Am(CO$_3$)$_2$Na·5H$_2$O(s) −6.9	AmCO$_3$OH(am) −5.63
Cm	CmCO$_3$OH(am) −5.53	CmCO$_3$OH(am) −4.6	Cm(OH)$_3$(s) −9.28	CmCO$_3$OH(am) −5.84	CmCO$_3$OH(am) −6.01	CmCO$_3$OH(am) −5.63
Ho	Ho$_2$(CO$_3$)$_3$(s) −5.07	Ho$_2$(CO$_3$)$_3$(s) −4.38	Ho(OH)$_3$(am) −3.01	Ho$_2$(CO$_3$)$_3$(s) −5.82	Ho$_2$(CO$_3$)$_3$(s) −5.81	Ho$_2$(CO$_3$)$_3$(s) −5.19
Nb	Nb$_2$O$_5$ −3.95	Nb$_2$O$_5$ −4.66	n.s.l.	Nb$_2$O$_5$ −4.06	Nb$_2$O$_5$ −3.76	Nb$_2$O$_5$ −3.97
Ni	Ni(OH)$_2$(beta) −4.41	Ni(OH)$_2$(beta) −2.63	Ni(OH)$_2$(beta) −5.57	Ni(OH)$_2$(beta) −4.24	Ni(OH)$_2$(beta) −4.61	Ni(OH)$_2$(beta) −4.25
Np	NpO$_2$:2H$_2$O −9.18	NpO$_2$:2H$_2$O −9.16	NpO$_2$OH (aged) −5.41	NpO$_2$OH (aged) −2.93	NpO$_2$OH (aged) −3.07	NpO$_2$:2H$_2$O −9.11
Pa	Pa$_2$O$_5$(s) −6.7	Pa$_2$O$_5$(s) −6.7	Pa$_2$O$_5$(s) −6.51	Pa$_2$O$_5$(s) −6.51	Pa$_2$O$_5$(s) −6.57	Pa$_2$O$_5$(s) −6.62
Pb	PbClOH(s) −5.03	PbClOH(s) −4.15	n.s.l.	Cerussite −6.19	Cerussite −6.09	PbClOH(s) −5.13
Pd	Pd(OH)$_2$(s) −5.44	Pd(OH)$_2$(s) −4.51	Pd(OH)$_2$(s) −4.76	Pd(OH)$_2$(s) −5.41	Pd(OH)$_2$(s) −5.46	Pd(OH)$_2$(s) −5.46
Pu	Pu(OH)$_4$(am) −8.04	Pu(OH)$_4$(am) −9.36	Pu(OH)$_4$(am) −9.31	PuO$_2$(OH)$_2$:H$_2$O −5.65	PuO$_2$(OH)$_2$:H$_2$O −5.67	Pu(OH)$_4$(am) −6.24
Ra	RaSO$_4$(cr) −6.54	RaSO$_4$(cr) −4.56	n.s.l.	RaSO$_4$(cr) −6.77	RaSO$_4$(cr) −6.98	RaSO$_4$(cr) −6.53
Se	FeSe$_2$(s) −8.23	Se(s) −14.51	n.s.l.	n.s.l	n.s.l.	FeSe$_2$(s) −6.39
Sm	SmOHCO$_3$(s) −7.41	SmOHCO$_3$(s) −6.16	Sm(OH)$_3$(am) −5.7	SmOHCO$_3$(s) −7.52	SmOHCO$_3$(s) −7.68	SmOHCO$_3$(s) −7.37
Sn	SnO$_2$(am) −7.16	SnO$_2$(am) −7.46	CaSn(OH)$_6$(s) −7.85	SnO$_2$(am) −6.98	SnO$_2$(am) −6.86	SnO$_2$(am) −7.07
Sr	Celestite −2.73	n.s.l.	n.s.l.	Strontianite −3.36	Strontianite −3.42	Celestite −2.82
Tc	TcO$_2$:1.6H$_2$O −8.39	TcO$_2$:1.6H$_2$O −8.38	n.s.l.	n.s.l.	n.s.l.	TcO$_2$:1.6H$_2$O −8.39
Th	ThO$_2$ (am,aged) −9.06	ThO$_2$ (am,aged) −9.04	ThO$_2$ (am,aged) −8.91	ThO$_2$ (am,aged) −8.15	ThO$_2$ (am,aged) −8.18	ThO$_2$ (am,aged) −8.94
U	UO$_2$ (am,aged) −8.69	UO$_2$ (am,aged) −8.94	CaU$_2$O$_7$:3H$_2$O −6.66	Becquerelite −5.55	Becquerelite −5.38	UO$_2$ (am,aged) −8.61
Zr	Zr(OH)$_4$ (am,aged) −7.93	Zr(OH)$_4$ (am,aged) −7.93	Zr(OH)$_4$ (am,aged) −7.73	Zr(OH)$_4$ (am,aged) −7.76	Zr(OH)$_4$ (am,aged) −7.81	Zr(OH)$_4$ (am,aged) −7.85

4 The Simple functions spreadsheet tool

The Simple Functions spreadsheet tool has been developed by Amphos 21 to determine the solubility limits of radionuclides and it is especially designed for Performance Assessment exercises. The development of this tool has been promoted by the necessity expressed by SKB of having a confident and easy-to-handle tool to calculate solubility limits in an agile and relatively fast manner.

The development of this tool started in 2005 /Enviros 2005/ and since then, it has been improved until getting the current versions /Grivé et al. 2010/.

The aim of this section is to briefly present this tool and its capabilities, although for a detailed discussion of the suitability and usage of this tool, the reader is addressed to the Simple Function spreadsheet user's guide /Grivé et al. 2010/.

This tool is based on an Excel© spreadsheet file and contains three types of information:

- **Input Data,** in which the user defines the groundwater composition where the solubility limits of radionuclides have to be determined

- **Common data,** containing data and equations needed to calculate the solubility and uncertainty of all the radionuclides of interest. They mostly refer to major elements.

- **Individual Element data,** containing the equations and the thermodynamic data of the aqueous species and solid phases needed for the solubility and uncertainty calculations for a given radionuclide.

As this tool does not pretend to substitute the complex geochemical codes, the aqueous speciation and solid phase system included is a simplification of the actual system, selected after an accurate and preliminary study following expert criteria described in /Grivé et al. 2010/.

In the SKB concept for a nuclear waste repository, the materials of the container are steel-based. Under anoxic conditions, Fe, which is the main component of this type of canisters, corrodes being magnetite the most important Fe-corrosion product formed on the canister surface. Further oxidation of magnetite causes the formation of Fe(III) oxides (e.g. goethite or hematite). The formation of this corrosion layer will affect the oxidation and reduction processes occurring in their vicinity, and also will modify the composition of the groundwater finally interacting with the radionuclides.

Fe corrosion processes are complex and kinetically controlled and therefore, the equilibration of a given groundwater with iron corrosion products is not simple. Experience gained when using specialised geochemical codes for this kind of calculations has shown that the parameters of the groundwater most affected by the interaction with Fe-corrosion products are pH, Eh and total iron aqueous concentration.

This is especially relevant for the redox-sensitive radionuclides, such as Uranium, given that the presence of corrosion products will determine the oxidation state of the radionuclide in solution and therefore, its solubility.

Therefore, and as stated in /Duro et al. 2006a/ solubility assessments can be done assuming:

- A groundwater without interacting either with the buffer or the canister, or
- A groundwater whose composition has been affected by the Fe corrosion products formed at the canister surface.

In the development of the Simple Functions Spreadsheet tool we have taken into account these two different assumptions. This has lead to the development of two different versions of the Simple Functions Spreadsheet:

- **Version A**, In which the user introduces the groundwater composition, including pH, Eh and Fe aqueous concentration. This version must be used for solubility assessments in groundwater composition that have not been interacted with canister corrosion products.

- **Version B**, in which the user introduces the groundwater composition, except Eh and Fe aqueous concentration. These two values are calculated by the Simple Functions Spreadsheet tool to be in equilibrium with Fe-corrosion products. The approaches followed for this calculation are described in Grivé et al. (2010). This version is designed for solubility assessments in which the user assumes that groundwater has interacted with Fe-corrosion products.

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Groundwater compositions

The groundwater compositions considered are those reported in Table A1, extracted from /SKB 2006a/.

We have completed some of these groundwater compositions by adding information on redox potentials taken from the original sources.

Table A-1. Groundwater compositions used in the calculations (from /SKB 2006a/). Shadowed cells: redox data for groundwater compositions used in this work (original data in bold). Concentrations in kmol/m³.

	Forsmark	Laxemar	Äspö	Finnsjön	Gideå	Grimsel: inter-acted glacial meltwater	"Most Saline" groungwater at Laxemar	"Most Saline" groungwater at Olkiluoto	Cement pore water	Baltic seawater	Ocean water	Maximun salinity from glacial upconing
pH	7.2	7.9	7.7	7.9	9.3	9.6	7.9	7	12.5	7.9	8.15	7.9
Na	0.089	0.034	0.091	0.012	0.0046	0.00069	0.349	0.415	0.002	0.089	0.469	0.25
Ca	0.023	0.0058	0.047	0.0035	0.00052	0.00014	0.464	0.449	0.018	0.0024	0.0103	0.27
Mg	0.0093	0.00044	0.0017	0.0007	0.000045	0.0000006	0.0001	0.0053	≤ 0.0001	0.010	0.053	0.0001
K	0.0009	0.00014	0.0002	0.00005	0.00005	0.000005	0.0007	0.0007	0.0057	0.002	0.01	0.0005
Fe	33×10^{-6}	8×10^{-6}	4×10^{-6}	32×10^{-6}	9×10^{-7}	3×10^{-9}	8×10^{-6}	6×10^{-5}	$\leq 10 \times 10^{-6}$	3×10^{-7}	4×10^{-8}	2×10^{-6}
HCO_3^-	0.0022	0.0031	0.00016	0.0046	0.00023	0.00045	0.00010	0.00014	≈ 0	0.0016	0.0021	0.00015
Cl^-	0.153	0.039	0.181	0.0157	0.0050	0.00016	1.283	1.275	≈ 0	0.106	0.546	0.82
SO_4^{2-}	0.0052	0.0013	0.0058	0.00051	0.000001	0.00006	0.009	0.00009	≈ 0	0.0051	0.0282	0.01
HS^-	≈ 0	3×10^{-7}	5×10^{-6}	–	$\leq 3 \times 10^{-7}$	–	$\leq 3 \times 10^{-7}$	$\leq 1.6 \times 10^{-7}$	≈ 0	–	–	$\leq 3 \times 10^{-7}$
Ionic Strength (kmol/m³)	0.19	0.053	0.24	0.025	0.006	0.0013	1.75	1.76	0.057	0.13	0.65	1.09
Eh (mV)	**−140**	**−280**	*−307/−73*	*−250/−68*	*−201/−60*	**−200**	**−314**	**−3**				**−400**
pe	*−2.37*	*−4.75*	**−5.21/−1.24**	**−4.23/−1.16**	**−3.41/−1.01**	*−3.39*	*−5.32*	*−0.05*				*−6.78*
Ref.Eh /pe	*1*	*2*	*3*	*3*	*3*	*4*	*4*	*5*				*2*

1) /SKB 2005/. 2) /SKB 2006b/. 3) /Bruno et al. 1997/. 4) /Duro et al. 2006/. 5) /Pitkänen et al. 1999/.