

SUBATECH

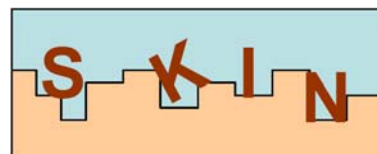
SKIN PROJECT

1st Annual Workshop Proceedings

EURATOM

EC 7th Framework Program Collaborative Project

“Slow processes in close-to-equilibrium conditions for radionuclides in water/solid systems of relevance to nuclear waste management”



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FOREWORD

The present document is the proceedings of the 1st Annual Workshop of the Euratom FP7 Collaborative Project SKIN (Slow processes in close-to-equilibrium conditions for radionuclides in water/solid systems of relevance to nuclear waste management). The workshop was hosted by AMPHOS (Amphos 21) and held in Barcelona 17th – 18th November 2011. It has 10 partners and 1 associated group. Annual workshops bring together, partners, associated group and external interested groups. The present proceedings will be followed by two additional proceedings corresponding to the forthcoming annual workshops to be held in 2012 and 2013, respectively. The 2nd Annual Workshop will be held in Switzerland in November 2012, hosted by Paul Scherrer Institute.

The proceedings aim to be available to a broad scientific community on the outcome of the SKIN project through the scientific-technical contributions. The proceedings give only very brief information about the project structure and the different activities around the project, such training measures and dissemination of knowledge. Such exhaustive information about the project can be found under http://www.emn.fr/z-subatech/skin/index.php/Main_Page.

TABLE OF CONTENTS

THE PROJECT	1
THE FIRST ANNUAL WORKSHOP.....	2
OBJECTIVES.....	2
RTD SESSIONS	2
STRUCTURE OF THE PROCEEDINGS.....	3
SUMMARY OF WP ACTIVITIES.....	2
RADIONUCLIDE INCORPORATION INTO CALCITE	4
A. <i>Selenium(IV) incorporation into calcite, experimental approach, status, and outlook.....</i>	<i>4</i>
B. <i>Neptunium(V) incorporation into calcite, experimental approach, status, and outlook</i>	<i>6</i>
SULFATES: RECRYSTALLIZATION OF BARITE IN THE PRESENCE OF RADIUM	7
A. <i>Context of the study.....</i>	<i>7</i>
B. <i>Radium uptake experiments</i>	<i>7</i>
C. <i>Co-precipitation and EXAFS.....</i>	<i>8</i>
D. <i>Perspective(s).....</i>	<i>8</i>
METHODS TO ASSESS RADIOISOTOPE MIGRATION IN CEMENTITIOUS MEDIA USING RADIAL DIFFUSION AND ADVECTION	10
SORPTION OF CS ON THE CALLOVO-OXFORDIAN CLAYSTONE	11
IDENTIFICATION OF IRREVERSIBILITY/REVERSIBILITY RELATIONS AT CLAY SURFACES: SOLUBILITY OF CLAYS.....	12
INTERACTION BETWEEN URANIUM AND IRON (III) OXIDES.....	14
DISCREPANCIES IN THORIUM OXIDE SOLUBILITY VALUES: ThO₂ SYNTHESIS AND CHARACTERIZATION....	17
STUDY THE KINETICS OF TcO₂(S) UNDER HYPERALKALINE CONDITIONS.....	19
THE INFLUENCE OF CLAY SLURRY INVASION ON THE DISSOLUTION OF SPENT NUCLEAR FUEL UNDER REDUCTIVE REPOSITORY ENVIRONMENTS.....	20
REDUCTION OF URANYL BY GAMMA-RADIATION IN AQUEOUS SOLUTION CONTAINING IRON (II)	22
MODELLING/THEORY	23
APPROACHES TO MODEL THE KINETICS OF TRACE ELEMENT UPTAKE IN HOST MINERALS.....	25
THEORY ON THE AFFINITY LAW.....	27
SYNTHESIS AND SAFETY ASSESSMENT: IMPACT OF UNCERTAINTIES IN SAFETY ASSESSMENT.....	28

THE PROJECT

SKIN (01/01/2011 – 31/12/2013 - 3 years) is a European Project accepted within the 7th Framework Programme of the European Atomic Energy Community (FP7 Euratom) for nuclear research and training activities. It is a collaborative project including 9 European countries and 1 Asian country: ARMINES/SUBATECH (France), Karlsruhe Institute of Technology (Germany), Forschungszentrum Jülich (Germany), Svensk Kärnbränslehantering AB (Sweden), AMPHOS 21 (Spain), Chalmers University of Technology (Sweden), Stockholm University (Sweden), Paul Scherrer Institute (Switzerland), Loughborough University (United Kingdom) and Peking University (China).

The objective of SKIN is to assess the relevant individual processes in the near-field and far-field to allow the development of robust methodologies for performance and safety assessment. In fact, due to the slow groundwater movement in confined deep geological formations, the system “radionuclides – minerals – engineered barrier materials – water” will be close to chemical equilibrium. These systems, controlling radionuclide mobility, have been studied for many years, but only a little attention has been given to the fact that, due to the long disposal time, individual very slow processes can have a significant impact on the mobility of radionuclides, despite achievement of local equilibrium states being achieved. The results would integrate and complete the FP7 Euratom Programme for the implementation of geological disposal of radioactive waste.

The work program is structured along 4 RTD work packages (WP2-5). They cover near-field and far field aspects to assess the slow processes close-to-equilibrium which results will be implemented in Performance Assessment/Safety Case. Experimental programs are performed in WP2 and WP3: WP2 focuses on the formation and on slow processes close-to-equilibrium of solid solutions in aqueous environments under waste repository near-field and far field aspects as well as cement related systems; WP3 focuses on the understanding of the kinetics of alteration of oxides from primary solids, as well as the secondary solid phases expected to form under repository conditions after the eventual release of the radionuclides present in the different waste. WP4 assesses the experimental results by geochemical thermodynamic modeling and its new partial-equilibrium approach and by the affinity law and its validity close to equilibrium. WP5 performs a synthesis of results of experimental, modeling and safety assessment approaches in the context of a full assessment of the literature, and inclusion of literature data. Specific work packages on knowledge management, education and training (WP6) and administrative management issues (WP1) are also included in the project.

The present proceedings document the outcome of the 1st Annual Project Workshop and give an overview of the outcome of the 1st project year.

THE FIRST ANNUAL WORKSHOP

Objectives

The Workshop combines different activities and meetings with the following objectives:

- Informing about the scientific progress
- Informing about the administrative status
- Discussing various topics of interest
- Informing/agreeing upon forthcoming reporting
- Agreeing upon the forthcoming work program

Emphasis was on scientific-technical topics with administrative issues kept to the minimum necessary.

RTD sessions

Two days of plenary sessions was programmed where the results from the different work packages were presented. Next to an overview of the achievements within the respective WP conducted by the WP leader, scientific highlights were presented. The following presentations were given within the project under the validation by the End Users Group.

WP2 “Experimental Programme 1” session (D. Bosbach, FZJ)

1. F. Heberling (KIT), Volker Metz (KIT), Stephanie Heck (KIT), Melanie Böttle (KIT): *Radionuclide incorporation into calcite and barite*
2. F. Brandt (FZJ), H. Hedström (CHT), N. Torapava (CHT), F. Heberling (KIT): *Recrystallization of Barite in the presence of Radium*
3. J. Hinchliff, N. Evans (Loughborough Univ.): *Methods to assess radioisotope migration cementitious media using radial diffusion and advection*
4. T. Suzuki-Muresan (Armines): *Sorption of Cs on the Callovo-Oxfordian clayston*
5. T. Suzuki-Muresan (Armines): *Identification of irreversibility/reversibility relations at clay surfaces : solubility of clays*

WP3 “Experimental Programme 2” session (L. Duro, Amphos 21)

1. M. Grivé, E. Colàs, L. Duro (Amphos 21): *Interaction between Uranium and Iron (III) oxides*
2. J. Vandenborre (Armines): *Discrepancies in thorium oxide solubility values: ThO₂ synthesis and characterization*
3. N. Evans, J. Hinchliff (Loughborough Univ.): *Study the kinetics of TcO₂(s) under hyperalkaline conditions*
4. D. Cui (Stockholm Univ.), Kastriot Spahiu (SKB): *The influence of clay slurry invasion on the dissolution of spent nuclear fuel under reductive repository environments*

5. C.L. Liu (PKU): *Reduction of Uranyl by γ -Radiation in Aqueous Solution Containing Iron (II)*

WP4 “Modeling and Theory” session (D. Kulik, PSI)

1. B. Thien, D. Kulik, E. Curti (PSI): *Approaches to model the kinetics of trace element uptake in host minerals*
2. S. Ribet, B. Grambow (Armines): *Theory on the Affinity Law*

WP5 “Synthesis and Safety Assessment” (L. Duro, AMPHOS21)

L. Duro, A. Valls (Amphos 21): *Presentation of the reference case*

Invited talk

M. Prieto (Oviedo Univ.): *Interfacial tension, metastability and solubility of solid solutions*

Structure of the proceedings

The proceedings present individual scientific and technical contributions.

SUMMARY OF WP ACTIVITIES

RADIONUCLIDE INCORPORATION INTO CALCITE

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A. Selenium(IV) incorporation into calcite, experimental approach, status, and outlook.

The equilibrium recrystallization of calcite is extremely slow, therefore we so far focused on coprecipitation experiments at supersaturated conditions to study radionuclide incorporation into calcite. Coprecipitation is investigated in three kinds of experimental settings to cover a large range of supersaturation. In mixed flow reactor (MFR) experiments radionuclide containing calcite can be precipitated homogeneously at steady state conditions onto calcite crystal seeds. Experiments are usually run at an calcite saturation index, SI(Calcite), between 0.3 and 1.0. This results in growth rates between 10^{-9} and 10^{-8} mol m⁻² s⁻¹. Besides the growth rate, partition coefficients can be derived from these experiments. Much simpler are “Free-Drift” experiments. In these experiments the system runs from an initial supersaturation state towards equilibrium. The reaction progress is monitored via pH measurements. The reaction rates can be derived from geochemical modeling of the solution composition at each time step. Conditions in these experiments are not homogeneous, they change with time, but Free Drift experiments are advantageous especially to cover higher supersaturation states, SI(Calcite) > 1.0 (up to 4). To realize coprecipitation experiments at very low supersaturation, aragonite to calcite recrystallization experiments are performed. Calcite is thermodynamically more stable than aragonite at standard conditions ($\log_{10} K_{SP}(\text{aragonite}) = -8.34$, $\log_{10} K_{SP}(\text{calcite}) = -8.48$) (Hummel et al., 2002). A solution in equilibrium with aragonite has an SI with respect to calcite of 0.14. Therefore aragonite dissolves and calcite precipitates at very low rates.

Eight MFR experiments on selenium(IV) coprecipitation with calcite were performed. The selenium environment in calcite was investigated by powder EXAFS measurements at the Se K-edge on Se-doped calcite from MFR experiments. During the SKIN project an additional EXAFS study on an Se(IV)-doped calcite single crystal was performed exploiting the polarization dependence of EXAFS measurements. By performing EXAFS measurements with three different orientation of the crystal relative to the x-ray beam the incorporation species could be characterized not only in terms of distances and coordination numbers of neighboring atoms, but also in terms of the orientation of SeO₃²⁻ molecules relative to the crystal structure. These investigations show that upon coprecipitation with calcite selenium(IV) is structurally incorporated onto a carbonate lattice site. Using this knowledge we can formulate a thermodynamic partition coefficient, D, for selenium(IV) incorporation into calcite:

$$D = \frac{X_{CaSeO_3} / X_{Calcite}}{c(SeO_3^{2-}) / c(CO_3^{2-})} \quad (\text{eq. 1})$$

where X_{CaSeO_3} and $X_{Calcite}$ are the mole fractions of selenite and carbonate in the solid phase and c denotes the corresponding concentrations in the aqueous solution. If we plot the ratio of the aqueous concentrations against the ratio of the mole fractions in the solid we can derive the partition coefficient from the slope of the regression line through the data points. The calculated partition coefficient is: $D = 0.02 \pm 0.01$.

The good representation of the data points by a straight line indicates that it should be possible to describe the system using an ideal solid-solution model.

$$D_{ideal} = \frac{K_{SP(Calcite)}}{K_{SP(CaSeO_3)}} \quad (\text{eq. 2})$$

For an ideal solid-solution the partition coefficient at equilibrium conditions is defined by the ratio of the solubility products of the two endmember phases. In case of selenite incorporation into calcite it is important to notice that the $CaSeO_3$ endmember is a hypothetical phase, as a solid with this composition in calcite structure does not exist. Therefore the solubility product is not known, but equation 2 can be used to estimate it. Using this relation we find a solubility product of: $\log_{10} K_{SP}(CaSeO_3) = -6.7 \pm 0.4$. The solubility of a stoichiometrically similar $CaSeO_3$ -phase, $CaSeO_3 \cdot H_2O$, is: $\log_{10} K_{SP}(CaSeO_3 \cdot H_2O) = -6.40 \pm 0.25$ (Olin et al., 2005). This means that the hypothetical endmember would be more stable than the known solid $CaSeO_3$ -phase, which is impossible, and suggests, that the selenium(IV) incorporation into calcite is kinetically controlled. It might argument that within the uncertainty limits of the parameters the solubilities are the same, which is still pretty unlikely, especially as a theoretical investigation of the system SeO_3^{2-} in calcite by V. Vinograd (unpublished) predicted a very high solubility for the hypothetical $CaSeO_3$ endmember of: $\log_{10} K_{SP}(CaSeO_3) = -0.34$. This implies that the equilibrium partition coefficient should be, $D = 7.2 \cdot 10^{-9}$.

Based on these findings it was decided to study the coprecipitation of selenium(IV) with calcite as a function of supersaturation over a large range of supersaturation conditions. To achieve coprecipitation at higher supersaturations than in MFR experiments Free Drift experiments were performed. The results of these experiments need to be interpreted with care as at high supersaturation not only calcite but also amorphous calcium carbonate and vaterite precipitated. Nevertheless it is intriguing that at all conditions an identical partition coefficient, $D = 0.02 \pm 0.01$, was obtained.

To achieve lower supersaturation as it typically sets up in MFR experiments an aragonite to calcite recrystallization experiment was started. However, the recrystallization process is extremely slow, and results are not yet available.

B. Neptunium(V) incorporation into calcite, experimental approach, status, and outlook

In a similar approach as with selenium(IV), the coprecipitation of neptunium(V) with calcite was studied in numerous MFR experiments. The incorporation species was characterized by EXAFS spectroscopy. The results indicate that neptunium(V) is structurally incorporated into calcite (Heberling et al., 2008). However, the charge balancing mechanism that enables the complex coupled substitution which is necessary to incorporate a NpO_2^+ molecule into the calcite structure is not yet known. During the SKIN project further investigations on the substitution scheme are planned, for example by exchanging the background electrolyte cations that might be responsible for charge compensation during the incorporation reaction.

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SULFATES: RECRYSTALLIZATION OF BARITE IN THE PRESENCE OF RADIUM

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A. Context of the study

The possible solubility control of Ra by coprecipitation of a $\text{Ra}_x\text{Ba}_{1-x}\text{SO}_4$ solid solution has been demonstrated in many cases and can be modeled reliably [1]. However, an open question is whether a Ra containing solution will equilibrate with solid BaSO_4 under repository relevant conditions. Here, Radium enters a system in which Barite is in equilibrium with the aqueous solution. Previous studies have indicated that Ra uptake is not limited by pure adsorption but involves a significant fraction of the bulk solid [2, 3].

Ra uptake experiments, thermodynamic calculations, structural analysis of the RaSO_4 endmember and complementary coprecipitation experiments were carried out to gain a deeper understanding of the Ra- BaSO_4 exchange process. Ultimately, the data obtained in this working package will support the assessment of safety margins in working package 4.

B. Radium uptake experiments

Batch experiments were carried out with the following starting conditions: $5 \cdot 10^{-6}$ mol/L of Ra, 0.1 mol/L NaCl and 5 or 0.5 g/L of barite. Two different types of barite with specific surface areas of 1.7 and 0.17 m^2/g were used for Ra-uptake experiments at room temperature. The evolution of the Radium and Barium concentration in solution with time was monitored via Gamma spectroscopy and ICP-MS.

The experimental results show a decrease of the Ra concentration to $3.5 \cdot 10^{-9}$ to $7 \cdot 10^{-9}$ mol/L within the first 70 days of the experiment at a solid/liquid ratio of 5 g/L. At a solid/liquid ratio of 0.5 g/L a slower decrease of the Ra concentration is observed to $2 \cdot 10^{-8}$ mol/L after 180 days. The decrease of the Ra concentration is apparently not related to the specific surface area of the barite crystals. A higher Ra retention capacity is consistently observed for the barite type with lower surface area. Barium concentrations are slightly above the calculated solubility in all experiments.

Different models describing the mechanism of Ra incorporation into barite have been calculated: (1) Ba – Ra exchange into the crystal volume, combining the Ra – Ba exchange with the Ba – Ba recrystallization rate at equilibrium conditions [3]; (2) the formation of a Ra-Ba-Phase on barite surfaces. According to model (1), the calculated results would indicate an enrichment of Ra in the liquid phase at 0.1 – 0.5 g/L, whereas the experiments with 5 g/L of barite would enrich Ra in the solid phase.

The formation of a Ra-Ba Phase on barite surface according to model (2) could be possible because all experiments are slightly supersaturated with regard to $\text{Ra}_x\text{Ba}_{1-x}\text{SO}_4$ after about one day. The most likely composition to precipitate has been derived from the Lippmann diagram [4]. Assuming an ideal solid solution and the precipitation of the most supersaturated composition, average $X_{\text{RaSO}_4(\text{s})}$ crystallized in a time interval (e.g. $t_1 - t_2$) can be estimated with GEMS-PSI. From the decrease of Ra with time, amounts of newly formed radiobarite are calculated. Crystallization rates calculated according to this model are in a similar range of 10^{-5} to 10^{-7} moles $\text{m}^{-2} \text{d}^{-1}$ for all experiments (normalized to the barite surface area). Calculated amounts of solid solution crystallized are similar for experiments at 5 g/L experiments (ca. 0.03 g/L solid solution), once a steady state is reached.

C. Co-precipitation and EXAFS

The work that has been performed at Chalmers university of Technology has so far been aimed at traditional co-precipitation, where the kinetic behavior of radium and barium has been studied at various temperatures and molar fractions. These results will be used to determine the Arrhenius constants of the co-precipitation, also the system will be studied until equilibrium is reached. These studies will be continued at higher temperatures.

EXAFS measurements have also been performed, and the bond distance between radium and oxygen has been determined, as well as the radium- sulfur distance.

D. Perspective(s)

Ra-uptake experiments will be extended to 90 °C to determine the retention capacity in comparison to room temperature. In addition, electron microscopy and spectroscopic methods will be applied to determine the spatial distribution of Ra within the radiobarites.

Radium-223 isotopic exchange at the surface of radium-226 and barium sulphate crystals will be studied. Two principle effects should be distinguished: isotopic-exchange and co-precipitation of radium-223 with radium-226 or barium in aqueous solution containing radium-226 or barium sulphate crystals. Equilibrium between solid and aqueous phases should be reached. The aliquots of aqueous phase will be taken to measure radium-223 and radium-226 or barium concentration. The EXAFS measurements of mixed radium-223 barium and radium-223/radium-226 crystals will be performed. Radium-223 which decays producing four alpha particles, weak gamma radiation and having a shorter half-

life is more suitable for kinetic experiments in comparison to radium-226. Radium-223 has a potential application in medicine as a pain reduction of patients with bone metastases [1-3].

First, milking of radium-223 from actinium-227 is to be done. Different resins are considered, DOWEX 50 WX 8 with sulfonic acid as a functional group, or Ln resin with di(2-ethylhexyl)orthophosphoric acid (HDEHP) as a functional group. The method should be developed as how to separate Ac-227 and Th-227 from Ra-227, actinium(III) and thorium(IV) should be bound stronger to a resin, which will allow for radium(II) to be eluted.

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METHODS TO ASSESS RADIOISOTOPE MIGRATION IN CEMENTITIOUS MEDIA USING RADIAL DIFFUSION AND ADVECTION

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The UK concept for geological disposal of intermediate level (ILW) and low level radioactive waste (LLW) is likely to include backfill materials based on admixtures of Ordinary Portland Cement (OPC). It is expected that these backfill materials will generate high pH conditions. The eventual corrosion of the metal canisters used for disposal will also promote a low Eh environment. It has been generally assumed that the safety functions of the cement within the near field of a Geological Disposal Facility (GDF) will include reduction of the solubility of many radionuclides and retardation of migration by sorption and incorporation.

The GDF will be subject to different pressure regimes throughout its development and operation as it equilibrates with the surrounding environment. Hydraulic gradients will be present and advection will be a contributory mechanism to diffusion for radioisotope migration. The work undertaken in WP2 of the SKIN project by Loughborough University involves the development of experimental methods that use radial flow through intact cylinders to evaluate the potential for diffusion and advection of relevant isotopes through Nirex reference vault backfill (NRVB). The initial results are very promising and the small scale and cost effectiveness of the approach means that multiple experiments can be undertaken encompassing the full range of physical (and chemical) variations.

For diffusion an appropriate concentration of the isotope of interest (⁹⁰Sr in the present experiments) is introduced into a cavity in the centre of the cylinder, which is then sealed, and placed in a solution previously equilibrated with the matrix. The increase in concentration of the isotope in the external solution is then determined at defined time intervals. For advection the ⁹⁰Sr is similarly introduced into the central core of the cylinder and then equilibrated water is forced under nitrogen pressure, from the central core to the outside of the cylinder where it is collected in a tray prior to analysis. The fate of the isotopes under study has been traced on a macro scale using autoradiography techniques. Both experimental set ups and results have been successfully modeled using conventional numerical solutions and the simulation package GoldSim.

SORPTION OF CS ON THE CALLOVO-OXFORDIAN CLAYSTONE

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The question raised in this study is whether a Kd value is justified for describing Cs sorption on the COx.

The use of a Kd value means that the sorption is reversible. This is the case for montmorillonite (Iijima et al., 2010) but not for illite. In certain conditions, Cs becomes fixed in the edge-interlayer regions of illite (Comans and Hockley, 1992; de Koning and Comans, 2004; Smith and Comans, 1996), leading to a partial “irreversibility”. It is a time-dependent process, the irreversibly sorbed cesium becoming important over time scales of a few weeks and longer (Comans and Hockley, 1992) This was explained by a diffusion process of caesium into the interlayers of the illite clay mineral. It was as well observed after a short contact time (~5 min) in the presence of relative high amount of alkali ions (K^+ , Cs^+ ; NH_4^+) leading to a collapse of the frayed edge sites (De Koning and Comans, 2004).

In the present experiments realized with COx samples, conditions to observe this partial irreversibility were present: the contact time was fixed between 1 and 5 months and the experiments were done in the presence of potassium for a wide range of Cs concentration. The results show however a complete reversibility of the sorption. One explanation is that illite from the interstratified illite/smectite fraction does not behave as illite and that the partial irreversibility expected with illite is not observed because of the low content of “pure” illite.

Reference

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IDENTIFICATION OF IRREVERSIBILITY/REVERSIBILITY RELATIONS AT CLAY SURFACES: SOLUBILITY OF CLAYS

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In a previous work (Suzuki-Muresan et al.), the solubility of clays was studied in conditions close-to-equilibrium at three temperatures (25, 50 and 90 °C). In those conditions, the dynamic equilibrium of dissolution/precipitation as mechanism describing the equilibrium between clays and solution was determined due to the isotopic exchange between the radiotracer ³²Si and total Si in solution. However, the high concentration in silicium at equilibrium indicates a control of solubility by the accessory mineral phases existing in the clays. The aim of the present work is thus to determine the accurate solubility of clays by purification method and to follow the isotopic exchange between the clay mineral surface and the solution enriched in isotopic silicium.

Two clays were chosen for the study:

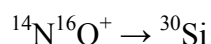
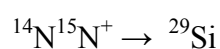
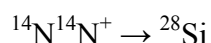
–illite/smectite ISCz1 from C.M.S. containing 0.5 wt% quartz and 1 wt% kaolinite

–illite IMT2 from C.M.S. containing 7.5% quartz, 2% microcline, 0.3% kaolinite and traces of chlorite

These two clays are purified on the base of the elutriation principle which consists to separate “the lighter particles of a powder from the heavier ones by means of an upward directed stream of fluid (gas or liquid) (McNaught and Wilkinson, 1997)”. The purification has started with the illite/smectite clay to recover the clay fraction under 2 µm. The XRD measurement after purification shows a small peak characteristic of quartz phase which indicates that the purification was efficient. The results also indicate that it is difficult to remove totally the quartz phase from I/S clay. The remaining quantity of quartz will be determined by TGA/DTA. In this method, the sample will be heated up to 800 °C to follow the transition Quartz(α) → Quartz(β) at 573°C. The granulometric distribution gives a median of (1.0±0.1) µm after purification to compare with (2.8±0.4) µm before purification. The EDX analyses on the I/S clay before and after purification compared with the data obtained by (Gailhanou et al., 2007) are similar. The next step is the purification of illite.

To study the surface reactivity and the mechanism governing the equilibrium of illite and illite/smectite compared with quartz in conditions close-to-equilibrium, batch experiments (10 g/L of clays) will be loaded in Teflon® reactor at three temperatures (25, 50 and 90 °C) in NaCl 0.01 M solution.

To follow all the studied phenomena, a natural isotope will be added once the system will reach the equilibrium. Between the three natural isotope of silicium $^{28,29,30}\text{Si}$ the isotope ^{29}Si has been chosen as a tracer. The isotopic exchange between ^{29}Si and ^{28}Si will be followed and the tracer ^{29}Si with enrichment up to 99.9% has been provided by Eurisotop (Si-28 \rightarrow 0.04%, Si-29 \rightarrow 99.9%, Si-30 \rightarrow 0.06%). First measurements in 0.7M HNO₃ solution were performed with a medium resolution (4000 Resolution, $\Delta m=0.014$) in the aim to determine the quantification and the detection limits. As silicium is a major element in environment, high background interference with quadrupole ICP-MS is expected due to the presence of quartz torch or particulates in the air and the polyatomic interferences such as



Thus, it is necessary to work in clean room and with a high resolution ICP-MS.

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INTERACTION BETWEEN URANIUM AND IRON (III) OXIDES

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Iron oxides are present in nature and also in the near and far field of the repository; they are the main products of canister corrosion and can be present among the engineered and geological barriers. Among the iron oxides, the amorphous *ferrihydrite* is one of the most widespread iron solids and an important precursor of more stable and crystalline iron oxides such as goethite or hematite (Cornell and Schwertmann, 2003). Ferrihydrite evolution with time and the final products formed depends on many factors, such as pH, time, temperature, etc. The presence of foreign species (such as uranium) in the system will affect the ferrihydrite ageing process. The ageing and transformation process of ferrihydrite will affect in turn the solubility and the retention/release process of uranium from the coprecipitates (Bruno et al. 1995, Duro, 1996).

The objective of present work is to deepen in the understanding of bounding processes between uranium and iron oxides at long time frames, in order to evaluate the role of these solids in the retention and release of uranium from the repository.

Several U(VI)-Fe(III) coprecipitates, aged from days to several years, were analysed using X-ray diffraction (XRD) and Extended X-Ray Absorption Fine Structure (EXAFS).

According to the XRD analysis of the samples at 3 weeks and 9 years, the bulk of U(VI)-Fe(III) coprecipitates can be assumed to evolve from a 2L ferrihydrite (3 weeks aging) to a 6L ferrihydrite-like structure (9 years aging) as shown in Figure 1. Similar results were obtained by Kukkadapu and co-workers (Kukkadapu et al., 2003) for Ni(II)-Fe(III) coprecipitates. The results obtained in the EXAFS (Fe K-edge) measurements were consistent with the XRD results, indicating a ferrihydrite-like structure of the bulk solids.

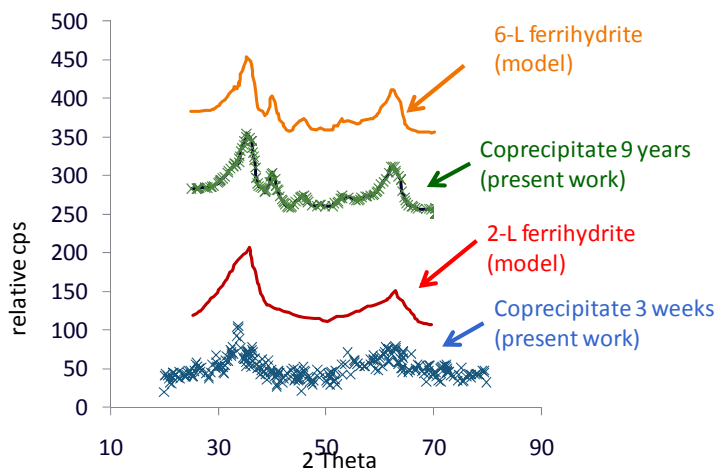


Figure 1. XRD analysis of the Fe(III)-U(III) coprecipitated samples aged for 3 weeks (blue) and 9 years (green) and comparison with XRD model spectra for 2-line ferrihydrite (red) and 6-line ferrihydrite (orange).

The results obtained in the EXAFS (U L_{III}-edge) measurements indicate 3.41-3.46 Å U-Fe distances. These distances are consistent with an edge-sharing bond between U(VI) and ferrihydrite. Furthermore, the measurements indicate that bonding environment of uranium in the coprecipitates evolves with ageing time, towards a schoepite-like structure. This would imply that the assessment of the efficiency of this retention process at these time frames would be given by the schoepite solubility limit.

Further work will be focused on additional EXAFS analysis (μ -XAS) in order to understand the distribution of the elements in the sample and the study of the effect of carbonate on the coprecipitate ageing process.

Note: XRD analysis was performed in the X-ray laboratory of Institut de Ciències de la Terra Jaume Almera (CSIC) and in the X-ray diffraction service of the Universitat Autònoma de Barcelona (UAB). Iron EXAFS analysis were performed using the Fe K-edge signal in the A1 Beamline at the German Electron Synchrotron facility (DESY/HASYLAB) in Hamburg. Uranium EXAFS analysis were performed using the U L_{III}-edge in the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble.

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DISCREPANCIES IN THORIUM OXIDE SOLUBILITY VALUES: ThO₂ SYNTHESIS AND CHARACTERIZATION

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The aim of this task is to study the solubility of ThO₂(s) in the pH range 3 to 7. Previous studies indicated that thorium oxide solubility is very much dependent on the material at the grain boundary. With the use of powdered material, the cleaning of the surface is expected to be more effective, so that artefacts derived from pre-altered surface phases will be minimised. The attainment of apparent solubility equilibrium will be followed by analysing ²³²Th with time and after equilibration half of the solution will be removed for subsequent desorption studies, ²²⁹Th traces will be added to the remaining solution/solid system and the experiment will be continued until establishment of constant ²²⁹Th concentrations. In all solution analyses, colloids will be removed by ultra-filtration but Th analyses of colloidal material will be included in the mass balance. Once ²²⁹Th uptake on the surface has reached a steady state, desorption experiments will be performed putting the solids with a ²²⁹Th rich surface into the previously conserved solution without ²²⁹Th. Typical duration of experiments is shorter than a year. Different analytical techniques will be used for solution and solid analyses: ICP-MS, SEM, XRD, BET method and Granulometry technique. Surface analyses will be improved using coupling to laser ablation.

Synthesis of the solid oxide has been performed with different calcinations temperatures (ambient, 700°C, 900°C, 1300°C) in order to obtain 4 crystallizations of oxide Thorium with different grains vs. grain boundaries ratio. Also separation of ThO₂ crystallized kernel from the coating layers of HTR of ThO₂ has been conducted. These two methodologies have provided samples of the oxide with different crystallinity, i.e., grain size.

Solubility measurements have been conducted in the acidic pH range and the results compared with available data in the literature (see Figure 1).

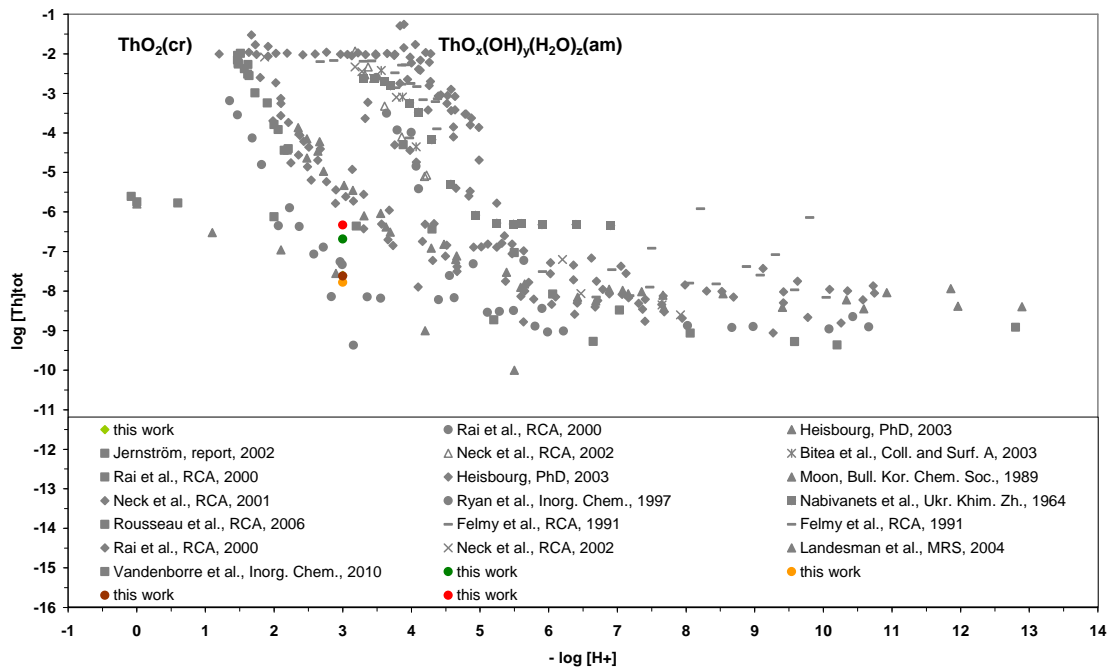


Figure 1. Comparison between the results of this work (color spots) and solubility measurements available in the literature (grey spots).

STUDY THE KINETICS OF TcO₂(s) UNDER HYPERALKALINE CONDITIONS

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The UK presents a high high inventory of ⁹⁹Tc in the wastes to manage. Under the expected GDF conditions of high pH and low Eh most technetium should be immobile as the solid phase TcO₂ (am). Nevertheless, not much is know about the behaviour of this solid phase.

Loughborough University task within this workpackage is to investigate the dissolution behaviour of amorphous Technetium (IV) oxide as a function of the following parameters:

- pH (10.5, 12.5 and 13.3)
- Aging of solid phase (1 hour to 1 years)
- Ionic strength (I = 1 and I =3)

These investigations involve isotopic exchange using ^{95m}Tc and structural determinations where appropriate.

To this aim, high purity TcO₂(s) must be produced electrochemically and a proportion left to age for 12 months, although experiments commence on the freshly produced TcO₂(s). The fate of the isotope in the solid phase is followed by using SEM and XRD.

Some of the limitations to this experimental task is the location and acquisition of sufficient pertechnetate to produce the required quantity of TcO₂(s), as well as the isolation of sufficient ^{95m}Tc. At the time of the annual workshop, Tc-95m had been purchased, received and was being extracted from the target, although its short (60day) half life may mean that more ^{95m}Tc will be needed before experiments can be completed.

THE INFLUENCE OF CLAY SLURRY INVASION ON THE DISSOLUTION OF SPENT NUCLEAR FUEL UNDER REDUCTIVE REPOSITORY ENVIRONMENTS

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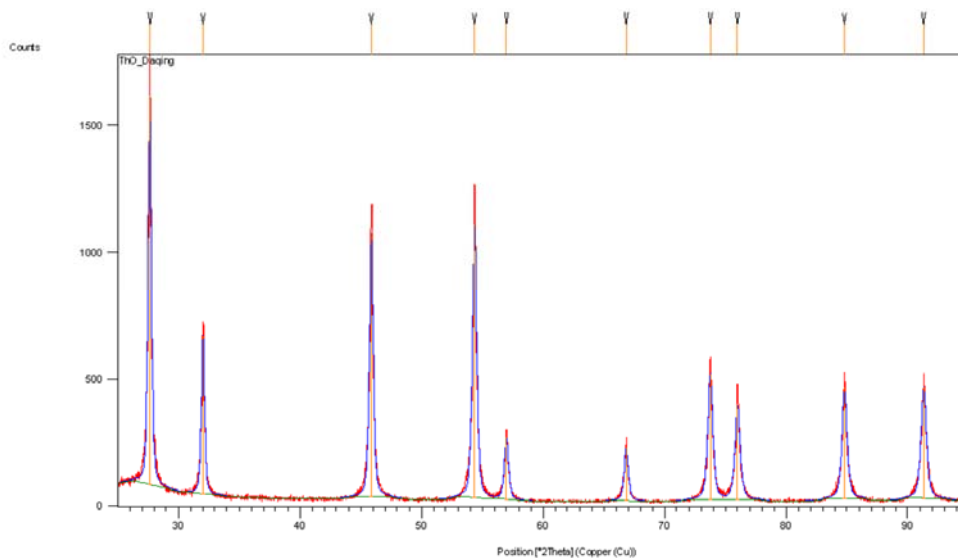
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The aim of this task is to evaluate the potential enhancing of SNF dissolution during a deglaciation period. When the diluted anoxic glacial melt water reaches the deep repository, the clay buffer may be partially or completely eroded, leaving a cavity filled with a slurry of colloidal clay particles. This can have several consequences, such as increasing the amount of U(VI) released from the spent nuclear fuel due to the fact that dissolved U(VI) sorbs strongly to the clay particles and the transport of particles is fast.

In order to eliminate the redox dependence in the experimental work, ThO₂(s) has been used instead of UO₂(s).

ThO₂(c) has been characterized by XRD & SEM, showing a crystalline material (see Figure 1)



Three different batch tests have been conducted, with the following parameters:

- Batch 1: 0.33g ThO₂ 142mL MQ solution pH 2.8.
- Batch 2: Membrane bag 000-10000 Dalton, 10 nm sized pores, holding 0.25 g synthesized Montmorillonite and 0.75g ThO₂ (prewashed 3 time with using ultrasonic bath, till clean solution. 430 mL MQ water
- Batch: 3 the same as batch 2, but without ThO₂.

Solution samples of the three batch experiments have been withdrawn at different times and analysed for Th concentration by means of ICP-MS. The results are shown in Figure 2.

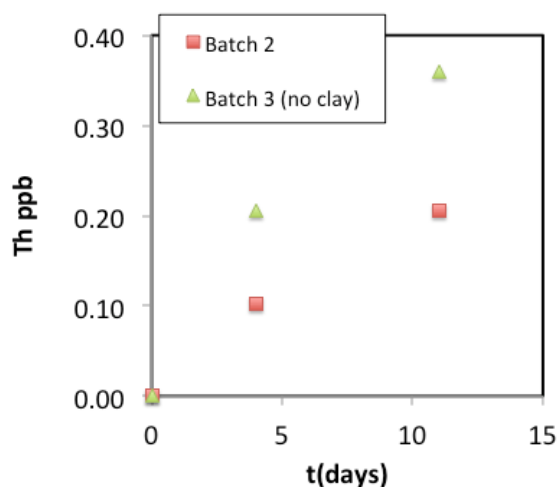


Figure 2. Concentration of Th measured in the samples of Batch 2 and Batch 3.

From the figure it can be seen that the concentration in the case of not having clay in the system is higher, showing the effect of sorption. The sorbed Th(IV) on clay can be measured at the end of the experiment by dissolving the clay mineral. If the amount of Th(IV) sorbed is much bigger than the difference between the last Th(IV) concentration in the batch experiments, it will be taken as an indication that proves that the Th(IV) sorption on clay slurry can enhance the ThO₂ dissolution. This work is under progress.

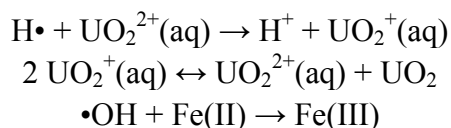
REDUCTION OF URANYL BY GAMMA-RADIATION IN AQUEOUS SOLUTION CONTAINING IRON (II)

C.L. Liu

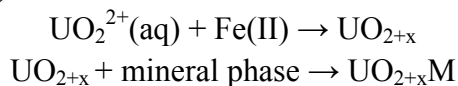
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The aim of the study is to assess the reductive precipitation of Uranium in presence of Fe(II) and the incorporation of reduction products in minerals. For an initial concentration of 1E-4 mol/L, uranyl cannot be reduced in presence of Fe(II). Over a total dose of 1000 Gy and a ratio iron / uranium > 7, γ -radiation can reduce 80% of the uranyl in the solutions containing Fe(II).

Radiolysis of water produces radicals and molecular product ($H\cdot$, e_{aq} , $\cdot OH$, H_2 , H_2O_2 and H_3O^+) where $H\cdot$ is a reducing radical and $\cdot OH$ is an oxidative radical. During radiolysis, the below redox mechanism may happen with the co-existence of U(V) and U(IV)



When uranyl and mineral phase containing Fe(II) are put together in contact, reactions at the interface may occur with the formation of a complex $UO_{2+x}M$ according to the following reactions



No precipitation of phases containing Fe is expected however, sorption on mineral phases, precipitation or competition between UO_{2+x} dissolution and UO_2^{2+} precipitation could be the possible reactions occurring during the radiolysis.

MODELLING/THEORY

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The irreversible uptake of radionuclides into host minerals is not yet properly accounted for in current thermodynamic models of repository-relevant systems. It is known that the overall uptake of M may differ from that expected either from adsorption or SS solubility equilibria.

Conversely, in the Task 4.1, a significant progress in this area was anticipated through accounting for the surface entrapment processes, namely for the interplay between surface adsorption, burial of M in a thin subsurface layer, diffusive transport through this layer, and incorporation in the bulk solid solution. Initially, we planned to investigate the “Surface / growth Entrapment Model” (SEMO) suggested by E.B. Watson (2004). However, a complementary “Surface Reaction Kinetics” model was published by D. DePaolo (2011), already after the commencement of SKIN project. In addition, literature research revealed that certain slow uptake processes have been described in 1980-es in soil chemistry using the “Adsorption- In-Diffusion” model by N.J. Barrow (1983). These findings during our 2011 work on Task 4.1 led to an emphasis on a comparative analysis of assumptions, parameters, limitations and quality of fits to the experimental data for all three above-mentioned trace element uptake kinetics model (see presentation for Task 4.1). This has been facilitated by the availability of program codes implementing the SEMO (courtesy of Prof. Watson) and the “Adsorption – In-Diffusion” model (Barrow, 1987). The reported advance forms a basis for the on-going stage of Task 4.1 work, namely the integration of three time-dependent models of metastable uptake into geochemical modeling code GEM-Selektor (<http://gems.web.psi.ch>) in order to merge them with the existing adsorption- and solid solution models into a new kind of partial-equilibrium solution models with time-dependent intrinsic metastabilities.

The affinity law for dissolution or precipitation reactions states that reaction rates close to equilibrium should be proportional to the affinity, while in the case of dissolution, far from equilibrium rates shall be large and independent from affinity. However, large deviations from this law are frequently observed, in which the roles of surface charge, selective dissolution, surface composition, etc. in such deviations are not yet clear. In the Task 4.3 it was foreseen that the reaction rate data (rate constants + overall rates) close to equilibrium would be collected and compared with those far from equilibrium in order to test the affinity law, to modify it, and to interpret the experimental data. In 2011 (see presentation for Task 4.3), the focus was on the models concerning the clay minerals like illite, smectite; literature data have been collected and presented.

No activity was planned for 2011 in Task 4.2.

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APPROACHES TO MODEL THE KINETICS OF TRACE ELEMENT UPTAKE IN HOST MINERALS

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The present task is focused on modeling of non-equilibrium trace element partitioning between a host mineral and aqueous solution that occurs during co-precipitation or recrystallization. In our presentation during the first annual workshop, the relevant concepts of kinetics of trace element uptake in minerals were introduced through a comparison of three existing modeling approaches.

Experiments have shown a growth rate dependency of trace element partitioning in host minerals, a time-dependent trace element partitioning during recrystallization, or a hysteresis between sorption and desorption of trace element depending on the ageing time. These deviations from equilibrium cannot be accounted using a simple aqueous solid-solution thermodynamic model. For this reason, three existing models of time-dependent trace element uptake in host minerals were evaluated and compared in context of the following questions: Why trace element uptake depends on the precipitation (re-crystallization) rate? What are the molecular mechanisms of such dependency? What should be the equilibrium (uptake) distribution?

In the *Surface Entrapment (SE) Model* (Watson, 2004), it is assumed that a growing crystal takes the composition of its surface, unless diffusivity in the thin near-surface region is effective during growth. In other words, there is a competition between growth rate and diffusivity. Compared to the expected equilibrium distribution of trace element between solid solution and aqueous electrolyte, at higher growth rate to diffusivity ratio, the more significant enrichment is predicted for structurally incompatible elements (e.g. Sr in calcite), and the more significant depletion is expected for structurally compatible elements (e.g. Cd in calcite). The SE model describes well the growth rate dependencies of trace elements distribution coefficients in calcite, but some parameters like the apparent surface layer diffusivity cannot be measured and must be determined by fitting.

The *Surface Reaction (SR) Kinetics Model* (DePaolo, 2011) is based on the dynamics of precipitation-dissolution process, represented as competition between a gross forward precipitation rate and a gross backward dissolution rate for each end-member (e.g. calcite and strontianite in the case of Sr uptake by calcite). Forward rates for host and trace elements or isotopes are connected via fractionation constants (model parameters). At equilibrium, these two rates are equal; their difference determines the net precipitation rate of the mineral and the trace element distribution coefficient. Concerning experimental results, the SR model provides similar curves similar to those from the SE model. However,

inferred mechanisms are quite different, and obtaining a proper value of the gross backward dissolution rate remains a challenge. The main advantage of this model is that it consists of a single resulting equation that is easy to solve even on a spreadsheet.

The Adsorption- Desorption- In-Diffusion (AD) Model (Barrow, 1983) considers adsorption and desorption as instantaneous processes. The adsorbed trace element concentration exceeding that in the bulk mineral triggers an in-diffusion process from surface toward the bulk mineral; contrary to the SE model, no out-diffusion is considered. This model does not account for the host mineral growth; it was applied to data on heavy metal- and anion adsorption on goethite, but not yet tested on other minerals and trace elements.

The on-going work is to embed the modified SE, SR and AD models into the geochemical code GEM-Selektor to make it possible simulating the uptake e.g. closed systems with several host minerals.

References

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THEORY ON THE AFFINITY LAW

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The present task concerns the theory of the chemical affinity law. The basic settings of the affinity law will be introduced in the following slides presented during the first annual workshop.

Numerous experimental observations note that the rate decreases when solution reach a composition close to the saturation of the mineral. Investigators have attempted to extrapolate far-from-equilibrium data to near-equilibrium conditions, sometimes with poor results because of the lack of understanding of the dependence of dissolution rate on the Gibbs free energy of the reaction.

The models attempted to describe the variations of the rate when approaching saturation are mostly based upon the transition state theory (TST), which predict a linear decrease of the rate close to equilibrium. The main hypotheses of the TST applied to solid/water reactions are that the activated complex is the same in the forward rate and backward rate and that there is only one rate limiting elementary reaction step in the reaction sequence leading to mineral dissolution. The TST based affinity rate law for mineral dissolution predicts that the rate will become zero at equilibrium, implying that the forward reaction rate (mineral dissolution) remains constant and it is counterbalanced by an equal backward reaction rate (mineral precipitation). This behavior appears valid for some minerals but others experiments in literature present a non-linear behavior.

The first slides introduce some definitions relating to the definition of the distance from equilibrium. Then the chemical affinity law is presented in relation with the transition state theory. Some examples, from literature, for which the linear case is valid, are shown: usually it is observed for simple oxides or hydroxides for which one limiting step (breaking of one type of bond between metal and oxygen) can be identified. Others cases, which are noted non-linear relating to the affinity law are then presented. The models attempted to simulate these types of behaviors are also shown in the next slides. It concerns mostly an introduction of “fitting” coefficients inside the previous chemical affinity law.

Our interest was turn towards the models concerning the clay minerals like illite, smectite. Literature data have been collected and presented.

Our main task in the SKIN project will be to understand the relationship between the coefficients of the rate law and the reaction mechanism. If the stoichiometry of forward dissolution reaction and backward precipitation are not the same, it shall be assessed how the associated changing surface composition will change the corresponding affinity term. Also, we will try to interpret isotopic data allowing assessing if even at zero net reaction rate at equilibrium, the dissolution-precipitation mechanism is continuing.

SYNTHESIS AND SAFETY ASSESSMENT: IMPACT OF UNCERTAINTIES IN SAFETY ASSESSMENT

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Uncertainties in the solubility and sorption of some elements may be reflected in high uncertainties in the results of the calculations used to support of safety assessment. The main objective of WP5 is to show to which extent some of the experimental results gathered within the SKIN project can reduce these uncertainties.

The assessment of the impact of SKIN on the conservatism will be done through a compartmental modelling approach. Three steps have been defined to achieve this objective:

1. To define a Reference case and to calculate the model using previous parameter values
2. To recalculate the model using new data obtained in SKIN project
3. To compare results obtained using literature or SKIN project data

A performance assessment reference case has been defined based on SR-Site system considered by SKB. The system consists of a deep geological repository for spent nuclear fuel in a crystalline host rock. The release of radionuclides from repository system will be calculated.

The reference case system considers five different compartments: waste, container, bentonite, granite and sink. The last compartment represents the surroundings of the system. The source term is considered in a way that radionuclides can be released by IRF (Instant Release Fraction) and/or can congruently dissolve with the matrix. Migration of radionuclides through the bentonite and the granite compartments occurs by diffusion and advection, respectively.

All data used to build up the compartmental model have been taken from the data report for the safety assessment SR-Site of SKB (TR-10-52) and the references therein.

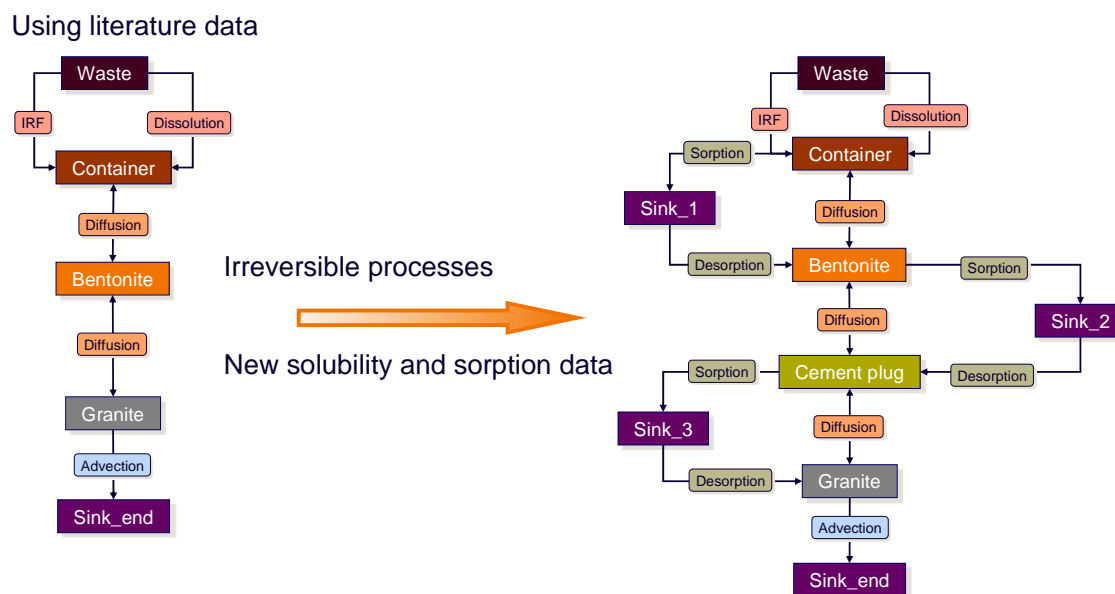


Figure 1. Scheme of compartmental model

In the second step, the model will be extended as shown in figure 1. Irreversible retention processes will be implemented by assuming sinks in the compartments. This model will implement all solubility and sorption data obtained during the SKIN project.

At the end, a comparison will be done between results obtained in the first and second steps. This will lead to determine the impact of the studies done in the frame of the SKIN project over the calculations that support safety assessment procedures.

References:

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SKIN PROJECT

“Slow processes in close-to-equilibrium conditions for radionuclides in water/solid systems of
relevance to nuclear waste management”

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