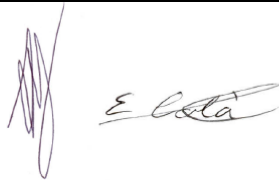




Handling of uncertainty in thermodynamic data

Final report

**Mireia Grivé,
Andrés Idiart,
Elisenda Colàs,
Lara Duro**

May 2013

Written by:	Revised by:	Validated by:
 Andrés Idiart Elisenda Colàs Mireia Grivé	 Mireia Grivé	 Lara Duro

Index

1. BACKGROUND AND INTRODUCTION	1
2. UNCERTAINTY ESTIMATES	3
2.1 SOURCES OF UNCERTAINTY	3
2.2 UNCERTAINTY CALCULATION.....	4
3. DISCUSSION ON THE SPECIFIC UNCERTAINTY VALUES IN SIMPLE FUNCTIONS TOOL.....	5
3.1 UNCERTAINTY ASSIGNED TO THERMODYNAMIC DATA.....	5
3.2 DEALING WITH UNCERTAINTY FOR SCARCE DATA.....	7
4. DETAILED EXAMPLES.....	16
4.1 URANIUM.....	18
4.2 RADIUM.....	21
4.3 AMERICIUM.....	23
5. SUMMARY AND CONCLUSIONS.....	27
REFERENCES.....	28

1. Background and introduction

Within the framework of the SR-Can safety assessment of SKB, the team of Amphos 21 conducted the solubility assessment of key radionuclides (Duro et al. 2006a, b, Grivé et al. 2010a). One of the outcomes was the development and implementation of an Excel© spreadsheet, named Simple Functions Spreadsheet, containing simple solubility functions for several elements included in the analyses (Grivé et al. 2010b). The calculations included in the Excel spreadsheet considered only those solid phases likely to form under the conditions of interest for SKB and those aqueous species accounting for, at least, 1% of the total aqueous concentration of the element investigated.

The Simple Functions Spreadsheet is a tool that calculates the solubility of radionuclides under a given range of groundwater compositions. It has been especially tailored to the specific requirements of Performance Assessment exercises: a confident and easy-to-handle tool to calculate solubility limits in an agile and relatively fast manner. Thus, only a simplified set of solid phases and aqueous species considered to be the most relevant in the environments of interest have been included. The spreadsheet also includes an estimation of the uncertainty of the calculated solubility that arises from the uncertainty in the thermodynamic data used in the calculations using an error propagation algorithm.

As part of the revision of the SR-Site Safety Assessment, SSM has requested SKB to provide more details and a sound reasoning on the validity of the different approaches used to assess uncertainty in solubilities, specifically arising from uncertainties in thermodynamic data. In this context, Amphos 21 has been requested by SKB to address SSM comments. As part of the work the consistency of the information related to this matter that has been published in the following SKB reports has been analysed:

- ✓ SKB (2011). Main report of the SR-Site project. SKB TR-11-01
- ✓ SKB (2010a). Radionuclide transport report for the safety assessment SR-Site. SKB TR-10-50
- ✓ SKB (2010b). Model summary report for the safety assessment SR-Site. SKB TR-10-51.
- ✓ SKB (2010c). Data report for the safety assessment SR-Site. SKB TR-10-52.

-
- ✓ SKB (2010d). Fuel and canister process report for the safety assessment SR-Site. SKB TR-10-46.
 - ✓ SKB (2006). Main report of the SR-Can project. SKB TR-06-09.
 - ✓ Grivé M, Domènech C, Montoya V, García D, Duro L. (2010b). Simple Functions Spreadsheet tool presentation. SKB TR-10-61.
 - ✓ Duro L., Grivé M, Cera E., Gaona X., Domènech C, (2006b). Determination and assessment of the concentration limits to be used in SR-Can. TR-06-32.
 - ✓ Grivé M., Domènech C., Montoya V., Garcia D., Duro L. (2010a). Determination and assessment of the concentration limits to be used in SR-Can Supplement to TR-06-32. SKB R-10-50.

The objective of this document is to not evaluate the uncertainty of all thermodynamic parameters, as this was already done for the solubility calculations and the development of the Simple Functions Spreadsheet during previous stages (Grivé et al. 2010b). Instead, the goal is to provide SKB with a review of the different existing approaches to assess the impact of thermodynamic data uncertainty on solubility and speciation, and above all: to frame how the approaches followed by SKB are in agreement with the ways of propagating uncertainty most commonly accepted by the scientific community.

The different alternatives to cope with uncertainty in the case of scarcity of data (e.g. ± 0.3 log units in the stability constant used by SKB in previous assessments) are also discussed.

Finally, detailed examples on the influence of uncertainty in the calculations of different radionuclide solubility values using the Simple Functions Spreadsheet are provided.

2. Uncertainty estimates

2.1 Sources of uncertainty

An important safety function in ensuring nuclear waste safety is the formation of solubility limiting phases that can decrease the radionuclide mobility in the repository (Ekberg et al. 2003). All the steps involved in the calculation and evaluation of these solubilities have some uncertainty associated (Ekberg and Emrén 1998, Serco 2008). The sources of uncertainty may be related to:

- the parameters that describe the *environmental conditions* of the disposal system, e.g. the chemical composition of the groundwater or the geological formation (i.e. mineral composition and spatial distribution) that is in contact with water;
- the *thermodynamic data* involved in the calculations, e.g. stability constants, enthalpies of reaction (if different temperatures are considered);
- the *conceptual and mathematical models* that describe the behaviour of the system.

This work aims at discussing, as requested by SSM, exclusively the uncertainties related to the thermodynamic data, specifically those involved in the solubility calculations included in the spreadsheet.

The solubility of an element depends not only on the specific properties of the controlling solid, but also on the properties of the aqueous species that contribute to its total aqueous concentration. Thus, the uncertainty in the solubility values includes the effects of both uncertainties in the thermodynamic data of the controlling solid and of the dominant aqueous species (Bernot 2005).

2.2 Uncertainty calculation

Two main approaches have been followed in the literature to determine uncertainties in solubilities (or in speciation) attributed to uncertainty in thermodynamic data:

- Derivative approach, based on error propagation theory (Wanner and Östhols 1999, Grivé et al. 2010b). These methods are fast and convenient for treating many equilibria, although they have some limitations. Namely, variables are assumed to have a Gaussian uncertainty distribution, and no covariance terms are included in the algorithm. Where dependencies between thermodynamic data are identified, the chain rule for the calculations of derivatives can be applied.
- Probabilistic approach based on simulations using the Monte Carlo (e.g. Cabaniss 1999), Latin Hypercube or other method, and sometimes based on tailor-made software packages for uncorrelated (e.g. Ekberg and Ödegaard-Jensen 2004, 2011, and references therein) and correlated thermodynamic data (Ekberg et al. 2011).

The validity and range of applications of the former approaches for uncertainty assessment has a relevant impact on the uncertainty of the PA solubility calculations.

As outlined above, the development of the Simple Functions Spreadsheet was motivated by the need of having a confident and at the same time easy-to-handle tool to calculate solubility limits in an agile and fast manner. Thus, probabilistic approach-based methods were out of the scope of the study because their implementation is much more complex, and they are not as fast as the derivative approach. Therefore, the methodology of the uncertainty analysis used in the Simple Functions Spreadsheet follows error propagation algorithms.

It must however be noticed that the Simple Functions Spreadsheet tool has also been tailored to be used together with the @RISK application (add-in to Microsoft Excel, see <http://www.palisade.com/risk/>) to perform probabilistic calculations with Monte Carlo simulations. This capability has been used in SKB (2010a) to assess both the impact of groundwater compositions and the variations in thermodynamic data.

3. Discussion on the specific uncertainty values in Simple Functions tool

A review of published uncertainties in the equilibrium constants have been carried out by Amphos 21 in previous works (Grivé et al. 2010b) in order to assign uncertainty ranges to the different thermodynamic constants involved in solubility calculations.

- When possible, the original error of the selected equilibrium constants has been used.
- When no error was reported in the selected original source, the range of variation between different bibliographic sources was taken as the uncertainty.
- Finally, when only one reference without an associated error was available, a default value of ± 0.3 log units was assigned as the uncertainty in $\log K_i$.

All these values have been included in the Simple Function Spreadsheet as input parameters to determine the uncertainty in the solubility calculations of the different elements.

In the following sections, a more extensive discussion on the methodology used to assess uncertainty is provided.

3.1 Uncertainty assigned to thermodynamic data

A summary of the literature sources used in the thermodynamic data selection for the SKB database (see Grivé et al. 2010a and references therein) and the Simple Functions Spreadsheet tool (Grivé et al. 2010b) is presented in Table 1. The selection is based mainly on the NAGRA/PSI database and on the different volumes of the NEA-TDB series. The thermodynamic data selection for elements not included in the NAGRA/PSI or NEA databases follows the same procedure of quality assurance as in those projects.

Table 1. Summary of the relevant sources of information for thermodynamic data selection in the Simple Functions Spreadsheet.

Element	Main source(s) of thermodynamic data	Report ^a
Sr	NAGRA-PSI	Duro et al. 2006a
Ra	NAGRA-PSI	Duro et al. 2006a
Zr	NEA	Grivé et al. 2010a
Nb	NAGRA-PSI	Duro et al. 2006a
Tc	NEA, NAGRA-PSI	Duro et al. 2006a
Ni	NEA	Grivé et al. 2010a
Pd	NAGRA-PSI	Duro et al. 2006a
Ag	Duro et al. 2006a	Duro et al. 2006a
Sn	Séby et al. 2001a, NAGRA-PSI	Duro et al. 2006a
Se	Séby et al. 2001b, Elrashidi et al. 1987	Duro et al. 2006a
Th	NEA	Grivé et al. 2010a
Pa	Baes and Mesmer 1976, Bard et al. 1985	Duro et al. 2006a
U	NEA	Grivé et al. 2010a
Np	NEA, NAGRA-PSI	Duro et al. 2006a
Pu	NEA, NAGRA-PSI	Duro et al. 2006a
Am, Cm	NEA, NAGRA-PSI	Duro et al. 2006a
Sm, Ho	Spahiu and Bruno 1995	Duro et al. 2006a
Pb	NAGRA-PSI	Grivé et al. 2010a

a: This column identifies the report where the data selection is described

Chemical thermodynamic data may have uncertainties due to both random and systematic errors (e.g. Wanner 2007). Another source of uncertainty may be the existence of important gaps in the database (i.e., lack of important aqueous or solid species in the database, relevant for solubility calculations).

Random errors are inherently unpredictable and are scattered about the true value. They can be estimated by comparing multiple measurements. Systematic errors are related to biases in measurement caused, for example, by imperfect calibration of an instrument used for measuring or by uncontrolled redox changes during the experiments. As a consequence of these errors, the result of the measurement could differ significantly from the actual value of the measured parameter.

All the measurements are prone to random error and they cannot be avoided. On the contrary, systematic errors and gaps in the database can be reduced and avoided.

Those uncertainties and shortcomings can usually be mastered by rigorous quality assurance in the selection of the thermodynamic data (Wanner 2007), as has been done in the selection of the data for the Simple Functions Spreadsheet. Provided that a rigorous data selection has been carried on, the number of systematic errors and gaps in the database, and as a consequence the uncertainty associated to this type of errors, should be kept to a minimum (Wanner and Östhols 1999, 2000).

The selection of the relevant uncertainty data is done by using the criteria and procedures established in NEA and NAGRA/PSI publications. When possible, the uncertainty reported in those publications has been adopted. In this sense, the uncertainties associated to the thermodynamic data should define a range within which the corresponding data can be reproduced with a probability of 95%.

In other cases the selection was based on a detailed review of other bibliographic sources (see Table 1). The error reported in the original source was then selected, when available. When no error was reported in the original source an uncertainty covering the most reliable range of independent data existing in the literature was selected. The reliability of published data was based on expert judgement.

When no error was reported in the original source and no more independent sources were identified, an uncertainty of ± 0.3 log units was assigned to the logarithm of the stability constant.

A detailed discussion on these uncertainty assessment processes is presented below.

3.2 Dealing with uncertainty for scarce data

Sometimes a detailed treatment of uncertainty is limited or impossible due to the availability of only one data point with no uncertainty assigned in the original source. The assignment of an uncertainty value in these cases is a highly subjective procedure (Wanner and Östhols 1999). For example, in Stenhouse et al. (2008, Appendix A) an estimate of ± 0.5 log units was considered in the cases where no uncertainty values were available.

In the Simple Functions Spreadsheet tool, a default value of ± 0.3 log units was assumed. This means the assumption that the value of the constant may vary from twice to half the central value:

$$\text{if } \log K = \log \beta \pm 0.3 \Rightarrow 2\beta > K > 0.5\beta$$

We must point out that the ± 0.3 log units uncertainty in logK for the species $\text{TcO}(\text{OH})^+$, $\text{Tc}(\text{CO}_3)(\text{OH})_2$, AgOH , PuOH^{2+} , AmHCO_3^{2+} , HoSO_4^+ , PbCl^+ , PbCl_2 , and PbCl_3^- corresponds to an actual uncertainty calculation from the original data sources (see NEA and NAGRA/PSI databases, Grivé et al. 2010a and Duro et al. 2006a for details).

The species whose logK uncertainty has been given a default value of ± 0.3 are listed in Table 2.

Table 2. Summary of species where the default value of ± 0.3 has been assigned to the stability constant in the Simple Functions Spreadsheet.

Element	Species	Reaction	logK ^o	$\Delta\log K^0$
Major	CaOH ⁺	$\text{Ca}^{2+} + \text{H}_2\text{O} = \text{CaOH}^+ + \text{H}^+$	-	0.30
			12.78	
	NaCO ₃ ⁻	$\text{Na}^+ + \text{CO}_3^{2-} = \text{NaCO}_3^-$	1.27	0.30
	NaHCO ₃	$\text{Na}^+ + \text{CO}_3^{2-} + \text{H}^+ = \text{NaHCO}_3$	10.08	0.30
	FeHCO ₃ ⁺	$\text{Fe}^{2+} + \text{CO}_3^{2-} + \text{H}^+ = \text{FeHCO}_3^+$	12.33	0.30
	CaSO ₄ (aq)	$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4$	2.30	0.30
	NaSO ₄ ⁻	$\text{Na}^+ + \text{SO}_4^{2-} = \text{NaSO}_4^-$	0.70	0.30
	FeHSO ₄ ⁺	$\text{Fe}^{2+} + \text{SO}_4^{2-} + \text{H}^+ = \text{FeHSO}_4^+$	3.07	0.30
	SrOH ⁺	$\text{Sr}^{2+} + \text{H}_2\text{O} = \text{SrOH}^+ + \text{H}^+$	-	0.30
			13.29	
Sr	SrCO ₃ (strontianite)	$\text{SrCO}_3(\text{s}) = \text{Sr}^{2+} + \text{CO}_3^{2-}$	-9.27	0.30
	SrSO ₄ (celestite)	$\text{SrSO}_4(\text{s}) = \text{Sr}^{2+} + \text{SO}_4^{2-}$	-6.63	0.30
Ra	RaCl ⁺	$\text{Ra}^{2+} + \text{Cl}^- = \text{RaCl}^+$	-0.10	0.30
	RaCO ₃ (s)	$\text{RaCO}_3(\text{s}) = \text{Ra}^{2+} + \text{CO}_3^{2-}$	-8.30	0.30
Pd	Pd(OH) ⁺	$\text{Pd}^{2+} + \text{H}_2\text{O} = \text{Pd(OH)}^+ + \text{H}^+$	-1.86	0.30
	Pd(OH) ₂	$\text{Pd}^{2+} + 2\text{H}_2\text{O} = \text{Pd(OH)}_2 + 2\text{H}^+$	-3.79	0.30
	Pd(OH) ₃ ⁻	$\text{Pd}^{2+} + 3\text{H}_2\text{O} = \text{Pd(OH)}_3^- + 3\text{H}^+$	-	0.30
			15.93	
Sm	SmOHCO ₃ (s)	$\text{SmOHCO}_3(\text{s}) + \text{H}^+ = \text{Sm}^{3+} + \text{CO}_3^{2-} + \text{H}_2\text{O}$	-7.70	0.30
Ho	Ho(SO ₄) ₂ ⁻	$\text{Ho}^{3+} + 2\text{SO}_4^{2-} = \text{Ho(SO}_4)_2^-$	4.90	0.30
	Ho(OH) ₃ (am)	$\text{Ho(OH)}_3(\text{am}) + 3\text{H}^+ = \text{Ho}^{3+} + 3\text{H}_2\text{O}$	17.80	0.30
Pb	PbClOH(s)	$\text{PbClOH}(\text{s}) + \text{H}^+ = \text{Pb}^{2+} + \text{Cl}^- + \text{H}_2\text{O}$	0.62	0.30

The relevance of the uncertainty assigned to the solubility of a given element must be critically evaluated through the assessment of the relative contribution of that particular element to the overall risk. Such contribution impact will depend, in turn, on the repository design. These aspects should be considered when allocating *effort* to the assessment of the uncertainties associated with that parameter (Serco 2008). It is important that the effort spent is *not disproportionate*. In general, a good estimate of uncertainty can be made by concentrating effort on the largest contributions to risk (Ellison and Williams 2012). With this in mind, the accuracy of the uncertainty and the impact on the solubility calculations of the species summarized in Table 2 have been evaluated by:

- Accuracy of the uncertainty: literature review;

- Impact on solubility calculations: performing calculations using the Simple Functions Spreadsheet (version A, see Grivé et al. 2010b), using the water compositions reported in Table 3. The Simple Functions Spreadsheet includes in the calculations a ranking of parameters as a function of their impact on the overall uncertainty (Grivé et al. 2010b). In this way, parameters whose uncertainty is not very important for solubility calculations (i.e. errors in their values do not affect to any significant extent the results) can be identified. More importantly, those key parameters for which accurate values are essential for the results to be meaningful can also be ranked.

Table 3. Composition of waters used in the calculations, from Duro et al. (2006b). Concentrations in mole·dm⁻³. Only the elements implemented in the Simple Function Spreadsheet are reported in the table.

	Forsmark reference water	Ice melting water
pH	7	9.6
Eh (mV)	-143	-200
[Na⁺]_{tot}	8.88·10 ⁻²	6.90·10 ⁻⁴
[K⁺]_{tot}	8.75·10 ⁻⁴	5.00·10 ⁻⁶
[Ca²⁺]_{tot}	2.33·10 ⁻²	1.40·10 ⁻⁴
[HCO₃][*]	1.77·10 ⁻³	4.50·10 ⁻⁴
[Cl]_{tot}	1.53·10 ⁻¹	1.60·10 ⁻⁴
[S]_{tot}^{**}	6.80·10 ⁻³	6.10·10 ⁻⁵
[Si]_{tot}	1.85·10 ⁻⁴	2.50·10 ⁻⁴
[Fe]_{tot}	3.31·10 ⁻⁵	3.00·10 ⁻⁹
Ionic strength	0.19	0.0012

* free hydrogenocarbonate concentration, no calcite equilibrium, no reduction to methane

** sulphate concentration, no reduction to sulphide

Major elements

Several species (CaOH⁺, NaCO₃⁻, CaSO₄(aq), etc) of this group have default uncertainty values of ± 0.3 log units. A quick overview seems to indicate that this uncertainty range is appropriate for those species. Some examples are provided below:

- Baes and Mesmer (1986) report uncertainty values in the range 0.1 to 0.3 for the hydrolysis of alkaline-earth cations. Thus, the uncertainty value of 0.3 for the species CaOH⁺ seems appropriate.

-
- Uncertainty values for NaCO_3^- , NaHCO_3 , FeHCO_3^+ or FeHSO_4^+ do not seem to be available in the literature.
 - In the case of $\text{CaSO}_4(\text{aq})$, literature values seem to range from the selected $\log K^\circ = 2.30$ (Nordstrom et al. 1990, Bell and George 1953) to $\log K^\circ = 2.11$ estimated by Sverjensky et al. (1997). For NaSO_4^- a range of values from $\log K^\circ = 0.70$ (Nordstrom 1990, Righellato and Davies 1930) to $\log K^\circ = 0.94$ (Pokrovski et al. 1995) have been identified. Thus, an uncertainty value of 0.3 seems appropriate for both species.

The impact of these species in solubility calculations has also been analysed:

- CaOH^+ is expected to be relevant only under very alkaline conditions. It should not be relevant at pH values below 11, that is, this species should not be relevant in the range of application of the Simple Functions Spreadsheet.
- NaCO_3^- , NaHCO_3 , FeHCO_3^+ and FeHSO_4^+ do not seem to play a key role in solubility calculations under the conditions of application of the Simple Functions Spreadsheet.
- For sulphates, $\text{CaSO}_4(\text{aq})$ and NaSO_4^- are relevant species for Sr and Ra solubility calculations (see Table 4) but the assignment of an uncertainty range of ± 0.3 log units is justified, as seen before.

Table 4. Solubility uncertainty calculation for Sr and Ra, including the parameters most contributing to uncertainty. $f_z(\%)$ is the degree of uncertainty (defined in percentage units)

Forsmark reference water				
Element	Solid Phase	Solubility limit (Log S)	Parameters contributing to uncertainty	$f_z(\%)$
Sr	Celestite	-3.16	$K_{sp}(\text{SrSO}_4)$	94.64
			$K^\circ(\text{CaSO}_4(\text{aq}))$	4.34
			$K^\circ(\text{NaSO}_4^-)$	0.63
Ra	$\text{RaSO}_4(\text{s})$	-6.76	$K_{sp}(\text{RaSO}_4)$	66.64
			$K^\circ(\text{CaSO}_4(\text{aq}))$	26.41
			$K^\circ(\text{NaSO}_4^-)$	3.81
Ice melting water				
Element	Solid Phase	Solubility limit (Log S)	Parameters contributing to uncertainty	$f_z(\%)$
Sr	Strontianite	-5.10	$K_{sp}(\text{SrCO}_3)$	99.59
Ra	$\text{RaSO}_4(\text{s})$	-5.88	$K_{sp}(\text{RaSO}_4)$	98.68
			$K^\circ(\text{CaSO}_4(\text{aq}))$	0.32

Strontium and Radium

Three strontium species (SrOH^+ , Strontianite and Celestite) and two radium species (RaCl^+ and $\text{RaCO}_3(\text{s})$) have default uncertainty values of ± 0.3 log units.

SrOH^+ does not seem to play a key role in solubility calculations under the conditions of application of the Simple Functions Spreadsheet.

The contribution of the species RaCl^+ may significantly affect the Ra solubility only in groundwaters with high chloride content like saline groundwaters, where chloride can reach very high concentrations. Further details on the contribution of this species are provided in the detailed example calculation reported in section 4.2.

In the case of strontianite, the original data from Busenberg and Plummer (1984) seems to indicate that the real uncertainty value could be even lower. Thus, the assignment of ± 0.3 log units is conservative. In analogy, the value assigned to $\text{RaCO}_3(\text{s})$ (± 0.3 log units) could also be justified.

In the case of celestite, no uncertainty has been encountered. However, for the analogue solid $\text{RaSO}_4(\text{s})$ a lower uncertainty value (± 0.09 log units) was found for its solubility product. Thus, the assignment of ± 0.3 log units for celestite is probably a conservative assumption.

As shown in Table 4, celestite, strontianite and $\text{RaSO}_4(\text{s})$ may be solubility limiting solids in some cases. Thus, the assignment of uncertainties to solubility products of those compounds may be of relevance. However, in the case of Sr or Ra, the concentration of those species in groundwaters may be governed by co-precipitation processes with major elements, leading to smaller Sr or Ra concentrations than the ones predicted from the solubilities of solids containing that element as major component (see discussion in Duro et al. 2006b). Only pure solid phases have been considered in the Simple Functions Spreadsheet, without considering the formation of mixed solid phases. Therefore, the main uncertainty in the calculation is the possibility of co-precipitation of strontium or radium with other solid phases present in the system.

Palladium

Three palladium species ($\text{Pd}(\text{OH})^+$, $\text{Pd}(\text{OH})_2$ and $\text{Pd}(\text{OH})_3^-$) have uncertainty values of ± 0.3 log units. Baes and Mesmer (1986) report uncertainty values in the range 0.1 to 0.2 for the formation of $\text{Pd}(\text{OH})_2(\text{aq})$. Thus, an uncertainty value of 0.3 is probably a conservative assumption.

The main parameter contributing to uncertainty is $K_{\text{sp}} \text{Pd}(\text{OH})_2(\text{s})$, although $K^\circ \text{Pd}(\text{OH})_2(\text{aq})$ may also have a contribution in the calculations (see Table 5).

Table 5. Solubility uncertainty calculation for Pd, including the parameters contributing the most to uncertainty.

Forsmark reference water				
Element	Solid Phase	Solubility limit (Log S)	Parameters contributing to uncertainty	$f_z(\%)$
Pd	$\text{Pd}(\text{OH})_2(\text{s})$	-5.40	$K_{\text{sp}} \text{Pd}(\text{OH})_2(\text{s})$	93.91
			$K^\circ \text{Pd}(\text{OH})_2(\text{aq})$	6.09
Ice melting water				
Element	Solid Phase	Solubility limit (Log S)	Parameters contributing to uncertainty	$f_z(\%)$
Pd	$\text{Pd}(\text{OH})_2(\text{s})$	-5.40	$K_{\text{sp}} \text{Pd}(\text{OH})_2(\text{s})$	93.77
			$K^\circ \text{Pd}(\text{OH})_2(\text{aq})$	6.23

Samarium and Holmium

One samarium and two holmium species, $\text{Ho}(\text{SO}_4)_2^-$, $\text{Ho}(\text{OH})_3(\text{am})$ and $\text{SmOHCO}_3(\text{s})$, have uncertainty values of ± 0.3 log units.

$\text{Ho}(\text{SO}_4)_2^-$ does not seem to play a key role in solubility calculations under the conditions of application of the Simple Functions Spreadsheet.

In the case of $\text{SmOHCO}_3(\text{s})$, the stability constant ($\log K_{\text{ps}} = -7.70$) has been estimated using as analogue values the equivalent solids for Nd ($\log K_{\text{ps}} = -7.50$) and Eu ($\log K_{\text{ps}} = -7.80$). Taking into account the values for those analogue compounds, the selection of an uncertainty range of ± 0.3 log units is considered appropriate.

Table 6. Solubility uncertainty calculation for Sm and Ho, including the parameters most contributing to uncertainty.

Forsmark reference water				
Element	Solid Phase	Solubility limit (Log S)	Parameters contributing to uncertainty	$f_z(\%)$
Sm	SmOHCO ₃ (s)	-6.63	$K^\circ \text{SmCO}_3^+$	57.34
			$K_{\text{sp}} \text{SmOHCO}_3(\text{s})$	42.01
			$K^\circ \text{Sm}(\text{CO}_3)_2^-$	0.57
Ho	Ho ₂ (CO ₃) ₃ (s)	-5.60	$K_{\text{sp}} \text{Ho}_2(\text{CO}_3)_3(\text{s})$	73.35
			$K^\circ \text{HoCO}_3^+$	25.04
			$K^\circ \text{Ho}(\text{CO}_3)_2^-$	1.54
Ice melting water				
Element	Solid Phase	Solubility limit (Log S)	Parameters contributing to uncertainty	$f_z(\%)$
Sm	SmOHCO ₃ (s)	-8.50	$K^\circ \text{Sm}(\text{CO}_3)_2^-$	74.40
			$K_{\text{sp}} \text{SmOHCO}_3(\text{s})$	24.71
Ho	Ho(OH) ₃ (am)	-5.57	$K_{\text{sp}} \text{Ho}(\text{OH})_3(\text{am})$	49.28
			$K^\circ \text{Ho}(\text{CO}_3)_2^-$	46.81

For $\text{Ho}(\text{OH})_3(\text{am})$, the uncertainty values for solubility products of analogue solids (e.g. $\text{Sm}(\text{OH})_3(\text{am})$) are in the range of ± 1.0 log units. As shown in Table 6, $\text{Ho}(\text{OH})_3(\text{am})$, may be the solubility limiting solid under certain conditions (e.g. in the case of ice melting water at pH=9.6). If the uncertainty of ± 0.3 log units is considered, the solubility of $\text{Ho}(\text{OH})_3(\text{am})$ contributes to uncertainty in a factor of 49%. However, if the uncertainty contribution for this solid is increased up to ± 1.0 log units, the contribution of the solubility of $\text{Ho}(\text{OH})_3(\text{am})$ to the uncertainty increases up to 92% (see the comparison in Table 7). Although the conditions under which this solid phase is

considered relevant are not the reference ones, the increase of the uncertainty to ± 1.0 log units for the solubility constant of this solid phase can be considered.

Table 7. Solubility uncertainty calculation for Ho if the uncertainty of $\text{Ho(OH)}_3(\text{am})$ is increased.

Ice melting water					
Element	Solid Phase	$\log K_{\text{ps}}$	Solubility limit ($\text{Log S} \pm \Delta \log \text{S}$)	Parameters contributing to uncertainty	$f_2(\%)$
Ho	$\text{Ho(OH)}_3(\text{am})$	$\log K_{\text{ps}}=17.80 \pm 0.30$	-5.57 ± 0.19	$K_{\text{sp}} \text{Ho(OH)}_3(\text{am})$	49.28
				$K^\circ \text{Ho(CO}_3)_2^-$	46.81
Ho	$\text{Ho(OH)}_3(\text{am})$	$\log K_{\text{ps}}=17.80 \pm 1.0$	-5.57 ± 0.45	$K_{\text{sp}} \text{Ho(OH)}_3(\text{am})$	91.52
				$K^\circ \text{Ho(CO}_3)_2^-$	7.82

Lead

PbClOH(s) has an uncertainty value of ± 0.3 log units. In this case, this solid does not seem to play a key role in solubility calculations under the conditions of application of the Simple Functions Spreadsheet.

4. Detailed examples

The methodology used in the Simple Functions Spreadsheet is based on the derivative approach to calculate through error propagation algorithms the uncertainties associated with the calculated solubility limits. This method has been chosen for its simplicity when compared to more sophisticated tools based e.g. on Monte Carlo simulations. The reason is that the focus of the work has been to develop a simplified tool for assessing solubility uncertainties to be implemented in an Excel spreadsheet for Performance Assessment calculations.

Element specific solubilities can be analytically related with all the variables and thermodynamic constants, which in a general way can be described as:

$$S = f(\text{pH}, T, [\text{ligands}], K\text{'s}, \dots) = f(Z_1, Z_2, \dots, Z_n) \quad (1)$$

where S is the total solubility of the element of interest and Z_i are the different variables or input parameters which must be known in order to calculate the solubility (e.g. pH, temperature, equilibrium constants, etc.). By means of error propagation theory, the uncertainty of S , named ΔS , can in turn be derived from the uncertainties in input parameters (ΔZ_i):

$$\Delta S = \sqrt{\left(\frac{\partial S}{\partial Z_1}\right)^2 \Delta Z_1^2 + \left(\frac{\partial S}{\partial Z_2}\right)^2 \Delta Z_2^2 + \dots + \left(\frac{\partial S}{\partial Z_n}\right)^2 \Delta Z_n^2} \quad (2)$$

Variables Z_i must be independent for this approximation to be valid. In order to comply with this condition, the chain rule can be applied for the calculations of the partial derivatives of S with respect to the different input parameters:

$$\frac{\partial S}{\partial Z_i} = \frac{\partial f}{\partial Z_i} + \sum_j \frac{\partial f}{\partial Y_j} \frac{\partial Y_j}{\partial Z_i} \quad (3)$$

where Y_j represents variables in the solubility function that implicitly depend on the variable Z_i . For all elements included in the analysis all derivatives are calculated analytically in the spreadsheet.

An outcome of this procedure is that the ranking of different parameters according to the effect of their uncertainty on the overall solubility uncertainty can be readily calculated as:

$$f_{Z_i}(\%) = \frac{\left(\frac{\partial S}{\partial Z_i}\right)^2 \Delta Z_i^2}{\Delta S^2} \cdot 100 \quad (4)$$

where $\left(\frac{\partial S}{\partial Z_n}\right)^2 \Delta Z_n^2$ represents the variance of Z_n .

In this section, some examples calculated with the Simple Functions Spreadsheet concerning the solubilities of uranium, radium, and americium are described and discussed in detail, showing the methodology of uncertainty calculation in a more practical way. Details about the speciation and solid phase stabilities under different groundwater conditions can be found in Duro et al. (2006b). The calculations in this section incorporate the thermodynamic data changes reported in Grivé et al. (2010a), and have been performed with Version A of the spreadsheet (Grivé et al. 2010b), designed to calculate radionuclide solubility limits in representative groundwater compositions supplied by the user.

In this exercise, two cases with different groundwater compositions (reported in previous sections, see Table 3) are calculated for each element, to underline the sensitivity of the uncertainty results on different input parameters. They correspond to the Forsmark reference water and the ice melting (Grimsel) water, as given in Duro et al. (2006b).

As a general observation, the most sensitive parameters are typically the solubility product of the solid phase and, to a lesser extent, the formation constant of the main

aqueous species of the studied element. However, there are some cases where other constants have an impact on the solubility uncertainty, as shown in the following examples.

4.1 Uranium

The first example involves the solubility of uranium under the two different groundwater compositions (Table 3). Under Forsmark groundwater conditions, with a neutral pH, the solubility of U is controlled by the solid phase $\text{UO}_2 \cdot 2\text{H}_2\text{O}(\text{am})$. In the ice melting water case, with a more alkaline pH, the controlling solid phase is uranophane. The main results of U solubility uncertainty for the two groundwater compositions are summarized in Table 8 and Table 9, together with the results in terms of contribution of the individual species to overall solubility uncertainty (in %).

In both cases, the solubility uncertainty is significant and is largely controlled by the uncertainties associated to the $\log K_{\text{sp}}$ values of the solid phases, especially large for uranophane. Therefore, the effect of other uncertainties is negligible. In this regard, the spreadsheet could be used to analyse which species would contribute to solubility uncertainty if the uncertainty in the $\log K_{\text{sp}}$ values of the solid phases were reduced. In the case of the Ice melting (Grimsel) groundwater, if the uncertainty for the uranophane solubility product was significantly reduced, by one order of magnitude (from 5 to 0.5 log units), the solubility uncertainty would be reduced accordingly by roughly one order of magnitude. In this case, the contribution to the uncertainty of $\text{UO}_2(\text{OH})_3^-$ (3.87%), $\text{UO}_2(\text{CO}_3)_3^{4-}$ (1.89%), and especially HCO_3^- (4.52%) would be of around 10% in total.

In the case of Forsmark water, if we reduced the uncertainty of the $\log K_{\text{sp}}$ value of $\text{UO}_2 \cdot 2\text{H}_2\text{O}(\text{am})$ by one order of magnitude (from 1.09 to 0.1), the contribution of HCO_3^- (19.73%), $\text{UO}_2(\text{CO}_3)_3^{4-}$ (6.98%), and $\text{U}(\text{OH})_{4(\text{aq})}$ (5.26%) to solubility uncertainty would be of more than 30% in total (although the solubility uncertainty is naturally reduced by one order of magnitude). It is remarkable that in both cases (neutral and alkaline conditions), the contribution to uncertainty of HCO_3^- and $\text{UO}_2(\text{CO}_3)_3^{4-}$ is significant even

when the uncertainty in the equilibrium constants for both species is as small as 0.02 and 0.04 log units, respectively.

The large uncertainty associated with the solubility product of solid phases is partially related to the Ostwald Step Rule which postulates that the precipitate with the highest solubility, that is, the least stable solid phase, will form first (Duro et al. 2006b). The thermodynamic data associated to these amorphous phases usually have large uncertainties, due to the nature of the solids themselves and the different degrees of crystallinity that they can present.

Table 8. Main results of U solubility for the two groundwater compositions.

Solubility limit	Forsmark	Ice melting
Solid phase	UO ₂ ·2H ₂ O(am)	uranophane
[U]	1.54·10 ⁻⁷	2.35·10 ⁻⁹
log[U]	-6.81	-8.628
Δ[U]	1.68E·10 ⁻⁷	5.96·10 ⁻⁹
% error	109%	253%
Δlog[U]	0.47	1.10

Table 9. Main results and uncertainty contribution for the species and solid phase considered in the U solubility calculations for two groundwater compositions.

U species	Reaction	logK ^o	ΔlogK ^o	Uncertainty contribution	
				Forsmark	Ice melting
UO ₂ OH ⁺	UO ₂ ⁺² + H ₂ O = UO ₂ OH ⁺ + H ⁺	-5.25	0.24	0.00%	0.00%
UO ₂ (OH) _{2(aq)}	UO ₂ ⁺² + 2H ₂ O = UO ₂ (OH) _{2(aq)} + 2H ⁺	-12.15	0.07	0.00%	0.00%
UO ₂ (OH) ₃ ⁻	UO ₂ ⁺² + 3H ₂ O = UO ₂ (OH) ₃ ⁻ + 3H ⁺	-20.25	1.05	0.00%	0.04%
UO ₂ (OH) ₄ ⁻²	UO ₂ ⁺² + 4H ₂ O = UO ₂ (OH) ₄ ⁻² + 4H ⁺	-32.40	0.68	0.00%	0.00%
(UO ₂) ₃ (OH) ₅ ⁺	3UO ₂ ⁺² + 5H ₂ O = (UO ₂) ₃ (OH) ₅ ⁺ + 5H ⁺	-15.55	0.12	0.00%	0.00%
(UO ₂) ₃ (OH) ₇ ⁻	3UO ₂ ⁺² + 7H ₂ O = (UO ₂) ₃ (OH) ₇ ⁻ + 7H ⁺	-32.20	0.80	0.00%	0.00%
UO ₂ CO _{3(aq)}	UO ₂ ⁺² + CO ₃ ⁻² = UO ₂ CO _{3(aq)}	9.94	0.03	0.00%	0.00%
UO ₂ (CO ₃) ₂ ⁻²	UO ₂ ⁺² + 2CO ₃ ⁻² = UO ₂ (CO ₃) ₂ ⁻²	16.61	0.09	0.01%	0.00%
UO ₂ (CO ₃) ₃ ⁻⁴	UO ₂ ⁺² + 3CO ₃ ⁻² = UO ₂ (CO ₃) ₃ ⁻⁴	21.84	0.04	0.09%	0.02%
(UO ₂) ₂ CO ₃ (OH) ₃ ⁻	2UO ₂ ⁺² + CO ₃ ⁻² + 3H ₂ O = (UO ₂) ₂ CO ₃ (OH) ₃ ⁻ + 3H ⁺	-0.86	0.50	0.00%	0.00%
UO ₂ ⁺	UO ₂ ⁺² + 0.5H ₂ O = UO ₂ ⁺ + 0.25O ₂ + H ⁺	-19.30	0.02	0.00%	0.00%
U(OH) ₃ ⁺	UO ₂ ⁺² + 2H ₂ O = U(OH) ₃ ⁺ + H ⁺ + 0.5O ₂	-37.22	1.00	0.00%	0.00%
U(OH) _{4(aq)}	UO ₂ ⁺² + 3H ₂ O = U(OH) _{4(aq)} + 2H ⁺ + 0.5O ₂	-42.52	1.40	0.07%	0.00%
U(CO ₃) ₄ ⁻⁴	UO ₂ ⁺² + 4CO ₃ ⁻² + 2H ⁺ = U(CO ₃) ₄ ⁻⁴ + 0.5O ₂ + H ₂ O	2.60	0.93	0.00%	0.00%
Solid phases	Reaction	logK^o	ΔlogK^o	Forsmark	Ice melting
UO₂·2H₂O(am)	UO ₂ ·2H ₂ O(am) + 2H ⁺ + 0.5O ₂ = UO ₂ ⁺² + 3H ₂ O	34.02	1.09	99.59%	
Uranophane	Ca((UO ₂) ₂ SiO ₃ (OH)) ₂ ·5aq+6H ⁺ = Ca ⁺² +2UO ₂ ⁺² +2H ₄ SiO ₄ +5H ₂ O	9.42	5.06		99.89%
Major Species	Reaction	logK^o	ΔlogK^o	Forsmark	Ice melting
CaOH ⁺	Ca ⁺² + H ₂ O = CaOH ⁺ + H ⁺	-12.78	0.30	0.00%	0.00%
FeOH ⁺	Fe ⁺² + H ₂ O = FeOH ⁺ + H ⁺	-9.50	0.10	0.00%	0.00%
Fe(OH) _{3(aq)}	Fe ⁺² + 0.25O ₂ (g) + 2.5H ₂ O = Fe(OH) _{3(aq)} + 2H ⁺	-4.80	1.06	0.00%	0.00%
Fe(OH) ₄ ⁻	Fe ⁺² + 0.25O ₂ (g) + 2.5H ₂ O = Fe(OH) ₄ ⁻ + 3H ⁺	-13.84	0.08	0.00%	0.00%
HCO ₃ ⁻	H ⁺ + CO ₃ ⁻² = HCO ₃ ⁻	10.33	0.02	0.25%	0.05%
CaCO _{3(aq)}	Ca ⁺² + CO ₃ ⁻² = CaCO ₃	3.22	0.14	0.00%	0.00%
CaHCO ₃ ⁺	Ca ⁺² + CO ₃ ⁻² + H ⁺ = CaHCO ₃ ⁺	11.44	0.09	0.00%	0.00%
NaCO ₃ ⁻	Na ⁺ + CO ₃ ⁻² = NaCO ₃ ⁻	1.27	0.30	0.00%	0.00%
NaHCO ₃	Na ⁺ + CO ₃ ⁻² + H ⁺ = NaHCO ₃	10.08	0.30	0.00%	0.00%
FeCO _{3(aq)}	Fe ⁺² + CO ₃ ⁻² = FeCO _{3(aq)}	4.38	1.31	0.00%	0.00%
FeHCO ₃ ⁺	Fe ⁺² + CO ₃ ⁻² + H ⁺ = FeHCO ₃ ⁺	12.33	0.30	0.00%	0.00%
HSO ₄ ⁻	H ⁺ + SO ₄ ⁻² = HSO ₄ ⁻	1.98	0.25	0.00%	0.00%
CaSO _{4(aq)}	Ca ⁺² + SO ₄ ⁻² = CaSO ₄	2.30	0.30	0.00%	0.00%
NaSO ₄ ⁻	Na ⁺ + SO ₄ ⁻² = NaSO ₄ ⁻	0.70	0.30	0.00%	0.00%
FeHSO ₄ ⁺	Fe ⁺² + SO ₄ ⁻² + H ⁺ = FeHSO ₄ ⁺	3.07	0.30	0.00%	0.00%
FeSO _{4(aq)}	Fe ⁺² + SO ₄ ⁻² = FeSO _{4(aq)}	2.25	0.05	0.00%	0.00%
FeCl ⁺	Fe ⁺² + Cl ⁻ = FeCl ⁺	0.14	0.23	0.00%	0.00%

4.2 Radium

The results of Simple Functions for Ra are summarized in Table 10 and Table 11 for both groundwater compositions. In this case the solubility is controlled by $\text{RaSO}_{4(s)}$ for both groundwater compositions. A small uncertainty in the equilibrium constant is associated with $\text{RaSO}_{4(aq)}$ (Table 11). As a consequence, the uncertainty in the solubility is also small in both cases, as shown in Table 10.

For the Forsmark water calculation, there is an important contribution of $\text{CaSO}_{4(aq)}$ (26.40%) to the solubility uncertainty.

Table 10. Main results of Ra solubility for the two groundwater compositions.

Solubility limit	Forsmark	Ice melting
Solid phase	RaSO_4	RaSO_4
[Ra]	$1.72 \cdot 10^{-7}$	$1.31 \cdot 10^{-6}$
log[Ra]	-6.76	-5.88
$\Delta[\text{Ra}]$	$1.90 \cdot 10^{-8}$	$1.19 \cdot 10^{-7}$
% error	11%	9%
$\Delta\log[\text{Ra}]$	0.05	0.04

Table 11. Main results and uncertainty contribution for the species and solid phase considered in the Ra solubility calculations for two groundwater compositions.

Ra species	Reaction	logK ⁰	ΔlogK ⁰	Uncertainty contribution	
				Forsmark	Ice melting
Ra(OH) ⁺	Ra ⁺² + H ₂ O = Ra(OH) ⁺ + H ⁺	-13.50	0.25	0.00%	0.00%
RaCO _{3(aq)}	Ra ⁺² + CO ₃ ⁻² = RaCO ₃	2.50	0.40	0.00%	0.92%
RaSO_{4(aq)}	Ra ⁺² + SO ₄ ⁻² = RaSO ₄	2.75	0.10	2.53%	0.07%
RaCl⁺	Ra ⁺² + Cl ⁻ = RaCl ⁺	-0.10	0.30	0.61%	0.00%
Solid phase					
Ra(SO₄)_s	Ra(SO ₄) _s = Ra ⁺² + SO ₄ ⁻²	-10.26	0.09	66.65%	98.68%
Major Species					
CaOH ⁺	Ca ⁺² + H ₂ O = CaOH ⁺ + H ⁺	-12.78	0.30	0.00%	0.00%
FeOH ⁺	Fe ⁺² + H ₂ O = FeOH ⁺ + H ⁺	-9.50	0.10	0.00%	0.00%
Fe(OH) _{3(aq)}	Fe ⁺² + 0.25O ₂ (g) + 2.5H ₂ O = Fe(OH) _{3(aq)} + 2H ⁺	-4.80	1.06	0.00%	0.00%
Fe(OH) ₄ ⁻	Fe ⁺² + 0.25O ₂ (g) + 2.5H ₂ O = Fe(OH) ₄ ⁻ + 3H ⁺	-13.84	0.08	0.00%	0.00%
HCO ₃ ⁻	H ⁺ + CO ₃ ⁻² = HCO ₃ ⁻	10.33	0.02	0.00%	0.00%
CaCO _{3(aq)}	Ca ⁺² + CO ₃ ⁻² = CaCO ₃	3.22	0.14	0.00%	0.00%
CaHCO ₃ ⁺	Ca ⁺² + CO ₃ ⁻² + H ⁺ = CaHCO ₃ ⁺	11.44	0.09	0.00%	0.00%
NaCO ₃ ⁻	Na ⁺ + CO ₃ ⁻² = NaCO ₃ ⁻	1.27	0.30	0.00%	0.00%
NaHCO ₃	Na ⁺ + CO ₃ ⁻² + H ⁺ = NaHCO ₃	10.08	0.30	0.00%	0.00%
FeCO _{3(aq)}	Fe ⁺² + CO ₃ ⁻² = FeCO _{3(aq)}	4.38	1.31	0.00%	0.00%
FeHCO ₃ ⁺	Fe ⁺² + CO ₃ ⁻² + H ⁺ = FeHCO ₃ ⁺	12.33	0.30	0.00%	0.00%
HSO ₄ ⁻	H ⁺ + SO ₄ ⁻² = HSO ₄ ⁻	1.98	0.25	0.00%	0.00%
CaSO_{4(aq)}	Ca ⁺² + SO ₄ ⁻² = CaSO ₄	2.30	0.30	26.40%	0.32%
NaSO₄⁻	Na ⁺ + SO ₄ ⁻² = NaSO ₄ ⁻	0.70	0.30	3.81%	0.01%
FeHSO ₄ ⁺	Fe ⁺² + SO ₄ ⁻² + H ⁺ = FeHSO ₄ ⁺	3.07	0.30	0.00%	0.00%
FeSO _{4(aq)}	Fe ⁺² + SO ₄ ⁻² = FeSO _{4(aq)}	2.25	0.05	0.00%	0.00%
FeCl ⁺	Fe ⁺² + Cl ⁻ = FeCl ⁺	0.14	0.23	0.00%	0.00%

The impact of aqueous species with an associated uncertainty of ΔlogK⁰ = 0.3 has been analysed in more detail. Some conclusions can be extracted:

- *RaCl⁺*: for Forsmark groundwater, if larger values of ΔlogK⁰ are considered, up to ΔlogK⁰ = 3, there is a negligible impact in the solubility uncertainty according to the spreadsheet. However, an increasing contribution is found, from 0.6% up to 38% for ΔlogK⁰ = 3, for the uncertainty contribution of this particular species. For Grimsel water, there is no impact at all.
- *CaSO_{4(aq)}* and *NaSO₄⁻*: For Grimsel water, there is no impact in the solubility uncertainty, but the contribution increases if their uncertainty is increased, especially for CaSO_{4(aq)}, with a contribution of up to 24% for ΔlogK⁰ = 3. The

case with Forsmark water is different, since the contribution of $\text{CaSO}_{4(\text{aq})}$ to uncertainty is as high as 26.4% considering a $\Delta\log K^0 = 0.3$. If this later value was increased to 3, the calculated contribution to uncertainty would be 97.29%, while the solubility uncertainty is increased by 500%.

The low impact of large uncertainty windows of the above-mentioned aqueous species is significant, since in this case the uncertainty in the solid phase equilibrium constant is very small.

The uncertainty associated with the $\log K^0$ values of these species has also been discussed in detail in section 3.2. Specifically, it has been mentioned that the main uncertainty in the calculation is the possibility of co-precipitation of radium with other solid phases present in the system (Duro et al. 2006b), a possibility that is not taken into account in the simplified calculations of the Spreadsheet tool.

4.3 Americium

The case of Americium deserves special attention. This element has been also used in Stenhouse et al. (2008, Appendix A) as an example to compare the results obtained in Duro et al. (2006b) using the Phreeqc code with a methodology to assess uncertainty based on Monte Carlo simulations, also using Phreeqc as the geochemical solver and the same set of input parameters (thermodynamic database, water composition, etc.).

Besides the reference Forsmark water in Table 3, the water composition used in the Simple Functions example in Grivé et al. (2010b) has also been used. The compositions of both waters are equivalent, with the only difference in pH, which is equal 7 in the former (Table 3) and 6 in the later (Table 12). The reason to use these two compositions is that the solubility controlling phase changes from $\text{Am}(\text{CO}_3)_2\text{Na}\cdot 5\text{H}_2\text{O}$ for pH 7 to $\text{Am}_2(\text{CO}_3)_3$ for pH 6, while the solubility is increased by one order of magnitude if pH = 6.

Table 12. Composition of water used in the calculations from Grivé et al. (2010b). Concentrations in mole·dm⁻³.

	Modified water Grivé et al. (2010b)
pH	6
Eh (mV)	-143
[Na ⁺] _{tot}	$8.88 \cdot 10^{-2}$
[K ⁺] _{tot}	$8.75 \cdot 10^{-4}$
[Ca ²⁺] _{tot}	$2.33 \cdot 10^{-2}$
[HCO ₃ ⁻]	$1.77 \cdot 10^{-3}$
[Cl] _{tot}	$1.53 \cdot 10^{-1}$
[S] _{tot}	$6.80 \cdot 10^{-3}$
[Si] _{tot}	$1.85 \cdot 10^{-4}$
[Fe] _{tot}	$3.31 \cdot 10^{-5}$
Ionic strength	0.19

The results of the Am solubility uncertainty calculation obtained with Simple Functions for the compositions of the three groundwaters are summarized in Table 13 and Table 14. The uncertainties are smaller in the case of Forsmark water due to the fact that the uncertainties associated to the log K_{sp} value of the solid phase $\text{Am}(\text{CO}_3)_2\text{Na} \cdot 5\text{H}_2\text{O}(\text{s})$ and contributing species are smaller than those for the other two water compositions. This case also shows a significant contribution (26.54%) of the aqueous species $\text{Am}(\text{CO}_3)^+$ (even though the uncertainty of its equilibrium constant is small) as this is expected to be one of the main americium species in solution.

By reducing the pH of the Forsmark water in one log unit (water used in Grivé et al. 2010b), the solubility increases one order of magnitude, and the associated uncertainty almost doubles. This is due to the fact that in this case the controlling solid is $\text{Am}_2(\text{CO}_3)_3$, which has a much larger uncertainty associated to its solubility product than the previous solid phase, while its contribution to solubility uncertainty is also larger (98.62%), as seen in Table 14.

Finally, the Ice melting (Grimsel) water leads to a much lower solubility, in this case controlled by $\text{Am}(\text{OH})_{3(\text{am})}$. The solubility uncertainty is not as large as the second case, because the contributing species and solid phase have smaller uncertainty associated to their thermodynamic data. In this case there is a significant contribution of the aqueous species $\text{Am}(\text{CO}_3)_2^-$ to total uncertainty.

As in previous examples, although the uncertainty associated to the $\text{CO}_3^{2-}/\text{HCO}_3^-$ equilibrium constant is very small, it has a contribution to the solubility uncertainty. This is related to the key role that carbonates play in the solubility calculations.

Table 13. Main results of Am solubility for the two groundwater compositions.

Solubility limit	Forsmark	Modified*	Ice melting
Solid phase	$\text{Am}(\text{CO}_3)_2\text{Na}\cdot 5\text{H}_2\text{O}$	$\text{Am}_2(\text{CO}_3)_3$	AmOH_3
[Am]	$2.86\cdot 10^{-6}$	$3.09\cdot 10^{-5}$	$9.27\cdot 10^{-8}$
log[Am]	-5.54	-4.51	-7.03
$\Delta[\text{Am}]$	$1.67\cdot 10^{-6}$	$3.42\cdot 10^{-5}$	$8.47\cdot 10^{-8}$
% error	59%	111%	91%
$\Delta\log[\text{Am}]$	0.25	0.48	0.40

* Same results as reported in Grivé et al. (2010b)

Table 14. Main results and uncertainty contribution for the species and solid phase considered in the Am solubility calculations for the different groundwater compositions.

Am species	Reaction	logK ^o	ΔlogK	Uncertainty contribution		
				Forsmark	Modified*	Grimsel
Am(OH) ⁺²	Am ⁺³ + H ₂ O = Am(OH) ⁺² + H ⁺	-7.20	0.50	0.03%	0.00%	0.00%
Am(OH) ₂ ⁺	Am ⁺³ + 2H ₂ O = Am(OH) ₂ ⁺ + 2H ⁺	-15.10	0.70	0.00%	0.00%	1.71%
Am(OH) ₃	Am ⁺³ + 3H ₂ O = Am(OH) ₃ + 3H ⁺	-26.20	0.50	0.00%	0.00%	0.00%
Am(CO ₃) ⁺	Am ⁺³ + CO ₃ ⁻² = Am(CO ₃) ⁺	8.00	0.40	26.54%	1.16%	0.21%
Am(CO ₃) ₂ ⁻	Am ⁺³ + 2CO ₃ ⁻² = Am(CO ₃) ₂ ⁻	12.90	0.60	0.26%	0.00%	21.36%
Am(CO ₃) ₃ ⁻³	Am ⁺³ + 3CO ₃ ⁻² = Am(CO ₃) ₃ ⁻³	15.00	1.00	0.00%	0.00%	0.01%
AmHCO ₃ ⁺²	Am ⁺³ + H ⁺ + CO ₃ ⁻² = AmHCO ₃ ⁺²	13.43	0.30	0.04%	0.17%	0.00%
Am(SO ₄) ⁺	Am ⁺³ + SO ₄ ⁻² = Am(SO ₄) ⁺	3.30	0.15	0.00%	0.02%	0.00%
Am(SO ₄) ₂ ⁻	Am ⁺³ + 2SO ₄ ⁻² = Am(SO ₄) ₂ ⁻	3.70	0.15	0.00%	0.00%	0.00%
AmCl ⁺²	Am ⁺³ + Cl ⁻ = AmCl ⁺²	0.24	0.03	0.00%	0.00%	0.00%
AmCl ₂ ⁺	Am ⁺³ + 2Cl ⁻ = AmCl ₂ ⁺	-0.74	0.05	0.00%	0.00%	0.00%
Solid phases						
Am(OH) ₃ (am)	Am(OH) ₃ (am) + 3H ⁺ = Am ⁺³ + 3H ₂ O	16.90	0.80			76.58%
Am ₂ (CO ₃) ₃ (s)	Am ₂ (CO ₃) ₃ (s) = 2Am ⁺³ + 3CO ₃ ⁻²	-33.40	2.20		98.62%	
Am(CO ₃) ₂ Na·5H ₂ O(s)	Am(CO ₃) ₂ Na·5H ₂ O(s) = Am ⁺³ + 2CO ₃ ⁻² + 5H ₂ O + Na ⁺	-21.00	0.50	72.98%		
Species						
CaOH ⁺	Ca ⁺² + H ₂ O = CaOH ⁺ + H ⁺	-12.78	0.30	0.00%	0.00%	0.00%
FeOH ⁺	Fe ⁺² + H ₂ O = FeOH ⁺ + H ⁺	-9.50	0.10	0.00%	0.00%	0.00%
Fe(OH) ₃ (aq)	Fe ⁺² + 0.25O ₂ (g) + 2.5H ₂ O = Fe(OH) ₃ (aq) + 2H ⁺	-4.80	1.06	0.00%	0.00%	0.00%
Fe(OH) ₄ ⁻	Fe ⁺² + 0.25O ₂ (g) + 2.5H ₂ O = Fe(OH) ₄ ⁻ + 3H ⁺	-13.84	0.08	0.00%	0.00%	0.00%
HCO ₃ ⁻	H ⁺ + CO ₃ ⁻² = HCO ₃ ⁻	10.33	0.02	0.14%	0.04%	0.14%
CaCO ₃ (aq)	Ca ⁺² + CO ₃ ⁻² = CaCO ₃	3.22	0.14	0.00%	0.00%	0.00%
CaHCO ₃ ⁺	Ca ⁺² + CO ₃ ⁻² + H ⁺ = CaHCO ₃ ⁺	11.44	0.09	0.00%	0.00%	0.00%
NaCO ₃ ⁻	Na ⁺ + CO ₃ ⁻² = NaCO ₃ ⁻	1.27	0.30	0.00%	0.00%	0.00%
NaHCO ₃	Na ⁺ + CO ₃ ⁻² + H ⁺ = NaHCO ₃	10.08	0.30	0.00%	0.00%	0.00%
FeCO ₃ (aq)	Fe ⁺² + CO ₃ ⁻² = FeCO ₃ (aq)	4.38	1.31	0.00%	0.00%	0.00%
FeHCO ₃ ⁺	Fe ⁺² + CO ₃ ⁻² + H ⁺ = FeHCO ₃ ⁺	12.33	0.30	0.00%	0.00%	0.00%
HSO ₄ ⁻	H ⁺ + SO ₄ ⁻² = HSO ₄ ⁻	1.98	0.25	0.00%	0.00%	0.00%
CaSO ₄ (aq)	Ca ⁺² + SO ₄ ⁻² = CaSO ₄	2.30	0.30	0.00%	0.00%	0.00%
NaSO ₄ ⁻	Na ⁺ + SO ₄ ⁻² = NaSO ₄ ⁻	0.70	0.30	0.00%	0.00%	0.00%
FeHSO ₄ ⁺	Fe ⁺² + SO ₄ ⁻² + H ⁺ = FeHSO ₄ ⁺	3.07	0.30	0.00%	0.00%	0.00%
FeSO ₄ (aq)	Fe ⁺² + SO ₄ ⁻² = FeSO ₄ (aq)	2.25	0.05	0.00%	0.00%	0.00%
FeCl ⁺	Fe ⁺² + Cl ⁻ = FeCl ⁺	0.14	0.23	0.00%	0.00%	0.00%

* Groundwater reported in Grivé et al. (2010b)

5. Summary and Conclusions

A review of the existing approaches to assess the impact of thermodynamic data uncertainty on solubility and speciation has been presented. The specific methodology used in the Simple Functions Spreadsheet tool has been discussed in this context.

A more detailed review on the specific uncertainty values used in the Simple Functions Spreadsheet tool, including a basis to the use of the default value of ± 0.3 log units when no uncertainty was available, has been provided. All cases are justified and discussed in the light of the assigned uncertainties. The only case where a change in the default uncertainty to ± 1 log units could be justified is the solubility constant of $\text{Ho}(\text{OH})_3(\text{am})$.

Finally, detailed examples are provided on the influence of uncertainty in the calculations of different radionuclide (Uranium, Americum and Radium) solubility values using the Simple Functions Spreadsheet.

From the detailed analyses presented in this report, the uncertainty assignment approach followed in the SR-Site solubility exercise is considered by and large sufficiently accurate and appropriate for the purpose.

References

- Baes C F, Mesmer R E, 1976** The hydrolysis of cations. New York: Wiley.
- Bard A J, Parsons R, Jordan J (eds), 1985** Standard potentials in aqueous solution. New York: Marcel Dekker.
- Bell R P, George J H B, 1953.** The incomplete dissociation of some thallos and calcium salts at different temperatures. Transactions of the Faraday Society 49, 619–627.
- Bernot P, 2005.** Dissolved concentration limits of radioactive elements. Report ANL-WIS-MD-000010 REV 05, Bechtel SAIC Company, Las Vegas, NV.
- Busenberg E, Plummer L N, Parker V B, 1984.** The solubility of strontianite (SrCO_3) in CO_2 - H_2O solutions between 2 and 91°C , the association constants of $\text{SrHCO}_3^+(\text{aq})$ and $\text{SrCO}_3^0(\text{aq})$ between 5 and 80°C , and an evaluation of the thermodynamic properties of $\text{Sr}^{2+}(\text{aq})$ and $\text{SrCO}_3(\text{cr})$ at 25°C and 1 atm total pressure. Geochimica et Cosmochimica Acta 48, 2021–2035.
- Cabaniss S E, 1999.** Uncertainty propagation in geochemical calculations: non-linearity in solubility equilibria. Applied Geochemistry 14, 255–262.
- Duro L, Grivé M, Cera E, Domènech C, Bruno J, 2006a.** Update of a thermodynamic database for radionuclides to assist solubility limits calculation for performance assessment. SKB TR-06-17, Svensk Kärnbränslehantering AB.
- Duro L, Grivé M, Cera E, Gaona X, Domènech C, Bruno J, 2006b.** Determination and assessment of the concentration limits to be used in SR-Can. SKB TR-06-32, Svensk Kärnbränslehantering AB.
- Ekberg C, Emrén A T, 1998.** Uncertainties in solubility calculations aimed at a repository for spent nuclear fuel. In Mosleh A, Bari R A (eds). Proceedings of the 4th International Conference on Probabilistic Safety Assessment and Management, New York, 13–18 September 1998. Vol 4, 2223–2228.
- Ekberg C, Ödegaard-Jensen A, 2004.** Computer programs for uncertainty analysis of solubility calculations: Windows version and other updates of the SENVAR and UNCCON. Program description and handling instructions. SKI Report 2004:20, Statens kärnkraftinspektion (Swedish Nuclear Power Inspectorate).
- Ekberg C, Ödegaard-Jensen A, 2011.** Uncertainties in chemical modelling of solubility, speciation and sorption. Accreditation and Quality Assurance 16, 207–214.
- Ekberg C, Meinrath G, Strömberg B, 2003.** A retraceable method to assess uncertainties in solubility estimations exemplified by a few americium solids. The Journal of Chemical Thermodynamics 35, 55–66.
- Ekberg C, Englund S, Liljenzin J-O, 2011.** Uncertainty analysis of correlated stability constants. Accreditation and Quality Assurance 16, 185–189.
- Ellison S L R, Williams A (eds), 2012.** EURACHEM/CITAC guide. Quantifying uncertainty in analytical measurement. 3rd ed.. EURACHEM/CITAC Working Group.

- Elrashidi M A, Adriano D C, Workman S M, Lindsay W L, 1987.** Chemical equilibria of selenium in soils: a theoretical development. *Soil Science* 144, 141–151.
- Grivé M, Domènech C, Montoya V, Garcia D, Duro L, 2010a.** Determination and assessment of the concentration limits to be used in SR-Can Supplement to TR-06-32. SKB R-10-50, Svensk Kärnbränslehantering AB.
- Grivé M, Domènech C, Montoya V, García D, Duro L, 2010b.** Simple Functions Spreadsheet tool presentation. SKB TR-10-61, Svensk Kärnbränslehantering AB.
- Nordstrom D K, Plummer L N, Langmuir D, Busenberg E, May H M, Jones B F, Parkhurst D L, 1990.** Revised chemical equilibrium data for major water–mineral reactions and their limitations. In Bassett R L, Melchior D (eds). *Chemical modeling of aqueous systems II*. Washington, DC, American Chemical Society. (ACS Symposium Series 416), 398–413.
- Pokrovski G S, Schott J, Sergeev A S, 1995.** Experimental determination of the stability constants of NaSO_4^- and $\text{NaB}(\text{OH})_4^0$ in hydrothermal solutions using a new high-temperature sodium-selective glass electrode – Implications for boron isotopic fractionation. *Chemical Geology* 124, 253–265.
- Righellato E C, Davies C W, 1930.** The extent of dissociation of salts in water. Part II. Uni-bivalent salts. *Transactions of the Faraday Society* 26, 592–600.
- Serco, 2008.** Strategy for the treatment of uncertainty in solubility, sorption and diffusion data for a UK HLW repository. Report to NDA. SA/ENV-1002, Serco, UK.
- Séby F, Potin-Gautier M, Giffaut E, Donard O F X, 2001a.** A critical review of thermodynamic data for inorganic tin species. *Geochimica et Cosmochimica Acta* 65, 3041–3053.
- Séby F, Potin-Gautier M, Giffaut E, Borge G, Donard O F X, 2001b.** A critical review of thermodynamic data for selenium species at 25°C. *Chemical Geology* 171, 173–194.
- SKB, 2006.** Long-term safety for KBS-3 repositories at Forsmark and Laxemar – a first evaluation. Main report of the SR-Can project. SKB TR-06-09, Svensk Kärnbränslehantering AB.
- SKB, 2010a.** Radionuclide transport report for the safety assessment SR-Site. SKB TR-10-50, Svensk Kärnbränslehantering AB.
- SKB, 2010b.** Model summary report for the safety assessment SR-Site. SKB TR-10-51, Svensk Kärnbränslehantering AB.
- SKB, 2010c.** Data report for the safety assessment SR-Site. SKB TR-10-52, Svensk Kärnbränslehantering AB.
- SKB, 2010d.** Fuel and canister process report for the safety assessment SR-Site. SKB TR-10-46, Svensk Kärnbränslehantering AB.
- SKB, 2011.** Long-term safety for the final repository for spent nuclear fuel at Forsmark. Main report of the SR-Site project. SKB TR-11-01, Svensk Kärnbränslehantering AB.
- Spahiu K, Bruno J, 1995.** A selected thermodynamic database for REE to be used in HLNW performance assessment exercises. SKB TR 95-35, Svensk Kärnbränslehantering AB.

Stenhouse M, Jégou C, Brown P, Meinrath G, Nitsche H, Ekberg C, 2008. Review of SR-Can: Evaluation of SKB's handling of spent fuel performance, radionuclide chemistry and geosphere transport parameters. External review contribution in support of SKI's and SSI's review of SR-Can. SKI Report 2008:17, Statens kärnkraftinspektion (Swedish Nuclear Power Inspectorate).

Sverjensky D A, Shock E L, Helgeson H C, 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb. *Geochimica et Cosmochimica Acta* 61, 1359–1412.

Wanner H, 2007. Solubility data in radioactive waste disposal. *Pure and Applied Chemistry* 79, 875–882.

Wanner H, Östhols E, 1999. TDB-3: guidelines for the assignment of uncertainties (Version of 1st June 1999). OECD, Nuclear Energy Agency.

Wanner H, Östhols, E 2000. TDB-1: guidelines for the review procedure and data selection (Version of 6th January 2000). OECD, Nuclear Energy Agency.