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**Radionuclide solubilities to be used  
in SKB 91**

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# **RADIONUCLIDE SOLUBILITIES TO BE USED IN SKB 91**

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**ABSTRACT (ENGLISH)**

We have performed thermodynamic calculations in order to assess the solubility limits (source term) for selected radionuclides. Equilibrium solubilities for U, Pu, Np, Am, Th, Ra, Sn, Tc, Zr, Sn, Ni, Sm, Pa, Nb and Pd have been calculated in four waters, representing average fresh and saline granitic groundwaters under oxidizing and reducing conditions, respectively.

The results from the calculations have been compared with the measured radionuclide concentrations in natural waters as well as in spent fuel leaching tests.

**ABSTRACT (SWEDISH)**

Vi har utfört termodynamiska beräkningar för att fastställa löslighetsgränserna (källtermen) för utvalda radionuklider. Jämviktslösligheter för U, Pu, Np, Am, Th, Ra, Sn, Tc, Zr, Sn, Ni, Sm, Pa, Nb, och Pd har beräknats i fyra vatten, vilka motsvarar standardmässiga söta och salta granitvatten, under oxiderande och reducerande förhållanden.

Resultaten från beräkningarna har jämförts med mätta koncentrationer av radionuklider i naturliga vatten och lakförsök av använt bränsle.

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## SUMMARY

The present exercise is part of the SKB 91 project. We have calculated the most probable solubilities for a series of selected radionuclides in four types of average granitic groundwaters. The radionuclides have been chosen among those which are relevant for safety assessment purposes and which have a chance to be solubility limited under repository conditions. In this respect, Sr, I, Cs and Rn are not considered in these calculations.

Equilibrium calculations have been performed for the following radionuclides: U, Pu, Np, Am, Th, Ra, Sn, Tc, Zr, Ni, Sm, Pa, Nb and Pd. Large input concentrations of these radionuclides have been set to equilibrate at 25<sup>0</sup> with four average granitic groundwaters which represent the measured compositions for fresh and saline groundwaters of the Finnsjön area under oxidizing and reducing conditions.

The calculations have been performed mostly by using the EQ3/6 code package including the thermodynamic data base (version 0288). For uranium and plutonium the SKBU and SKBPu data bases have been used. In some other cases we have used the PHREEQE code in addition to the following data bases: ZZ-Hatches for Zr, Se, Ni Pb and Nb, Baes and Mesmer for Sn and Pa and Baeyens and McKinley for Pd. The behaviour of Sm was discussed by analogy with Am.

The calculated equilibrium concentrations, the solubility limiting phase and the predominant aqueous speciation are reported. The calculated data are compared to the experimental results from spent fuel leaching tests as well as to the observed radionuclide concentrations in natural water systems.

The results of the calculations are in good agreement with the observed radionuclide concentrations for U, Pu, Np and Tc under reducing conditions, Am, Th and Sn. The solubilities appear to be conservative for Np in oxic conditions, Ra, Zr, Ni, Pa, Nb and probably Pd. No solubility limit is found for Tc and Se under oxic conditions.

## RADIONUCLIDE SOLUBILITIES TO BE USED IN SKB 91

Solubility limits are often used to constrain the possible migration of radionuclides in the near-field. Particularly, for those elements which solubility is sufficiently low. Under radiolytically induced oxidation the surface of the spent nuclear fuel will dissolve and release its radionuclide content. In the actual repository most of the minor radionuclides will co-precipitate forming solid solutions with each other, thus limiting their dissolved concentration under their individual solubility limit. However, the quantification of these processes is still not fully understood and consequently, individual solubility limits are taken as a conservative upper constrain.

The solubilities in this report are best-estimate values. We will not give any uncertainty ranges or alternative values, since the solubilities will be modelled as fixed parameters in the SKB 91 safety assessment exercise. The reason for this is that the object with SKB 91 is to highlight the effect of variations in the site geology means to the overall safety of the repository. Therefore all near-field parameters will be kept constant through the exercise.

## ELEMENTS TO BE STUDIED

The elements that are important in the safety assessment are shown in table 1.

Se	*	Ni	*
Sr	(probably never solubility limited)	Nb	*
Zr	*	Am	*
Tc	*	Pu	*
Pd	*	Np	*
Sn	*	U	*
I	(never solubility limited)	Pa	*
Cs	(never solubility limited)	Th	*
Sm	*	Ra	*
C	(probably never solubility limited)	Rn	(never solubility limited)
Cl	(never solubility limited)	Pb	*

\* Covered in this report

Table 1 Radioelements considered in SKB 91.

## GROUNDWATER COMPOSITION

The groundwater studied in SKB 91 are two typical Finnsjön-waters (Ahlbom et al, 1989<sup>1</sup>), one saline and one high in carbonate (Table 2.)

	Fresh (ppm)	Saline (ppm)
Ca	75.0	1600.0
Na	23.0	120.0
Mg	6.3	1700.0
K	3.2	13.0
Fe	9.0	0.016
Si	6.0	6.0
Cl	61.0	5500.0
Br	0.3	29.0
F	0.6	1.2
NO <sub>3</sub>	0.5	-
SO <sub>4</sub>	8.9	380.0
HCO <sub>3</sub>	220.0	48.0
pH	6.9	7.0
Eh(mV)	-200/650	-200/650

Table 2

*Groundwater compositions.*

Only these two waters are considered in the safety analysis. Chemical effects on the groundwater caused by bentonite reactions are neglected.

## SOLUBILITIES

Solubilities are calculated for reducing (-200mV) and oxidizing ( $fO_2 = 0.2$  atm) conditions.

SALINE	Oxidizing conditions conc/film phase	dom. spec	Reducing conditions conc/film phase	dom. spec
U	$3 \times 10^{-6}$ Schoepite	$UO_2(CO_3)_2^{2-}$ $UO_2(CO_3)_3^{4-}$	$2 \times 10^{-7}$ $UO_2(\text{fuel})$	$U(OH)_4$
Pu	$3 \times 10^{-8}$ $Pu(OH)_4$	$PuO_2^+$	$5 \times 10^{-8}$ $Pu(OH)_4$	$Pu^{3+}$ $PuSO_4^+$
Np	$4 \times 10^{-4}$ $NaNpO_2CO_3$	$NpO_2^+$ $NpO_2Cl$	$2 \times 10^{-8}$ $Np(OH)_4$	$Np(OH)_4$
Am	$6 \times 10^{-8}$ $AmOHCO_3$	$AmCO_3^+$ $Am^{3+}$	$5 \times 10^{-8}$ $AmOHCO_3$	$AmCO_3^+$ $Am^{3+}$
Th	$2 \times 10^{-10}$ $ThO_2$	$Th(OH)_4$	$2 \times 10^{-10}$ $ThO_2$	$Th(OH)_4$
Ra	$2 \times 10^{-7}$ $RaSO_4$	$Ra^{2+}$	$2 \times 10^{-7}$ $RaSO_4$	$Ra^{2+}$
Sn	$2 \times 10^{-8}$ $SnO_2$	$Sn(OH)_4$	$2 \times 10^{-8}$ $SnO_2$	$Sn(OH)_4$
Tc	high	$TcO_4^-$	$2 \times 10^{-8}$ $TcO_2$	$[TcO(OH)_2]_2$
Zr	$9 \times 10^{-11}$ $ZrO_2$	$Zr(OH)_5^-$	$8 \times 10^{-11}$ $ZrO_2$	$Zr(OH)_5^-$
Se	high	$SeO_4^-$	$1 \times 10^{-4}$ $Fe_3Se_4$	$HSe^-$
Ni	$2 \times 10^{-4}$ $NiFe_2O_4$	$Ni^{2+}$	$2 \times 10^{-5}$ $Ni_3S_4$	$Ni^{2+}$
Sm	$7 \times 10^{-4}$ $Sm(OH)_3$	$Sm^{3+}$	$7 \times 10^{-4}$ $Sm(OH)_3$	$Sm^{3+}$
Pa	$3 \times 10^{-7}$ $Pa_2O_5$	$PaO_2(OH)$	$3 \times 10^{-7}$ $Pa_2O_5$	$PaO_2(OH)$
Pb	$2 \times 10^{-5}$ $PbCO_3$	$PbCl^+$	$7 \times 10^{-16}$ $PbS$	$PbCl^+$
Nb	$1 \times 10^{-5}$ $Nb_2O_5$	$Nb(OH)_5$	$1 \times 10^{-5}$ $Nb_2O_5$	$Nb(OH)_5$
Pd	$1.5 \times 10^{-6}$ $Pd(OH)_2(s)$	$Pd(OH)_2(aq)$	$1.5 \times 10^{-6}$ $Pd(OH)_2(s)$	$Pd(OH)_2(aq)$

Table 3 Solubilities in the saline Finnsjövater.

FRESH	Oxidizing conditions conc/lm phase	dom. spec	Reducing conditions conc/lm phase	dom. spec
U	$3 \times 10^{-4}$ Schoepite	$\text{UO}_2(\text{CO}_3)_2^{2-}$ $\text{UO}_2(\text{CO}_3)_3^{4-}$	$2 \times 10^{-7}$ $\text{UO}_2(\text{fuel})$	$\text{U}(\text{OH})_4$
Pu	$3 \times 10^{-9}$ $\text{Pu}(\text{OH})_4$	$\text{PuO}_2^+$	$2 \times 10^{-8}$ $\text{Pu}(\text{OH})_4$	$\text{Pu}^{3+}$ $\text{PuSO}_4^+$
Np	$2 \times 10^{-3}$ $\text{NpO}_2(\text{OH})$	$\text{NpO}_2^+$ $\text{NpO}_2\text{CO}_3$	$2 \times 10^{-9}$ $\text{Np}(\text{OH})_4$	$\text{Np}(\text{OH})_4$
Am	$2 \times 10^{-8}$ $\text{AmOHCO}_3$	$\text{AmCO}_3^+$ $\text{Am}^{3+}$	$2 \times 10^{-8}$ $\text{AmOHCO}_3$	$\text{AmCO}_3^+$ $\text{Am}^{3+}$
Th	$2 \times 10^{-10}$ $\text{ThO}_2$	$\text{Th}(\text{OH})_4$	$2 \times 10^{-10}$ $\text{ThO}_2$	$\text{Th}(\text{OH})_4$
Ra	$1 \times 10^{-6}$ $\text{RaSO}_4$	$\text{Ra}^{2+}$	$1 \times 10^{-6}$ $\text{RaSO}_4$	$\text{Ra}^{2+}$
Sn	$3 \times 10^{-8}$ $\text{SnO}_2$	$\text{Sn}(\text{OH})_4$	$3 \times 10^{-8}$ $\text{SnO}_2$	$\text{Sn}(\text{OH})_4$
Tc	high	$\text{TcO}_4^-$	$2 \times 10^{-8}$ $\text{TcO}_2$	$[\text{TcO}(\text{OH})_2]_2$
Zr	$2 \times 10^{-11}$ $\text{ZrO}_2$	$\text{Zr}(\text{OH})_5^-$	$2 \times 10^{-11}$ $\text{ZrO}_2$	$\text{Zr}(\text{OH})_5^-$
Se	high	$\text{SeO}_4^-$	$1 \times 10^{-9}$ $\text{Fe}_3\text{Se}_4$	$\text{HSe}^-$
Ni	$9 \times 10^{-5}$ $\text{NiFe}_2\text{O}_4$	$\text{Ni}^{2+}$	$1 \times 10^{-4}$ $\text{Ni}_3\text{S}_4$	$\text{Ni}^{2+}$
Sm	$1 \times 10^{-4}$ $\text{Sm}_2(\text{CO}_3)_3$	$\text{Sm}^{3+}$	$1 \times 10^{-4}$ $\text{Sm}_2(\text{CO}_3)_3$	$\text{Sm}^{3+}$
Pa	$3 \times 10^{-7}$ $\text{Pa}_2\text{O}_5$	$\text{PaO}_2(\text{OH})$	$3 \times 10^{-7}$ $\text{Pa}_2\text{O}_5$	$\text{PaO}_2(\text{OH})$
Pb	$2 \times 10^{-6}$ $\text{PbCO}_3$	$\text{PbCO}_3$	$2 \times 10^{-15}$ $\text{PbS}$	$\text{PbCO}_3$
Nb	$1 \times 10^{-5}$ $\text{Nb}_2\text{O}_5$	$\text{Nb}(\text{OH})_5$	$1 \times 10^{-5}$ $\text{Nb}_2\text{O}_5$	$\text{Nb}(\text{OH})_5$
Pd	$1,5 \times 10^{-6}$ $\text{Pd}(\text{OH})_2(\text{s})$	$\text{Pd}(\text{OH})_2(\text{aq})$	$1,5 \times 10^{-6}$ $\text{Pd}(\text{OH})_2(\text{s})$	$\text{Pd}(\text{OH})_2(\text{aq})$

Table 4 Solubilities in the fresh Finnsj water.

## URANIUM

The thermodynamic data base used in these calculations is the SKBU 1 (Bruno and Puigdomenech, 1988<sup>2</sup>), which has been previously validated for its use in the EQ3/6 code package (Puigdomenech and Bruno, 1988<sup>3</sup>). Most of the data used in the SKBU 1 thermodynamic data base agrees with the recommendations from the uranium group of the NEA-TDB project (Grenthe et al, 1990<sup>4</sup>).

Under oxidizing conditions the solubility limiting phase for uranium is schoepite,  $\text{UO}_2(\text{OH})_2$  (s). This phase and/or related  $\text{UO}_2 \cdot x\text{H}_2\text{O}$  solid phases have been found in spent fuel leaching tests under oxidizing conditions (Forsyth et al, 1986<sup>5</sup>).

Schoepite has also been identified in early stages of the oxidative alteration of uraninite in geological conditions (Finch and Ewing, 1990<sup>6</sup>). The uranium (VI) aqueous speciation is dominated by carbonate complexes. The carbonate complexes  $\text{UO}_2(\text{CO}_3)_3^{4-}$  have been identified by laser spectroscopy in spent fuel leaching solutions under oxidizing conditions (Bruno et al, 1988<sup>7</sup>). The calculated solubilities are in good agreement with the observations from spent fuel leaching tests in contact with air (Forsyth and Werme, 1992<sup>8</sup>).

Under reducing conditions  $\text{UO}_2$  is stable and  $\text{UO}_2$  (fuel) is the solubility limiting phase. The aqueous speciation is dominated by the  $\text{U}(\text{OH})_4$  (aq) complex. The calculated solubilities are in good agreement with the observations from spent fuel leaching experiments under reducing conditions.

Neither the solid nor the aqueous speciation are affected by the small changes in the salinity of the groundwater. The solubility of schoepite in non-saline groundwater is due largely to its higher carbonate content.

## PLUTONIUM

The thermodynamic data base used in these calculations is the one provided with the EQ3/6 code package (version 0288). We have introduced some modifications in this database and these are discussed in a recent report concerning Pu solubilities (Puigdomenech and Bruno, 1991<sup>9</sup>).

$\text{Pu}(\text{OH})_4$  (s) is the solubility limiting phase in both reducing and oxidizing conditions. The various  $\text{Pu}(\text{OH})_4$  (s) morphologies and their stability under the effect of radiolysis are discussed in Puigdomenech and Bruno, 1991.

Under oxidizing conditions,  $\text{PuO}_2^+$  is the dominating aqueous species, while  $\text{Pu}^{3+}$  and  $\text{PuSO}_4^+$  appear to be the predominant ones under reducing conditions. Nevertheless, Pu has been found to be present mostly as Pu(V) at very low concentrations in both sea water and J-13 groundwater under reducing conditions. This has been explained by the slow kinetics of disproportionation of Pu(V) to Pu(III) and Pu(IV) at trace concentrations.

The small changes in salinity of the chosen groundwaters do not affect neither the solubility nor the speciation of Pu. The calculated solubilities of plutonium agree with the measured Pu concentrations in spent fuel leach tests under oxidizing conditions (R. Forsyth et al, 1986<sup>10</sup>). However, the calculated Pu solubilities under reducing conditions are 2-3 orders of magnitude larger than the measured Pu concentrations in spent fuel dissolution experiments (R.S. Forsyth and L.O. Werme, 1989<sup>11</sup>).

## TECHNETIUM

The thermodynamic data base used in these calculations is the one provided with the EQ3/6 code package (version 0288). However, some oxide and sulphide solid phases were removed from the data base due to the lack of sufficiently good data. The critical data concerning the solubility of the hydrous  $\text{TcO}_2$  (s) and its redox equilibrium with  $\text{TcO}_2$  have been derived from the experimental data by Meyer et al, (1989<sup>12</sup>).

Under oxidizing conditions the solubility of Tc is very large and practically non-limited. The aqueous speciation is dominated by the  $\text{TcO}_4^-$  ion. The measured Tc concentrations from spent fuel leaching tests in J-13 groundwater in contact with air are  $\log[\text{Tc}] = -6.3 \pm 0.5$ .

Under reducing conditions the hydrous  $\text{TcO}_2$  is the solubility limiting phase, while  $[\text{TcO}_2(\text{OH})_2]_2$  (aq) is the predominant aqueous species. This is in good agreement with the experimental findings, although recent work has shown the relative importance of Tc(IV) hydroxy carbonate complexes (Eriksen et al, 1992<sup>13</sup>). The measured Tc concentrations from spent fuel dissolution experiments under reducing conditions are somewhat erratic depending on how well the redox conditions are kept (L.O. Werme, personal communication). The calculated Tc(IV) solubilities agree with the lowest Tc concentrations measured in these experiments.

## NEPTUNIUM

The thermodynamic data base used in these calculations is the one provided in the EQ3/6 code package (version 0288). This is based in the compilations by R.J. Lemire (Lemire and Tremaine, 1980<sup>14</sup> and Lemire, 1988<sup>15</sup>).

Under oxidizing conditions two different solid phases control the Np solubility, depending on the salinity of the groundwater. In groundwaters with high NaCl contain,  $\text{NaNpO}_2\text{CO}_3$  (s) is the solubility limiting phase. This corresponds to an idealised morphology of a series of  $\text{Na}_x(\text{NpO}_2)_{1-x}\text{CO}_3$  solid phases which can be formed. The calculated Np(V) solubilities appear to be in good agreement with the ones obtained in solubility experiments. However, these are 5 orders of magnitude larger than the ones obtained with J-13 groundwater in spent fuel leaching tests in contact with air (Wilson and Bruton, 1989<sup>16</sup>).  $\text{NpO}_2^+$  and  $\text{NpO}_2\text{Cl}$  are the predominant aqueous species. In non-saline groundwaters the solubility of Np in oxidizing conditions is limited by the precipitation of  $\text{NpO}_2(\text{OH})$  (s). The aqueous speciation is dominated by  $\text{NpO}_2^+$  and  $\text{NpO}_2\text{CO}_3^-$  due to the relative concentrations of carbonate and chloride in these waters.

Under reducing conditions  $\text{Np}(\text{OH})_4$  (s) is the stable solid phase, while  $\text{Np}(\text{OH})_4$  (aq) is the predominant aqueous species. The calculated solubilities are in good agreement with the reported Np concentrations from spent fuel leaching tests (Wilson and Bruton, 1989<sup>16</sup>).

## AMERICIUM

The thermodynamics data base used in these calculations is the one provided with the EQ3/6 code package (version 0288). The solid and aqueous speciation are not affected neither by the salinity of the groundwater nor by its redox potential.

$\text{Am}(\text{OH})\text{CO}_3$  (s) is the solubility limiting phase, while  $\text{AmCO}_3$  and to a lesser extent  $\text{Am}^{3+}$  are the predominant aqueous species. The Am(III) solubility in saline groundwater is somewhat higher because the lower carbonate content decreases the degree of saturation of the hydroxy-carbonate solid phase.

The measured Am(III) in spent fuel dissolution experiments are 1-2 orders of magnitude lower than the predicted solubilities (Wilson and Bruton, 1989<sup>16</sup>).

## THORIUM

The thermodynamic data base used in the calculations is the one provided with the EQ3/6 code package (version 0288).

The thorium (IV) oxide,  $\text{ThO}_2$  (s), is the solubility limiting phase, both under oxidizing and reducing conditions.  $\text{Th}(\text{OH})_4$  (aq) is the predominant aqueous species. Both the speciation and the calculated thorium concentrations are in good agreement with the observations from laboratory experiments geochemical studies (Langmuir and Herman, 1980<sup>17</sup>) and natural analogue studies as the Poços de Caldas project (Bruno et al, 1990<sup>18</sup>).

There is no effect of salinity in the solubility and speciation of Th(IV) in granite groundwaters.

## RADIUM

The thermodynamic data base used in the calculations is the one provided with the EQ3/6 code package (version 0288). This thermodynamic data set is based mainly in analogies with the Ba(II) chemistry (Langmuir and Riese, 1985<sup>19</sup>).

Radium sulphate,  $\text{RaSO}_4$  (s) is the solubility limiting phase in all cases. The aqueous cation  $\text{Ra}^{2+}$  is the dominant aqueous species. The Ra(II) solubility is lower in saline groundwaters because their higher sulphate content.

Ra(II) concentrations measured in spent fuel leach tests and natural waters are 3 to 4 times lower. This is because Ra(II) is either source term controlled or co-precipitates with other major cations (Langmuir and Riese, 1985<sup>19</sup>).

## TIN

The thermodynamic data base used in the calculations is the one provided with the EQ3/6 code package (version 0288).  $\text{SnO}_2$  (s) is the solubility limiting phase in all cases, while  $\text{Sn}(\text{OH})_4$  (aq) is the predominant aqueous species. The thermodynamic data for both species are poorly known (Baes and Mesmer, 1976<sup>20</sup>). However, the calculated Sn(IV) concentrations appear to be in good agreement with the observations from natural water systems.

## ZIRCONIUM

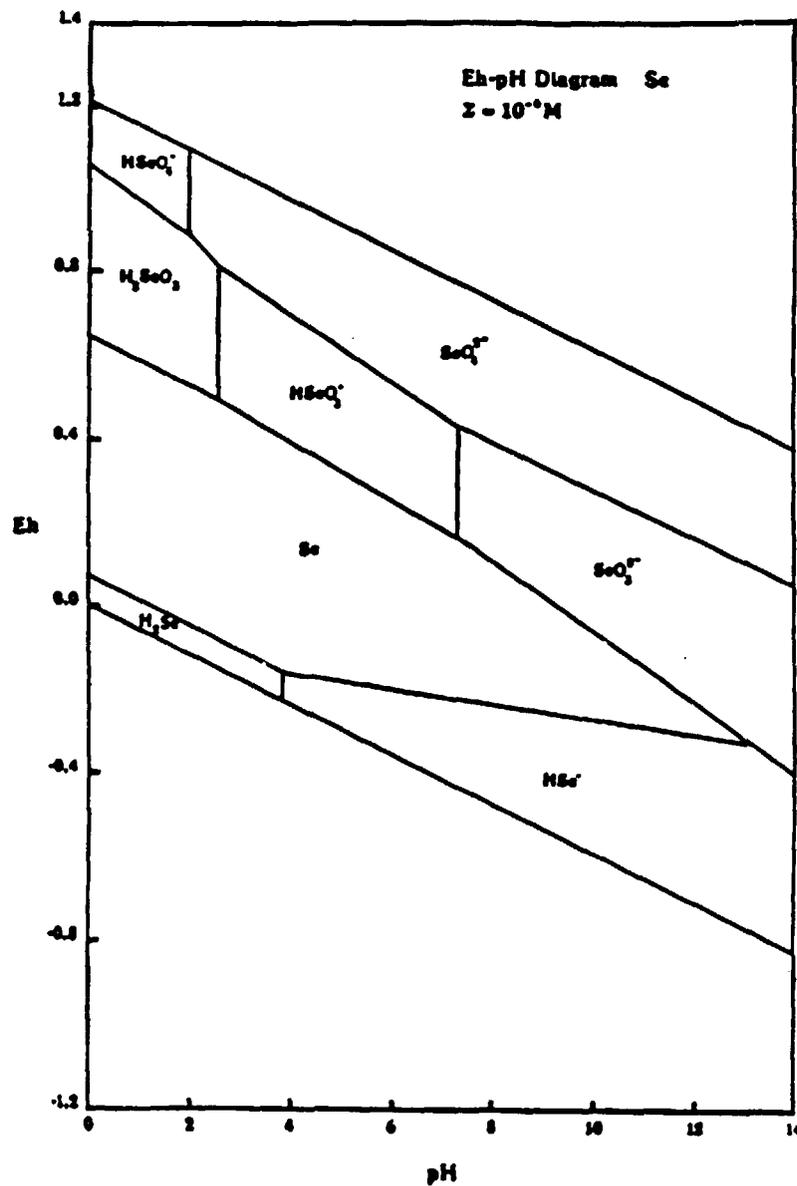
The thermodynamic data base used in these calculations has been the one provided in the ZZ-Hatches code package (NEA, 1989<sup>21</sup>). The solid and aqueous speciation is dominated by the hydroxide complex formation. The original hydrolytic data has been selected and compiled by Baes and Mesmer (1976<sup>20</sup>). Solubility and speciation is similar to that of Ac(IV). Different degrees of crystallisation have been recognized for  $ZrO_2(s)$  which is the solubility limiting phase in all calculations. We have selected the most soluble phase as the limiting one, according to the step Oswald rule. The aqueous speciation is dominated by the  $Zr(OH)_5^-$ . This complex has been determined in very alkaline conditions (1-9 M NaOH) and its stability should be well established. However, the stability of the neutral  $Zr(OH)_4(aq)$  is only estimated (Baes and Mesmer, 1976<sup>20</sup>). We expect from the behaviour of other tetravalent ions the  $Zr(OH)_4(aq)$  complex to be the dominant one under granitic groundwater conditions. Although, this would have a positive effect on the mobility of the aqueous Zr(IV), the calculated solubilities should be reasonably conservative. Zr concentrations in natural waters are normally lower than the ones we have calculated. They are usually controlled by the solubility of the very insoluble  $ZrSiO_4$  (zircon) phase. However, we have preferred to use  $ZrO_2(s)$  as the solubility limiting phase as a consequence of the Ostwald's kinetic step rule ("The less stable phase is the first to precipitate").

## SELENIUM

Selenium is an essential trace element (recommended human consumption values, 50-200  $\mu g/day$ ). However, at high levels it causes toxicity (threshold value: app 750  $\mu g/day$ ). Severe toxicity occurs at levels higher than 5000  $\mu g/day$ , producing loss of hair, nails and skin.

The selenium chemistry resembles very much that of sulphur with stable (-II), (0), (+IV) and (+VI) oxidation states under natural water conditions. The thermodynamic data base used in these calculations has been the one provided in the ZZ-Hatches code package (NEA, 1989<sup>21</sup>). In reducing granitic groundwaters, both saline and non-saline, the solubility of selenium is limited by the precipitation of selenides, particularly of Fe, Cu and Pb. These selenides are normally found in association to metal sulphide ores. Because of the similarity in charge and ionic radius ( $S^{2-}$ : 0.191 nm and  $Se^{2-}$ : 0.184<sup>22</sup>) substitution and co-precipitation of these anions commonly occurs. Therefore, the calculated solubility limits taking into account the precipitation of the  $Fe_3Se_2$  solid phase should be considered as a first approximation. Solid solution models should be applied in this case.

Under oxic conditions the calculation of Se solubilities is far more complex. Selenium should be present as selenite ( $SeO_3^{2-}$ ) under mildly oxidizing conditions and as selenate ( $SeO_4^{2-}$ ) in very oxidizing environments (see the predominance diagram). The only known solubility limiting phase for selenite, at reasonable levels, is  $MnSeO_3(s)$  which gives Se concentrations of the order of magnitude of  $10^{-7}$  molar. However, in oxic conditions it is more reasonable to expect that Se mobility is controlled by sorption reactions.



Calculated Pourbaix diagram for  $[Se]_{tot} = 1$  micromolar, according to Neal and Balistrieri<sup>23</sup>.

Selenite is known to sorb more strongly to minerals than selenate. This has been recently rationalized by an EXAFS investigation of the sorption of both anions on Fe(III) oxi-hydroxides. The authors<sup>24</sup> have shown that the sorption of selenite occurs through the formation of an inner sphere surface complex of the type:  $>FeOOH_2-SeO_3$ , while the selenate anion builds a weaker outer sphere surface complex with the following composition:  $>FeOOH_2-H_2O-HSeO_4$ . This of course has consequences in the mobility and bioavailability of selenate with respect to

selenite. Nevertheless, in spite of the fact that the biogeochemical cycling of selenium is rather effective, the average Se concentrations in rivers and oceans are in the order of magnitude of  $10^{-7}$  molar. This would indicate that sorption onto mineral phases is a rather efficient scavenger for Se under oxidizing conditions.

#### NICKEL

The thermodynamic data base used in these calculations has been the one provided in the ZZ-Hatches code package (NEA, 1989<sup>21</sup>). The compilation of Ni(II) thermodynamic data by Baeyens and McKinley<sup>25</sup> has also been taken into account. In granitic groundwaters and under reducing conditions the solubility of Ni is limited by the precipitation of Ni(II) sulphides, both in fresh and saline waters. Again, due to the similarities between Fe(II) and Ni(II), co-precipitation and solid solution formation with pyrite is expected to be the dominant process. Therefore, the calculated solubilities should be largely conservative.

Under oxic conditions nickel is expected to be associated to iron(III)-oxihydroxides, either by sorption reactions and/or by co-precipitation phenomena. The consideration of trevorite  $\text{NiFe}_2\text{O}_4$  as solubility limiting phase is bound to be conservative due to the fact that this ferrite phase is only formed at high temperatures. This was already observed in the trace element modelling work performed within the Poços de Caldas project<sup>18</sup>. However, the calculated solubilities for Ni in oxic conditions are rather large, even in the case when trevorite is taken into account. Therefore, we believe that the calculated solubilities in these conditions are conservative. Nickel concentrations in natural waters range between 0.001 and  $1\text{E-}7$  mole/litre<sup>26</sup>. The dominating aqueous species is the free  $\text{Ni}^{2+}$  cation for all the waters used in the calculations.

#### SAMARIUM

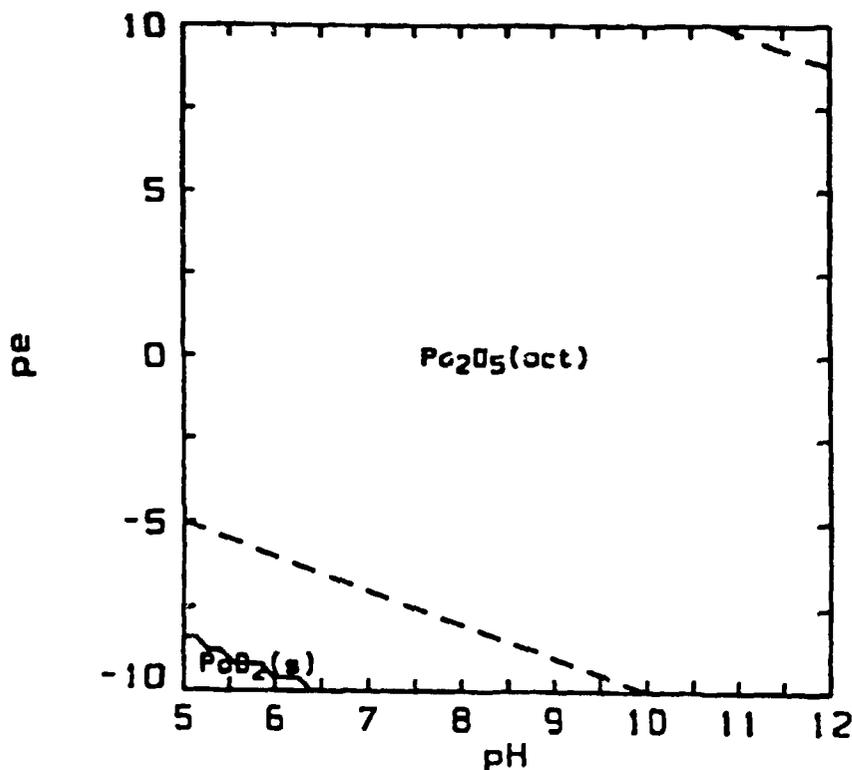
Samarium follows the behaviour of the rest of rare earth elements. In the non-saline granitic groundwaters the normal samarium(III) carbonate is the solubility limiting phase, while  $\text{Am}(\text{OH})_3$  is the most stable solid phase in the saline groundwaters. The mixed  $\text{Sm}(\text{OH})\text{CO}_3$  solid phase is not present in the data base used for these calculations<sup>1</sup>. This phase has been positively identified as the most stable one under granitic groundwater conditions for many rare earth elements and for Am(III). Therefore, it is reasonable to assume that this would be also the solubility limiting phase for Sm(III). The estimated solubilities of the  $\text{Sm}(\text{OH})\text{CO}_3$  solid phase are one order of magnitude lower than the calculated in this report. Hence, the reported Sm solubilities have to be considered as conservative.

#### PROTACTINIUM

Pa(V) is the only stable oxidation state of protactinium under natural water conditions (see the following Pourbaix diagram). It is slightly soluble and has a strong tendency to precipitate unless it is solved in strong acid and/or large fluoride concentrations. However, the stability of the precipitating solid phase varies largely upon ageing. In the thermodynamic data base used in this calculations a crystalline form of  $\text{Pa}_2\text{O}_5$  has been used as solubility limiting phase. By using a less crystalline form of the Pa(V) oxide, as reported by Baes and Mesmer<sup>20</sup> we obtain

Pb solubilities in granitic groundwaters of the order of magnitude of 1 micromolar. This should be regarded as a conservative limit. The aqueous speciation is dominated by the free  $\text{PbO}_2^+$  ion, under all the conditions of these calculations.

$$[\text{PbO}_2^+]_{\text{TOT}} = 1.00 \mu\text{M}$$



#### LEAD

The thermodynamic data base used for these calculations is one provided with the ZZ-Hatches code package<sup>21</sup>.

The calculated solubilities are very dependent on the redox potential of the groundwater. Under reducing conditions PbS (galena) is expected to be the solubility limiting phase. This would imply very low Pb solubilities, in the order of  $10^{-16}$  mole/litre. It is difficult to compare with the observed lead concentrations in groundwater since most of the data show Pb levels under the detection limit of the analytical techniques ( $5\text{E}-9$  mole/litre). The important point is that in reducing groundwaters Pb solubilities are under the above mentioned detection limit. Under oxidizing conditions the calculated solubilities are of the order of magnitude of 1-10 micromolar, depending on the salinity of the groundwater. The solubility limiting phase appears to be  $\text{PbCO}_3(\text{s})$ . In natural waters and under oxic conditions

solubilities range between 0.002-1E-7 mole/litre<sup>26</sup>. This is because most of the soluble lead is associated to particles under oxic conditions. Lead(II) builds strong inner sphere surface complexes with Fe(III)-oxides.

Lead(II) aqueous speciation is mainly dominated by  $PbCO_3(aq)$  in fresh granitic groundwaters and by  $PbCl^+$  and  $PbCl_2^0$  in saline groundwaters.

#### NIOBIUM

The speciation of Nb in natural waters is dominated by pentavalent species. The solubility of these species is limited by the precipitation of the oxide  $Nb_2O_5(s)$ . The solubility limits for Nb(V) have been calculated by using the thermodynamic data set given in the ZZ-Hatches code package<sup>20</sup>. The solubility product used in these calculations refers to the less stable  $Nb_2O_5$  phase. Therefore the calculated solubilities have to be regarded as conservative. There are no analytical data available on the observed Nb concentrations in natural waters.

#### PALLADIUM

The EQ3/6 database used is lacking data for Pd. Calculation with a PHREEQE database (Baeyens and McKinley, 1989<sup>25</sup>) shows a  $1,5 \times 10^{-6}$  mole/l solubility for palladium in Böttstein water (very similar to Finnsjön). This value is independent of redox potential.

#### COMMENTS TO CALCULATIONS

##### Crystallinity

The calculations were made assuming that no highly-crystalline actinide oxides would form. In that case, the solubility of U, Th, Pu and Np would be several orders of magnitude lower. The Ostwalds kinetic step rule ("the less stable phase is the first to precipitate") has been consequently applied.

#### CONCLUSIONS

The results of the calculations are in good agreement with the observed radionuclide concentrations for U, Pu, Np and Tc under reducing conditions, Am, Th and Sn. The solubilities appear to be conservative for Np in oxic conditions, Ra, Zr, Ni, Pa, Nb and probably Pd. No solubility limit is found for Tc and Se under oxic conditions.

The major uncertainties arise in the determination of the dependence of the solubility of Np on the redox state. Research efforts should concentrate on the determination of the redox potential of the Np(V)/Np(IV) couple and its dependence on pH, carbonate and phosphate concentration.

A large degree of optimization in the definition of the source term from the near field will be achieved when a reasonable chemical model for the spent fuel/bentonite/groundwater system is derived. This model should incorporate a thermodynamic approach to the co-precipitation of radionuclides with the major geochemical components.

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