Final synthesis report

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANAGEMENT

SKIN

DELIVERABLE 5.5

COLLABORATIVE PROJECT (CP)

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1. Overall synthesis

The SKIN project has provided a new methodological approach to radionuclide migration in nuclear waste disposal configurations. Indeed, a look only from the solution side, as it is frequently done, is not sufficient: the mineralogical point of view needs to be clearly incorporated into the overall approach, if one wants to assess the role of solid phases in limiting radionuclide migration. Until now, research on radionuclide migration was dominated by short term experiments, yet new observations close to equilibrium are quite different than those far from equilibrium. These new observations include aging of solubility-controlling solid phases; post-sorption processes on the solid influencing the chemical state of the sorbed radionuclides, allowing for in-diffusion or entrapment of trace elements, etc…

The impacts of the results of the SKIN project are expected to be quite different in the near and far field. The near field is characterized by strong chemical gradients and far-from-equilibrium environments, even though local equilibrium/partial equilibrium persists in a global disequilibrium. This leads to the coexistence of various dissolution and precipitation reactions, as well as to aging of initial precipitates over periods of many thousands of years. The evolution of the solution composition might lead to re-dissolution of initial precipitates and formation of new precipitates of different composition. Understanding of the temporal evolution of the reaction network is important for quantifying source terms, corrosion processes of containers, evolution of engineered barrier materials interfaces, etc... Of particular interest is the question on how radionuclides behave during these transformations. Typical concepts in safety assessment like “solubility” or “sorption” become quite ambiguous terms under such conditions. In contrast, in the far field, only small phase transformations are expected. But even in this case, some surface modifications and entrapment of radionuclides in solids might occur.

Ageing of initial solids can influence the binding forces of adsorbed material on ageing surface, and recrystallization may lead to entrapment or to changing the structure of adsorbed substance. Close to equilibrium, the dynamics of dissolution and precipitation rates are still only poorly known, including the question of inhibition. Such processes can often only be studied by looking at isotopic exchange, a technique rarely used in migration studies.

The new methodological approach allowed the SKIN project to address a number of important physical/chemical issues related to the safety of nuclear waste disposal, which were long time overlooked in classical safety analyses. In fact, the hypothesis of solid-liquid phase equilibrium (solubility, sorption) is a key concept in safety assessment. Slow phase transformation, solid state diffusion and incorporation of radionuclides and solid solution formation may occur, which are not yet taken into account in most cases. Neglecting these slow processes close to equilibrium leads mostly to over-conservative assessments. Even if safety margins appear to be large, better knowledge of these margins provides additional confidence. The equilibrium sorption and solubility constraints provide for various repository concepts redundant barriers against safety-relevant release of actinides. A typical solubility value for Am in water at the interface of a nuclear waste glass to clay pore water is 10^{-9} M [1]. Taking for clay rock a typical sorption constant, K_d, of 5000 $mL.g^{-1}$, and using the measured dispersion coefficient of 0.01, a pore diffusion coefficient of 10^{-10} $m^2.s^{-1}$, a clay rock porosity of 20%, a permeability of 10^{-13} $m.s^{-1}$, and a typical hydraulic gradient of $0.5 m.m^{-1}$, it is possible to obtain a migration distance across the clay rock after 1000 years beyond 1 m, and a maximum Am concentration $<10^{-29}$ M, well below drinking water standards; for longer times, Am concentrations will dissapear due to radioactive decay. If sorbed Am become irreversibly trapped inside the solid phase, it is not anymore available for migration, and actual solution concentrations may be much lower than those calculated. One may argue that it is not necessary to know whether such processes occur, since our calculations show already today that there is no risk for migration to the environment. Nevertheless, better understanding of these slow incorporation processes provides higher confidence in the real safety margins, especially regarding nuclides like ^{79}Se presenting higher solubility and lower sorption than Am.

Mechanistic understanding and open questions

One of the key problems was to distinguish thermodynamic and kinetic constraints for enrichment factors of radionuclides at the surface, compared to bulk incorporation, governed for example by surface complexation. The term “equilibrium” does hardly ever apply to the overall system, but only to some sub-systems, hence, we speak of “local” or “partial” equilibrium under conditions of global disequilibrium. For example, even though minerals like calcite or barium sulfate are in solubility equilibrium with the aqueous solution, this is not necessarily true for minor/trace components of the system, such as radionuclides. The example of Radium incorporation in barite has shown that the presence of trace elements like Ra in aqueous solution can lead to a complete recrystallization of the solid under apparent solubility equilibrium. Even if equilibrium is achieved between trace elements in solution and on the solid surface (adsorption equilibrium), there is disequilibrium between the trace element content at the surface and in the bulk of the solid. It is not simple to distinguish incorporation processes from surface layer formation or even from sorption processes. To understand and to quantify the underlying mechanism one needs to consider slow kinetics at long experimental times.

The kinetic interpretation of solubility equilibrium may give some insight into the surface incorporation. In studies of isotope exchange on clay surfaces it became obvious that despite the macroscopic equilibrium (“constant Si concentrations in solution”), concurrent dissolution and precipitation proceed, though with equal rates. It is easy to imagine that radionuclides may become embedded in the solid during the precipitation reaction.

Crystallographic distinction between lattice-compatible and incompatible elements alone is not sufficient to assess the potential for radionuclide incorporation in a host mineral. The example of Se(IV) on calcite shows that even for those structurally incompatible elements, incorporation can occur at the surface and in the sub-surface region, leading to enrichments million times higher than in bulk mineral phase. Such entrapment phenomena are strongly dependent on the degree of supersaturation. At present, those phenomena cannot be taken into account in safety assessment because quantification for a disposal site would require the ability to predict supersaturation ratios in the overall evolution of the near field. A detailed study (beyond the scope of SKIN) would be necessary to identify the potential degrees of supersaturation with respect to a large suite of mineral phases at repository-relevant conditions. Under such conditions, one may expect that the geochemical system of natural water in contact with engineered barrier materials and waste matrices will be closer to equilibrium than in laboratory systems. Many literature studies on incorporation of radionuclides in solid host phases are conducted at high degrees of supersaturation; such data may not be relevant to repository conditions.

There are also questions concerning the persistence of entrapment with ageing time. For example, the long-term data (>10 yr) for U(VI) sorption on iron hydroxide show a significant modification of the speciation of uranium at the surface with time. Such processes cannot yet be modelled, and the consequences for uranium mobilization can neither be predicted. In this particular case, we do not know whether the retention factors increase or decrease with time. Not only the sorbed substance changes the speciation at the iron oxide surface, but also a recrystallization of the iron oxide with time occurs. Both processes seem to be coupled in a way that the recrystallization leads to a reorganization of adsorbed uranium on the surface.

As far as recrystallisation and uptake mechanisms are concerned, we can distinguish a few kinetic steps and three principal uptake mechanisms (diffusion; overgrowth or surface restructuring; entire recrystallization of the solid) depending on the solid material and the environmental constraints. Yet we do not know, what factors (nucleation/growth pathway? surface free energy?) govern the distinction between the different mechanisms. Figure 1-1 shows two major trends. For the quite different solids studied, we qualitatively obtain a relation between the rate of dissolution (or surface site detachment) and either (A) the rate of neo-formation of a solid by dissolution/precipitation in case of $BaSO_4$, deduced from Ra uptake data, showing neo-formation of Ra containing crystals of 10 µm during experimental time or (B) surface restructuring at different degrees: (1) restructuring of many mono-layers in the case of calcite (based on data of ^{45}Ca exchange from Curti et al. [2]), (2) restructuring of a single mono-layer in case of alkali rare earth carbonate corresponding to 10^4 times smaller surface detachment rates in equilibrium than at undersaturated conditions, (3) reaction of only a few surface sites in case of ZrO_2, and (4) absence of any visible reaction of the ThO_2 grain surface with a detachment rate 10^9 times slower than for calcite, leading to the dominance of detachment from defect sites, grain boundaries, etc.

It appears that dissolution rates of at least 10^{-15} m·s^{-1} are necessary to occur during 100 days for surface restructuring beyond a mono-layer. Figure 1-1 illustrates results of the present evaluation in a quantitative manner: data for low reaction rates correspond to solids with very low solubility. Under these conditions and for experiments with powders, the solubility equilibrium is achieved well before a mono-layer becomes exchanged. Surface isotopic exchange rates are then directly proportional to detachment rates. For higher reaction rates, the exchange with a mono-layer occurs fast, but for all solids except $BaSO_4$, exchange with the sub-surface atomic layers increase only very slowly with increasing reaction rates. In the case of $BaSO_4$, isotopic exchange seems not to occur on an existing solid phase, but by dissolution of this existing phase and precipitation of a new one. Reasons for this different behavior are not yet known.

We used a reaction progress for 100 days as a reference period, as this corresponds to typical experimental times. If less than a monolayer on the solid phase is involved in the reaction over this time, both reaction modes cannot be distinguished. Dissolution rates are taken from literature [3] (Calcite, hydroxyapatite-HAP, $BaSO_4$, Quartz, UO_2, ThO_2, ZrO_2) or are obtained by data modelling ($NaREE(CO_3)_2$ or Illite) in the SKIN project. In the case of illite, dissolution rates are normalized to edge surface areas. The number of monolayers involved in the reaction is obtained from modeling or interpretation of the experimental data: for the rare earth carbonates, data are taken directly from the first order dissolution/precipitation model used in the project to model the uptake of ^{152}Eu.

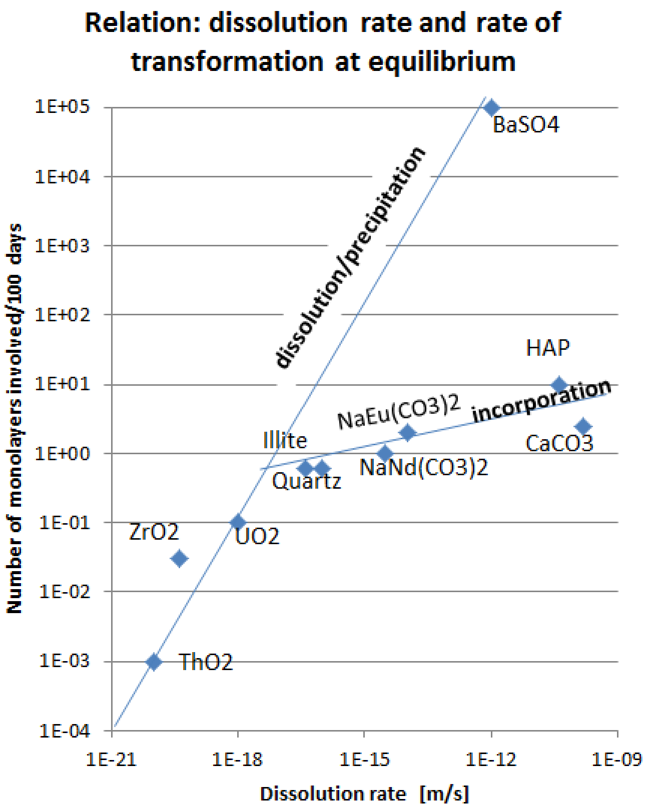

Figure 1-1: Relation between dissolution rates of various solids and the degree of exchange of mono-layers at the surface both from literature and from present work. Number of monolayers exchanged for 100 days taken from the data discussed in the text assuming linear extrapolation. The rate data are from James et al. [3]. The value for ThO_2(cr) is obtained directly from the rate data from Hubert et al. [4] at pH 3.1 and the translation of this rate into monolayer exchange rates. In all other cases monolayer exchange rates are obtained from isotopic exchange data. Data for quartz and illite are from [5], for illite the values correspond to exchange rates at edge sites. Data for calcite are from Curti et al. [2]

The data in Figure 1-1 show that relevant time scales vary largely: in case of $BaSO_4$ recrystallisation occurs in relatively short time, but what is the final state in the long term? We followed the evolution of Ra uptake over 2 years, but what about the long term evolution? In case of calcite: some 10 mono layers are involved in isotopic exchange over 100 days, but how many layers may exchange Ca atoms with the solution in hundreds of years? In case of silicates, less than a monolayer is involved in exchange reactions, even if they are assumed to occur only on edge sites. However, in 10000 years, some incorporation of trace elements in clay minerals may occur well beyond the edge sites.

Modelling

In this project, advanced tools were implemented (on the basis of GEM-Selektor code package, http://gems.web.psi.ch) for modelling the time-dependent non-equilibrium entrapment of trace radionuclides in solid-solution phases using the principle of partial equilibrium. In particular, the unified uptake kinetics model (UUKM) will ultimately allow modelling of slow kinetic processes even in complex geochemical systems coupled with transport of reactive chemical species [6]. The modelling of Ra-barite interaction experiments impressively demonstrated that kinetic effects may well extend over years, before equilibrium conditions are approached. Incorporation of compatible or incompatible trace elements at the surface and/or in the bulk of crystalline phases can now be quantified both at close-to-equilibrium and at far-from-equilibrium conditions. Neglecting such effects in geochemical models of reactive transport is likely to produce biased results. We believe that slow kinetic processes will need to be further explored in the future (both on experimental and modelling sides) in order to provide safer predictions on the fate of radionuclides in geological repository systems.

2. Impact on safety analyses

In general, the experimental data generated in the SKIN project and the models developed show that safety margins in nuclear waste disposal concepts are larger than typically anticipated. Large fractions of transportable radionuclides may become removed from the migration path by partly irreversible entrapment in the various solid phases along the migration transport path. Impact of uncertainties in solubility values and coupled sorption/solubility processes on radionuclide release from spent nuclear fuel provide new insight into safety margins. Some examples are discussed in the following.

The use of Ra-Ba co-precipitation in safety assessment

In various European spent fuel repository concepts, radium becomes a major dose contributor at long time perspective (after ca. ~300 k years), given the large amounts of ^{238}U disposed off. Solubility constraints for Ra release are important in quantifying dose contributions. The possibility of using its co-precipitation with Ba would be beneficial to safety, because the solubility of Ra in equilibrium with (Ra,Ba)SO_4 is much lower than this calculated with radium sulfate as solubility limiting phase. A scientific debate on the limits of use of formation of a (Ra,Ba)SO_4 solid solution constraints on Ra release in safety assessment is ongoing.

The first use of Ra-Ba co-precipitation in safety assessment was in the Project Opalinus Clay Safety Report /Nagra Technical Report NTB-02-05 (p.145) based on two technical reports [7-8]. Calculations using RaSO_4(s) as solubility limiting solid phase resulted in Ra concentrations of 4.8×10^{-8} M. In case of co-precipitation, a reduction of Ra concentrations by a factor of 1/5641 to a value of 8.6×10^{-12} M was calculated from the Ra/Ba ratio of 1/5641 in the material balance of the disposal vault, assuming ideal solid solution formation.

Reviewing these calculations, the regulatory body in Switzerland (HSK) pointed to the central role of the temporal evolution. The solid solution model of NAGRA implies that the Ra inventory of the waste is homogeneously distributed in the clay. This is not correct, in particular for the early stages of Ra-release. For this stage the higher solubility of 5×10^{-8} M has to be used. The lower NAGRA value may be more realistic at a later stage but without a detailed kinetic study HSK will use 5×10^{-8} M as a reference value [9].

In the international review organized by OECD-NEA the following comments were made: Except for radium, co-precipitation is not considered. This is conservative, but leads to predictions that significant quantities of some actinides (e.g. ^{230}Th, ^{231}Pa, ^{229}Th) are released into the buffer. This is at variance with experience based on analogy with uranium ores. Co-precipitation is a “reserve FEP” and Nagra should give consideration to incorporating it into models as more data become available [10].

The approach of considering Ra-Ba co-precipitation in the far field considered the presence of Ba in the clay rock and the bentonite was thus criticized because pure $RaSO_4$(s) would determine the solubilities inside the damaged canister and this is generally used in the solubility calculations.

In the SR-Site safety assessment [11] the barium present in the spent fuel was considered to co-precipitate with radium, representing an improvement as to the possibility of Ra-Ba-sulfate co-precipitation inside a damaged canister.

Scoping calculations for spent fuel of burn-up 40 MWd/kgU show that Ba and Ra inventories per canister grow with time: Ba reaches a constant level after ~500 y and in case of contact with groundwater will precipitate as $BaSO_4$(s), while ^{226}Ra reaches its peak after ~300000 y after disposal [12].

Two potential scenarios were addressed:

- In case of simultaneous release of Ra with Ba, the former will be readily incorporated into precipitating $BaSO_4$ to form a $(Ra,Ba)SO_4$ solid solution. Using a fuel dissolution rate of 10^{-7}/year and a congruent release of Ba, the calculated Ra and Ba concentrations after one year of contact at disposal time 300,000 years (when ^{226}Ra content is largest) are 1.3×10^{-12} M and 4.9×10^{-9} M, respectively. The resulting solid phase has a calculated composition $(Ba_{0.99942}Ra_{0.00057})SO_4$. The dissolved Ra is in the 10^{-11} M range; about 10^3 times lower than from equilibrium with $RaSO_4$(s). With the lowest value of sulfate concentration considered (3×10^{-4} M), Ra solubility increases to 7.1×10^{-10}M. Not considering co-precipitation and using $RaSO_4$(s) solubility under these conditions results in Ra concentrations are of 1.13×10^{-6} M.
- In the case of fuel dissolution inside a damaged canister, it is considered in SR-Site that the oxidized uranium resulting from fuel dissolution is precipitated as UO_2(s) on the surface of iron and its corrosion products. When ^{226}Ra is released from a secondary source, like a UO_2 precipitate away from the fuel, there is not sufficient experimental information to establish when and how the system will

reach equilibrium with the already precipitated barite resulting from fuel dissolution. In order to obtain further evidence for the co-precipitation kinetics in this case, an experimental study of the barite re-crystallisation and its co-precipitation with Ra was carried out [13]. The experimental investigation of the uptake of ^{226}Ra and ^{133}Ba by two different barite powders (0.31 and 3.2 m^2/g) in aqueous solutions indicates that there may be a significant uptake of Ra into the bulk of barite crystals. The kinetics of Ra-uptake in barite shows that the uptake rate drops significantly within 400 days, even though a zero exchange rate cannot be unambiguously demonstrated.

By using larger Ra concentrations and by analysis of the solid phase using ToFs the SKIN project provided a better understanding of the slow re-crystallization towards the thermodynamic aqueous-solid solution equilibrium. For the first time, experimental proof was obtained by direct microanalysis (ToF-SIMS) that Ra is taken up more or less homogeneously in the entire recrystallized solid (not just on the surface), implying that such systems can indeed be treated thermodynamically as solid solutions. The Swedish authorities required various reaction scenarios to be clarified concerning the use of Ra-Ba-sulfate co-precipitation as an argument in safety assessment.

a) If Ba is released early from spent nuclear fuel and precipitates as secondary phase, can there be redissolution of the precipitates and loss of some of the Ba when Ra-ingrowth reaches a maximum? SKB considers the impact to be weak since diffusive Ba release is very slow and Ra release from secondary UO$_2$ precipitates is also very slow.

b) Is it sure that Ba is released proportionally to fuel matrix dissolution, considering that barium zirconates may be present in spent fuel [14-15]. SKB argues that this is only an issue for fuel which has experienced in the reactor at very high temperatures (> 1500°C). Such fuel is not expected in the repository.

c) Is is possible that Sr is inhibiting uptake of Ra in barite? SKB points to the fact that also (Sr, Ba)-sulfate with high content of Sr can immobilize large amounts of Ra [16-18]. Numerical modeling of (Ba,Sr,Ra)SO$_4$ indicates that Ra is fixed in the solid phase in the near field of a radioactive waste repository [19] and the Sr present in the waste should not affect considerably the uptake of Ra by barite.

The representation of fuel dissolution in presence of clay slurry in safety assessment

When the buffer is partially or completely eroded, a cavity filled with slurry of water containing colloidal clay particles may exist in the deposition hole. If the canister is breached under such circumstances, the clay particles are not expected to affect the oxidative fuel dissolution rate. Dissolved U(IV) would, however, be expected to sorb strongly to the clay particles. This sorption increases the amount of U(IV) released in solution from the re-precipitated UO_2(s) or the fuel matrix. In this case, the amount of U(IV) sorbed on clay particles may be calculated as the K_d value for U(IV) on clay particles multiplied by the U(IV) concentration in solution, determined by UO_2(s) solubility. No limit is posed to the U(IV) release rate from UO_2(s) to satisfy U(IV) solubility limits in the canister void. In the case when all re-precipitated UO_2(s) is dissolved due to sorption to clay particles, the remaining U(IV) needed to saturate clay particles is released from the fuel matrix, resulting in an increase of the fuel dissolution rate. To calculate this enhanced U release, the scenario dependent concentration of clay particles and water flow need to be considered. The eroded void volume of the deposition hole is assumed to be filled with clay particles that enhance the dissolution rate of the UO_2 fuel matrix. The void ratio when the transport of bentonite is by colloid dispersion corresponds to a dry density of 37.6 $kg.m^{-3}$. This concentration will not be maintained in a large void in the deposition hole, since there will be a concentration gradient from the source of the colloids to the fuel.

If one assumes that a clay slurry with 10 g clay/L enters and leaves the canister with a flow of 100 liters/year, then the total amount of clay is 100 L/y *10 g/L=1000 g clay/y. This amount of slurry will contain at equilibrium an amount of U(IV) sorbed in the clay slurry of 2.5 10^{-3} mol U(IV) per kg clay slurry, corresponding to a dissolution rate of 3.4 10^{-7}/year-comparable with the average fuel dissolution rate used in SR-Site.

One of the central assumptions in this case is that the concentration of U(IV) in the canister void is equal to the solubility of UO_2(s) even in the presence of clay particles. If this is not true, clay particles will sorb less U(IV) and the impact of clay on UO_2(s) dissolution would even be smaller. .

From the result obtained in the SKIN project with ThO_2(s) as a surrogate for UO_2(s), it can be concluded that UO_2(s) dissolution rate is expected to be sufficiently low, so that U(IV) concentrations in the canister void will be lower than the equilibrium value during the residence time of the clay slurry in the canister void. In this case, the amount of U(IV) sorbed on clay particles (proportional to sorption coefficient (K_d) and concentration of U(IV) in solution) will be lower than that in a solution with the U(IV) concentration at UO_2 solubility level.

This is clearly seen from the experimental data, where $[Th]_{(ThO2+clay)} < [Th]_{(only\ THO2)}$. Therefore it can be expected that [U](t) should be lower or much lower than $[U]_{(solubility\ of\ UO2)}$ in a very long period of time, even longer than the time of clay staying in SNF canister void. Therefore, we may conclude that the invasion of clay slurry to canister void during the glacial period can enhance fuel dissolution, but not as much as conservatively assumed before (Equation1 [11]), because the U concentration in the canister void is lower than that in clay slurry free conditions.

In any case, the work should be continued in order to better constrain the boundaries and average values of U(IV) to be used for calculating the transport of uranium in the presence of a clay slurry.

Impact of uncertainties in solubility values in safety assessment

High uncertainties in the solubility and sorption of some elements may be reflected in high uncertainties in the results of the calculations used to support safety assessments. The main objective of WP5 of SKIN has been to study the impact of the project in reducing the uncertainty of solubility and sorption data. The evaluation of the impact of new data obtained within SKIN project (together with results of previous studies of literature and field data) is assessed trough compartmental modelling. A PA reference case has been defined based on the Swedish SR-Site exercise and calculated with AMBER. Additionally, MC-PhreeqC has been tested as a complementary tool of AMBER to integrate uncertainty analyses.

A simplified system has been calculated where thorium was the only radionuclide considered. The impact of the uncertainty associated with the solubility product of ThO_2 has been assessed. Firstly, a compilation of solubility data of ThO_2 from literature has been performed obtaining a wide range of values depending on the range of pH. That exercise is carried out with PhreeqC and MC-PhreeqC. The obtained output is used as input for the AMBER PA case.

Figure 2-1 shows the results obtained from the MC-PhreeqC model. The relationship between the solubility constant for ThO_2 (x axis), the calculated thorium concentrations in the cell (left axis, red) and the calculated saturation index (right axis, blue) is shown. Only solubility constants below -49.5 (dotted vertical line in Figure 2-1) lead to the precipitation of thorium hydroxide (saturation index = 0 and thorium concentrations below 10^{-10} M) under the flow regimes considered in the calculation. Th concentration becomes dominated by the balance of the dissolution rate and the flow rate when solubility constants are over -49.5, for the flow rate regimes tested.

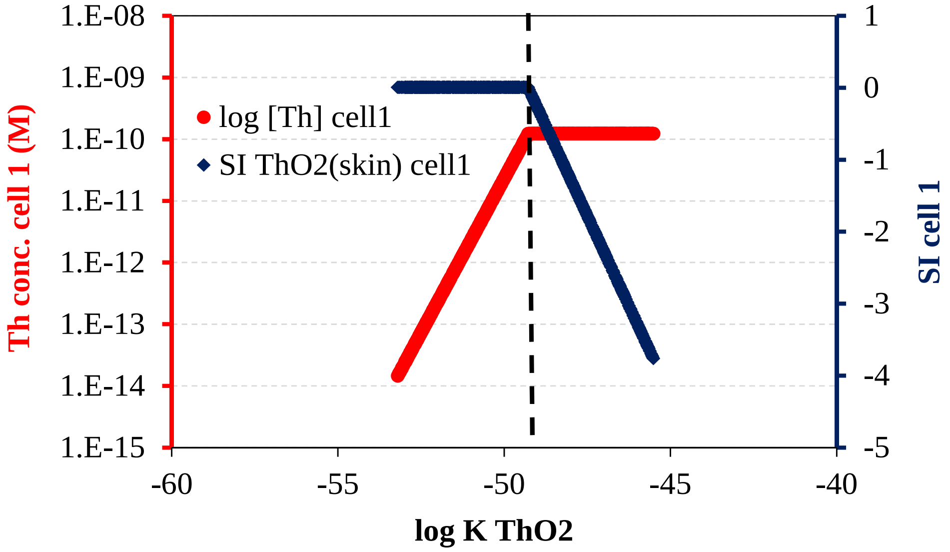

Figure 2-1: **Relationship between the solubility constant for thorium hydroxide ("x" axis), the calculated thorium concentrations in the cell (left axis, red) and the calculated saturation index (right axis, blue).**

Probability and cumulative distribution functions for Th concentration indicate that, in the 80% of the cases, Th concentration is not limited by solubility limit. The final conclusions would indicate that the concentration of thorium is a steady state value, given mostly by the balance between dissolution rate and flow rate, under the conditions of the simplified system.

Results obtained from the incorporation of MC-PhreeqC output in AMBER show that the concentration is not limited by solubility when the solubility of Th in Bentonite is below around 10^{-11} M.

3. Future work

Radionuclides from nuclear waste behave in many aspects similar to the non-radioactive isotopes present in the natural environment or to homologue chemical elements. The natural isotopes are involved in the overall geochemical mass transfer processes between various solid and fluid phases. These processes are often ongoing for hundreds of millions of years. How long will take to incorporate the radionuclides from the nuclear waste in the pre-existing geochemical cycle? The SKIN project has opened the door to study such very slow processes close to equilibrium, using the concept of entrapment in mineral solid solutions. However, the link between growth of crystalline solid phases and their capacity for entrapment of trace elements needs to be more clearly established. We are still not capable to quantify the exchange pool of mineral volumes along the transport path and the degree of incorporation of radionuclides from waste in the global exchanges in the mineral-water system. Nevertheless, we know that the present sorption models, taking the surface as inert, largely underestimate the available exchange pool, and ignore irreversible uptake. It is, for example, still not possible to quantify ^{41}Ca entrapment in repository rocks with a lot of calcite. The proof of incorporation in some tens to hundreds of monolayers in few hundreds of days exists, but could ^{41}Ca be incorporated within an entire micrometer sized calcite crystal if much longer time would be available, as it was observed in short time for Ra incorporation in $BaSO_4$?

More quantitative approaches need to be developed to assess the magnitude of the safety margins. In this context, an important issue in future work could be the study of entrapment processes in reactive transport models. One needs also to include organics in the assessments.

Finally, a large knowledge base for the significance of entrapment processes in trace element transport is hidden in natural and archaeological analogue systems. It should be possible to use the scientific tools generated in the SKIN project to analyse entrapment processes occurring in natural chemical gradients in a quantitative manner.

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