

Progress Report 2009

Laboratory for Waste Management
Nuclear Energy and Safety Research Department

Cover photo

Left: Optical image of a more than 100 000 years old alteration zone, formed between a natural cement and limestone (a sedimentary rock) in Maqarin, Jordan. The inset shows a scanning electron microscope image of the interface, illustrating the length scale and morphology of different mineral phases which were analyzed by synchrotron-based micro X-ray diffraction (micro-XRD).

Right: Micro-XRD images collected at the microXAS beamline of the SLS with a spatial resolution of $1 \times 1 \mu\text{m}^2$. Tobermorite, a crystalline calcium-silicate-hydrate (CSH) mineral, was identified in the interface between the cement (ettringite), and the limestone (calcite).

PAUL SCHERRER INSTITUT



Progress Report 2009

Laboratory for Waste Management

Nuclear Energy and Safety Research Department

Preface

The main task of the Laboratory for Waste Management is to carry out an R&D programme to strengthen the scientific basis for radioactive waste management.

The Laboratory serves an important national role by supporting the Swiss Federal Government and Nagra in their tasks to safely dispose of radioactive wastes from medical, industrial and research applications as well as from nuclear power plants. The activities are in fundamental repository chemistry, chemistry and physics of radionuclides at geological interfaces and radionuclide transport and retardation in geological media and man-made repository barriers. The work performed is a balanced combination of experimental activities in dedicated laboratories for handling radioactive elements, field experiments and theoretical modelling. The work is directed towards repository projects and the results find their application in comprehensive performance assessments carried out by Nagra. In particular, a major priority for LES over the next decade or so will be to contribute to the Sachplan Geologische Tiefenlagerung (“Sectoral Plan”).

This report summarises the activities and results achieved in the reporting period. It is organised as an overview followed by individual reports on the six waste management group/sub-programme activities.

We gratefully acknowledge the help of the Institute’s management and of Nagra in our work.

Table of Contents

1	OVERVIEW	7
1.1	Introduction.....	7
1.2	General.....	7
1.3	Performance assessment (PA).....	8
1.4	Foundations of repository chemistry.....	9
1.5	Repository near field.....	10
1.5.1	Clay systems.....	10
1.5.2	Cement.....	11
1.6	Repository far field.....	12
2	GEOCHEMICAL MODELLING	15
2.1	Overview.....	15
2.2	Thermodynamic databases and software.....	15
2.2.1	PSI/Nagra Chemical Thermodynamic Data Base 12/07.....	15
2.2.2	Estimations of SIT parameters by charge considerations only.....	15
2.2.3	GEM-Selektor program package.....	16
2.3	Solid solutions.....	17
2.3.1	Ion exchange on montmorillonite using a solid solution approach.....	17
2.3.2	Solubility of hydrotalcite –pyroaurite solid solutions.....	17
2.3.3	From atomistic simulations to thermodynamic modelling: (Ca,Sr) CO ₃ Aq-SS system.....	18
2.3.4	Radium interaction with clays and minor minerals (JAEA-LES).....	19
2.3.5	Uptake of anions by selected minerals.....	20
2.4	References.....	21
3	TRANSPORT MECHANISMS	23
3.1	Overview.....	23
3.2	Data acquisition from experiments on the field and laboratory scales.....	23
3.2.1	Field experiments in the Mont Terri Rock Laboratory.....	23
3.2.2	Reactive transport modelling of laboratory Cs diffusion experiments.....	25
3.3	Predictive modelling of in-situ repository evolution.....	25
3.3.1	Reactive transport modelling of geochemical evolution of SMA repository near field.....	25
3.3.2	Reactive transport modelling of Ni diffusion through bentonite.....	25
3.3.3	Reactive transport modelling of Ra retardation in bentonite.....	26
3.3.4	Diffusion report.....	27
3.4	Understanding the radionuclide transport mechanisms.....	27
3.4.1	Effects of heterogeneous mineral distributions on solute transport.....	27
3.4.2	Influence of clay particle arrangement on molecular diffusion coefficients in clays.....	29
3.4.3	Molecular modelling of hydronium transport in the interlayer of montmorillonite.....	29
3.5	"Know-how" transfer, connection with universities, benchmarking of coupled codes and networking.....	30
3.5.1	Fluid-rock interaction modelling.....	30
3.5.2	Benchmarking of coupled codes.....	31
3.5.3	Forthcoming projects.....	31
3.6	References.....	31
4	CLAY SORPTION MECHANISMS	33
4.1	Overview.....	33
4.2	Performance assessment.....	33
4.2.1	Generic sorption databases.....	33
4.2.2	Comparison of the current Opalinus Clay sorption database with one predicted from illite sorption data.....	33
4.2.3	Bottom-up approach (blind predictions).....	34
4.3	Other activities.....	35
4.3.1	MX-80 bentonite physico-chemical characteristics and sorption.....	35
4.3.2	MX-80 pH buffering.....	35
4.3.3	Effect of temperature on the sorption of Cs onto illite.....	35
4.4	Surface analysis investigations.....	35
4.5	PhD Project.....	36
4.6	References.....	37

5	CEMENT SYSTEMS	39
5.1	Overview	39
5.2	Sorption studies with dose-determining radionuclides	39
5.3	Uptake of neptunium by cementitious materials.....	40
5.3.1	Macroscopic studies.....	40
5.3.2	Synchrotron-based studies	41
5.4	Uptake of U(VI) by cementitious materials.....	42
5.4.1	Spectroscopic investigations of U(VI) uptake processes	42
5.4.2	Aqueous-solid solution thermodynamic model of U(VI) uptake by C-S-H phases.....	43
5.5	CI project	44
5.6	References.....	47
6	COLLOID CHEMISTRY	49
6.1	General.....	49
6.2	Activities in the CFM project	49
6.3	Other colloid activities.....	50
6.4	Future work.....	51
7	DIFFUSION PROCESSES	53
7.1	General.....	53
7.2	Diffusion in Opalinus Clay	53
7.3	Use of micro-beam techniques for studying the diffusion of strongly sorbing tracers	54
7.4	Assessment of heterogeneities (Amicam).....	54
7.5	Water dynamics in water-clay systems.....	54
7.6	Transport phenomena in compacted clay systems (TRAPHICCS).....	55
7.7	References.....	56
8	PUBLICATIONS.....	57
8.1	Peer reviewed journals and reports	57
8.2	Publications in books	58
8.3	Conference proceedings.....	58
8.4	Conferences/Workshops/Presentations	59
8.5	Invited talks	62
8.6	Other presentations	62
8.7	Other reports	62
8.8	Internal presentations	62
8.9	Others/Teachings	63

1 OVERVIEW

M.H. Bradbury

1.1 Introduction

The progress made in the Laboratory for Waste Management (LES) over the period from January 1, 2009 to December 31, 2009 is summarised in the first part of the report. The activities carried out in the individual groups are described in chapters 2 to 7 and are either predominantly “experimental” or “modelling” in their nature. However, there are strong interactions between groups and between experimentalists and modellers.

The MicroXAS Beamline, which was formally within LES, was officially transferred to the Laboratories for Synchrotron Radiation (SYN), Energy and Environmental Science; as of May 1, 2009. LES was heavily involved in the construction and development of this beamline, but now that the beamline has been fully operational for more than three years, there was a consensus between NES and SYN that a complete transfer of the group to SYN was in the best long term interests of the group and its activities. LES's connection to the beam line is now as a “user” and is no longer active in operational aspects. X-ray absorption spectroscopy studies are still seen as an important component in the research activities of LES, particularly as a means of gaining insights into reactions occurring at the molecular level at solid surfaces. LES has strong links with the beamline in, for example, joint PhDs and Post Docs, which will be maintained and developed as appropriate.

1.2 General

The governmental planning instrument, Sachplan Geologische Tiefenlagerung (“Sectoral Plan”), sets out site selection criteria for the deep geological disposal of low and intermediate level waste (SMA), and long-lived intermediate level waste, high level waste and spent fuel (HAA) in Switzerland. The Sectoral Plan has two main parts. Part 1 is the conceptual part and was approved by the Federal Council on April 2, 2008. In Part 2 of the Sectoral Plan, 3 implementation steps are foreseen. Stage 1 is the identification of 6 potential regions for an SMA waste repository and 3 potential regions for a HAA repository. These regions were announced in Bern through the Department of Energy on November 6, 2008. Stage 2 involves the selection of 2 sites each for SMA and HAA for more detailed evaluation. The final selection of 1 site each for SMA and HAA is foreseen in stage 3, and will be followed by an application for a general licence (as part of the

Nuclear Energy Law) in circa 2014/2016. Currently LES is carrying out work related to Stage 2.

The Lab is (or will be) involved in three projects in the 7th EU Framework Programme. LES is work package leader in one of them; WP4, Redox Reactions of Radionuclides, in ReCosy, “Redox Phenomena Controlling Systems” (start date April 1, 2008, duration 4 years). An EU collaborative project entitled “Processes of Cation Diffusion in Clay Rocks” (CatClay) has been approved and will begin in early 2010 (duration 4 years). Due to negotiation difficulties with the EU the start date of ACTINET I3 has been delayed to 2010. The microXAS beamline (supported by LES) is part of the core group of pooled facilities. The planned duration is 3 years.

Multi- and bi-lateral co-operations with external institutions and universities are considered to be of high importance and have continued in 2009. The main ones are summarized in Table 1.1.

The joint project between JAEA (Japan) and LES, set up to investigate the partitioning of Ra(II) between aqueous solutions, bentonite and argillaceous rocks, in the presence/absence of minor minerals (barite, calcite and witherite), was extended for 1 year and will now be completed in March 2010.

A guest scientist from Japan, Dr. Akira Kitamura (Research Scientist at JAEA) completed his 1-year sabbatical in March 2009 in the XAS sub-programme. Plans are already well advanced for a further Japanese scientist to join the LES team in 2010.

The third and last Marie-Curie Euratom Fellowship, “Microscale investigations of the speciation and mobility of U(VI) in cementitious materials”, MISUC, finished on August 31, 2009. Dr. Nathalie Macé secured a position at her home institute; CEA, Saclay.

In connection with the commissioning of a 32 element detection system intended for studying very lowly loaded samples and active measurements on the microXAS beamline, the intention is to advertise a post doc position early in 2010. The post doc will be in LES but based almost 100% at the microXAS beamline.

Table 1.1: National and international co-operations

Co-operations
Nagra Major financial contribution Various technical working groups
Multinational 7 th FP (III: ACTINET-I3, CP: ReCosy, Cat Clay) OECD/NEA (sorption III project) Mont Terri Project (<u>D</u> iffusion <u>R</u> etardation) Grimsel Test Site (<u>C</u> olloid <u>F</u> ormation <u>M</u> igration)
Universities Bern, CH. (mineralogy, petrography, water chemistry) Surrey, UK; EPFL, CH. (cement systems, molecular modelling) UC London, UK (molecular modelling) Mainz, D. (cement, montmorillonite) Strasbourg, F. (glass) Tübingen, D. (geosphere transport)
Research Centres CEA*, France (near and far field) CIEMAT, Spain (clay systems) EAWAG, Switzerland (cement) EMPA*, Switzerland (cement) INE, KIT*, Germany (near and far field; TRLFS) JAEA, Japan (Ra in bentonite/argillaceous rocks) IFR, FZD*, Germany (XAS, TRLFS) SCK/CEN, Belgium (clays) *formal co-operation agreements

In March 2009 Dr. Nathalie Diaz filled the vacant post doc position: “Assessing heterogeneities on the microscopic scale and implementation of such structures in a 3D transport model for compacted argillaceous materials.” (The finances were provided on a 50:50 basis between CEA and PSI) LES won the department internal competition for the NES financed post doc position with a proposal entitled “Two dimensional investigations of reactive transport processes at heterogeneous interfaces”. Dr. Mohamed Hayek took up this position on November 1, 2009. A proposal for a further post doc position to develop a multi-scale modelling approach to diffusion in clays has been accepted by the Forshungskommission (FoKo) and is fully funded by PSI as a Research Committee (FK) project.

Three PhD studies were being carried out in LES during 2009: “Thermodynamic stability and radionuclide binding mechanisms in hydrotalcite-like solid solutions” (finishing date circa June 2010); “Uptake of iodide species by selected mineral phases

relevant to radioactive waste repository environments: a combined radiochemical and spectroscopic study” (finishing date September 2011); and “Simulation of geochemical processes in enhanced geothermal systems” (finishing date October 2011). The second PhD is funded partially through the Virtual Institute of Advanced Solid-Aqueous Radiogeochemistry (INE, KIT) and the last through the Competence Centre for Environment and Sustainability.

An additional PhD position, for which finance has already been approved (Swiss National Science Foundation, SNF), with the title “Quantitative analysis of micro-heterogeneous systems: A joint employment of complementary micro beam techniques: Determination of narrow diffusion profiles: microXAS and laser ablation” commenced in September 2009. Two additional PhD projects entitled “The influence of Fe(II) on clay properties, the sorption of Fe(II) on clays and competitive sorption investigations: a combined macroscopic and microscopic study” and “Diffusion and retardation in clay mineral interlayers, DRIL” have been approved internally in PSI by the FoKo and have been submitted to SNF for further evaluation and eventual funding. Finally, a joint PhD project with the Laboratory for Neutron Scattering (Dr. F. Juranyi), and based there, entitled “Water Dynamics in Clays”, is financed by the SNF. This work is a continuation of the PhD project of F. Gonzalez carried out in the Diffusion Mechanisms Group and completed last year.

LES is participating in “Nuclear Environmental Chemistry” at ETH Zurich (lectures and exercises on nuclear waste management) within the MSc courses “Nuclear Energy Systems” and “Landfilling, Nuclear Repositories and Contaminated Sites”.

On February 25/26, 2009, the Waste Management Program Committee met for their annual meeting. The work performed within LES and the future plans were discussed as usual. The focus of this meeting was on reactive transport modelling (AN-44-09-09). The valuable help and input from the members of the committee, both at the meeting, and throughout the year, is appreciated by the whole Lab.

1.3 Performance assessment (PA)

The announcement in November 2008 of the 6 potential regions for SMA and 3 potential regions for HAA radioactive waste repositories, completed the first Stage of Part 2 of the “Sectoral Plan”. LES has contributed to the regional selection process by providing a generic study on the influences of mineralogy and water chemistry on sorption, and a

series of generic sorption databases for provisional performance assessment studies used in the selection of regions. These sorption databases covered the major rock type categories; argillaceous rocks (five SDBs), crystalline (five SDBs) and calcareous rocks (one SDB), and the range of water chemistries expected in Switzerland (pHs and ionic strengths), as well as considering reducing and oxidising conditions (NAB 08-50). This NAB was subsequently refined by re-defining and describing more fully the processes by which SDBs for argillaceous rocks in future performance assessment studies will be derived, NTB 09-03. In order to show that the proposed procedures were indeed valid, a comparison was made between the sorption values obtained by applying the methodology described in NTB 09-03 to the Opalinus Clay system and those in the SDB for OPA (NTB 02-19) used in the Entsorgungsnachweis (Nagra 2002). The outcome of the comparison is documented in NTB 09-07 which is currently under review. It may be said that the results are very positive.

A report summarising the physico-chemical characteristics of MX-80 bentonite, and sorption isotherms measured for Cs(I), Sr(II)/Ca(II), Ni(II), Eu(III), Th(IV), U(VI), Cl(-I), I(-I) and Se(IV) has been prepared as a Nagra NTB.

A state of the art reactive transport code, OPENGEOSYS-GEMS, is being used to predict the geochemical evolution of cementitious repository near fields, including bentonite seals, bentonite-sand backfillings, in different host rocks as an input to performance assessment studies. In particular, quantifying the influence of pore blocking, through secondary mineral formation, on gas transport is one of the main aims of these investigations.

Since modelling with reactive transport codes is becoming an ever increasing activity in LES, and increasingly important in performance assessment applications, benchmarking is an essential on-going activity. Simulations of radionuclide transport performed with Frac3D were benchmarked against COMSOLE and Tough2-EOS9nT. Several codes are benchmarked in the Mont Terri field diffusion experiments. As a result of the intensive and close co-operation with the Department of Environmental Informatics at the Helmholtz Centre for Environmental Research – UFZ Halle-Leipzig, Germany, the necessary development, support and benchmarking of the reactive transport code OPENGEOSYS is ensured.

A comprehensive report on diffusion measurements and data in argillaceous rocks from both the Swiss programme, and other international programmes, has

been compiled together with evaluations of the transport models used in performance assessment.

As further contributions to the information base required for the provisional PAs being performed for the 6 proposed repository regions, LES will deliver reports and databases on the following topics by the end of 2010.

- Update to the thermodynamic database
- Solubility limits (bentonite and cement porewaters)
- Diffusion report: evaluation of diffusion experiments in clay rocks
- Update of transport databases
- Update of sorption databases (bentonite, cement, clay host rocks)
- Interim report on the effects of the pH plume on sand/bentonite mixtures (“clogging”)

The planning of the contributions from LES to the procedures for selecting 2 sites for each repository type over the next circa 3 years, in terms of the required reports on specific topics and databases for PA and their associated deadlines, is well advanced. As indicated in the LES Annual Report for 2008 the proportion of time spent in LES directly for PA activities will certainly increase over the coming years up to the application for general licences for the realisation of SMA and HAA radioactive waste repositories which will be applied for in 2014/2016.

1.4 Foundations of repository chemistry

The update of the Nagra/PSI Chemical Thermodynamic Database 01/01 to the PSI/Nagra TDB 12/07 was completed on schedule in May 2009. This was an important early milestone to achieve since the thermodynamic data needed to be fixed so that water chemistries, solubilities and sorption databases could be calculated/developed within a consistent framework. The SIT equation has been used in the TDB update for extrapolating laboratory data to zero ionic strength. Gaps in the SIT interaction coefficients were filled with “default values”. All of the documentation related to the update will be completed during 2010.

The work performed in the framework of the OECD/NEA TDB iron review project has finally finished, after a long over-run.

The stand-alone GEMS kernel program for use in coupled modelling codes has been documented and is currently under testing in several coupled codes.

Characterisation and modelling of solid solution systems has continued; ion exchange on

montmorillonite has been modelled using a solid solution approach, solubility data for hydrotalcite – pyroaurite solid solutions have been interpreted using a Lippmann solubility diagram, in the JAEA – LES project on radium interaction with clays and minor minerals, uptake data have been modelled in terms of the formation of non-ideal solid solutions between RaSO_4 and BaSO_4 .

Trace Sr incorporation into calcite has been successfully modelled by atomic simulation methods.

The results of Γ sorption measurements on natural pyrite samples indicate only a very weak uptake which in natural systems would be insufficient for pyrite to function as an Γ scavenger. XANES measurements on polished surfaces of pyrite exposed to selenate (Se(IV)) solutions under anoxic conditions, indicated that the sorbed Se was present as Se(0) .

1.5 Repository near field

1.5.1 Clay systems

A series of experiments with MX-80 bentonite were carried out to check the buffer capacity of the amphoteric surface hydroxyl groups and the previous predictions made for the initial pH of the porewater in the compacted material. Model calculations agreed well with the experimental data and confirmed the extremely high buffer capacity of MX-80.

A large part of the work carried out in the present year on pure clay minerals (TRAPHICCS) was concerned with consolidating the diffusion data measured on Na-montmorillonite compacted to dry-bulk densities of 1300 and 1600 kg m^{-3} . Extensive diffusion data sets for $^{85}\text{Sr}^{2+}$, $^{22}\text{Na}^+$, $^{134}\text{Cs}^+$ and $^{36}\text{Cl}^-$ in Na-montmorillonite, Na-illite and kaolinite under different chemical conditions are now available. Also, diffusion experiments using bivalent anions, i.e. SO_4^{2-} and SeO_4^{2-} , are nearing completion. No reliable experimental diffusion data could be measured so far for Cs^+ . (A new series of experiments have begun.) In general, a substantial reduction of the uncertainties in the data could be achieved by the use of equipment with gradient-free advectively flushed confining filter plates, and by using filter plates with smaller pore sizes. It is now clear that using thin clay samples (~1 mm) in through-diffusion tests is not a suitable technique.

During the past year the OPENGEOSYS-GEMS coupled code has been used to investigate the role of Ra-Sr-Ba solid solutions in the retardation of Ra in bentonite. Numerical simulations showed that Ba, Sr, and Ra, which form sulphate solid solutions, also partition to the cation exchange sites of

montmorillonite, which is the major clay mineral constituent. At high montmorillonite contents, most of the Ra partitions to montmorillonite, while incorporation of Ra in sulphate solid solutions is more important at low montmorillonite contents. It was found that a decrease in Ra exchange due to low montmorillonite contents - which may occur in sand-bentonite mixtures - is compensated by the formation of solid solutions, and so the migration distance of aqueous Ra is similar at different montmorillonite/water ratios.

The crystal chemistry and surface reactivity of phyllosilicate minerals is a key issue for modelling the ion mobility and retardation in clay rich rocks. The Car-Parrinello molecular dynamics simulation techniques are used to predict the structure and dynamics of hydronium solvation in mono-, bi- and tri-hydrated Na-montmorillonite. The simulations have shown that, similar to bulk water, the free energy barrier for a classical proton transfer between interlayer water molecules is comparable with the thermal kinetic energy of molecular motion, and is therefore not a limiting factor for proton diffusion. The diffusivity of hydrogen in the interlayer is controlled by the structural re-arrangements of the solvating water molecules.

Molecular dynamics (MD) techniques have been widely used to predict and understand the diffusive transport of ions and molecules in the interlayers of clay minerals. The major limitation of such simulations is the system size, and it is currently not feasible to model realistic ensembles of clay particles using a full atomistic description of the system. On the other hand, macroscopic continuum models are not able to capture the essence of the transport along the mineral-fluid interfaces. Therefore, a model is being developed to link the nano-scale diffusion coefficients from molecular modelling, and the laboratory scale diffusion coefficients based on an explicit model for the pore structure.

The influence of Fe(II) concentrations in the bentonite porewater on the diffusive transport of Ni through bentonite has been modelled using a mechanistic sorption model ported into the reactive transport code MCOTAC. The sorption model includes surface protonation, surface complexation and cation exchange reactions. The simulations were conducted for one-dimensional spatial geometry and assuming sorption competition. Charge balance was explicitly formulated for the surface complexation reactions. Selectivity coefficients and surface complexation data were taken from previous work and from derived Linear Free Energy Relationships.

EXAFS investigations on samples prepared under anaerobic conditions have demonstrated that the amphoteric strong sorption sites of montmorillonite are selective for Ni(II), Th(IV) and U(VI), confirming the non-competitive sorption behaviour of these radionuclides as measured previously in batch sorption tests. In general, only metals in a like valence state are likely to compete with one another.

1.5.2 Cement

Investigations on the uptake of iodide (^{125}I) and chloride (^{36}Cl) were carried out at varying solid-to-liquid ratios on hardened cement paste and on samples which had been altered to the portlandite-controlled stage of degradation ($\text{pH} = 12.5$). The sorption values of ^{125}I are about an order of a magnitude larger than those of ^{36}Cl and the influence of the total chloride concentration found previously was confirmed. However, the mechanism is, as yet, not understood.

The uptake of methanol, ethanol, formaldehyde, acetaldehyde, formic acid and acetic acid was determined in compact cement samples (0.5 L volume) in connection with the potential formation of small, ^{14}C containing organic molecules produced during the anaerobic corrosion of steel in a cementitious near field. Although the sorption was very weak, it could be quantified accurately using the approach developed in this study.

Sorption studies carried out in previous years indicated an unexpectedly strong uptake of Np(V) by C-S-H phases ($R_d = 10^2 \text{ m}^3 \text{ kg}^{-1} - 2 \cdot 10^3 \text{ m}^3 \text{ kg}^{-1}$). These investigations were continued this year and showed that Np(V) sorption was indeed strong and occurred in two stages: a fast initial sorption process occurring within a few hours ($R_d = (8 \pm 2) \cdot 10^1 \text{ m}^3 \text{ kg}^{-1}$), followed by a slower step. The latter process reached steady state after ~ 25 days equilibration ($R_d \leq (6 \pm 2) \cdot 10^2 \text{ m}^3 \text{ kg}^{-1}$) and during this time the redox potential steadily decreased to a value $< 0.1 \text{ V}$. Hence, the observed decrease in the redox potential suggests that Np(V) was reduced to Np(IV) during the uptake of Np(V) by C-S-H. A thermodynamic model of Np uptake by C-S-H is in the process of being developed.

The work on the interaction with U(VI) with HCP and C-S-H phases was completed. Previous investigations suggested that the coordination environment of U(VI) in C-S-H and HCP resembled that of U(VI) bound in uranyl-silicate minerals, such as soddyite or uranophane. However, the local structure of U(VI) could not be fully resolved by EXAFS. TRLS measurements at 4 K provided additional information on the surface speciation at low U(VI) concentrations. The emission spectra of U(VI) taken up by C-S-H and

HCP are very similar and correspond to the spectrum determined for soddyite. These findings further imply that C-S-H is the uptake-controlling cement phase for U(VI) in cement. Therefore, since C-S-H phases will be present in the cementitious near field over very long periods of time, this ensures that U(VI) will be bound over equally long time scales.

On the basis of U(VI) sorption isotherm measurements and spectroscopic data, a model for the uptake of U(VI) by C-S-H was developed based on the in house sub-lattice CSH3T solid solution model for C-S-H phases. The model was capable of describing the experimental data well.

As part of its contribution to the Mont Terri field experiment on cement-Opalinus Clay interaction (CI project), LES carried out studies on ~ 100000 year old samples from the natural analogue site at Maqarin (Jordan). Thin sections were prepared from Maqarin samples containing reaction products at clay-cement interfaces, and studied using optical microscopy, scanning electron microscopy coupled with microanalysis (SEM/EDS), and microXRD. Ettringite and tobermorite were the major crystalline components identified at the interface using a $\sim 10 \times 10 \mu\text{m}^2$ micro-beam. Structure refinement of tobermorite is currently being performed using the XRD data collected at the microXAS beamline at the SLS (beam size $\sim 1 \times 1 \mu\text{m}^2$). An important component of this work is the application and further development of the micro-diffraction technique being carried out in a post doc study due to end in April 2010.

In the present concepts for low and intermediate level waste and long-lived intermediate level waste repositories, large quantities of cementitious materials are present. Upon re-saturation of the repository, mineral alteration processes at the cement - host-rock and cement-/backfill interfaces are expected. This may influence the transport and retention properties of the barrier system, and, in particular, the release of gas produced as the result of anaerobic iron corrosion and the degradation of organics. (Pore clogging effects.) State-of-the-art geochemical models for cementitious systems, compacted bentonite and argillaceous rocks have been incorporated into the reactive transport code OPENGEO SYS-GEMS to predict the geochemical evolution in the cementitious near fields. The major geochemical processes such as dissolution/precipitation of mineral phases, formation of solid solutions, cation exchange and surface complexation on mineral phases are accounted for. To verify and test the model, laboratory results on cement degradation in contact with bentonite (Gunma University, Japan) have been simulated. The model

accurately reproduces the experimentally observed evolution of the interfaces between concrete and clays.

1.6 Repository far field

The modelling results for the sorption of radionuclides (Ni(II), Co(II), Eu(III), Th(IV), U(VI)) on montmorillonite and illite have been used successfully to predict sorption isotherms measured on MX-80 and Opalinus Clay, respectively, illustrating the success of the “bottom –up” approach

Generally, the influence of temperature on sorption is poorly quantified. As a beginning to a broader investigation in 2010 on this topic, the sorption of Cs was measured on Na-illite as a function of Cs concentration at pH ~ 7, at 25 °C and 90 °C. An overall decrease in Cs sorption by a factor of ~4 was observed with increasing temperature.

The diffusion of ^{134}Cs and ^{60}Co was studied using a gradient free diffusion set up in which the confining filters were advectively flushed. This set up reduces the strong effects of filters on the overall diffusion behaviour of the system (filter-clay-filter sandwich) and allows a more accurate determination of the diffusion properties of the clay. The dual porosity like behaviour observed in earlier experiments with ^{60}Co was confirmed, and the data indicated a faster than expected diffusion of ^{60}Co .

The diffusive behaviour of strongly sorbing tracers in porous media may be (significantly) influenced by micro-heterogeneity (spatial distribution of minerals and their nature, different types of porosity). High-resolution techniques for measuring the spatial distribution of elements on a micrometer scale e.g. laser-ablation/mass spectroscopy and micro-XRF, will be used to measure diffusion fronts/profiles in Opalinus Clay.

To assess the influence of spatial heterogeneities in clay samples, solute diffusion simulations using the COMSOL-Multiphysics code are being performed in which mineral distributions in samples are explicitly taken into account. 3D clay fraction distributions in Opalinus Clay have been reconstructed based on sets of 2D tomograms obtained at the PSI-TOMCAT beam line.

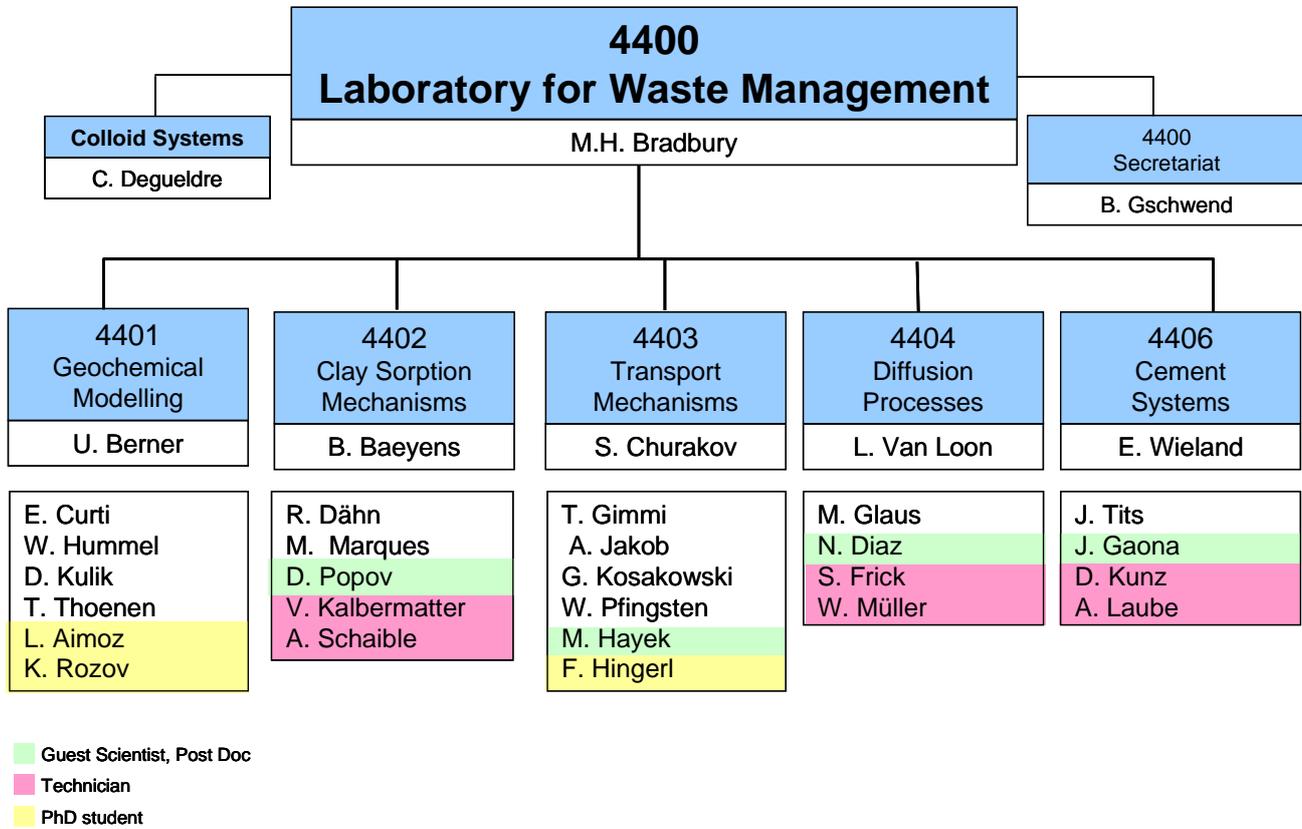
In house and literature diffusion data measured on different argillaceous rocks have been compiled and showed a relationship between the diffusion accessible porosity and the effective diffusion coefficient. An extended version of Archie's Law has been used to describe the relationship over the whole range. This extended relationship can be used to estimate the effective diffusion coefficient of radionuclides in argillaceous rocks from the porosity.

In the framework of the long-term diffusion/retention experiment (DR) in Mont Terri, diffusion measurements in Opalinus Clay of ^{85}Sr , ^{133}Ba and $^{75}\text{SeO}_4^{2-}$ were completed in 2009. The diffusion of ^{134}Cs will be continued for at least one more year. A simplified semi-analytical model describing the diffusive transport of aqueous species has been developed to calculate the sensitivity of the field measurements to three lumped parameters i.e. apparent diffusion coefficient in the rock, ratio of the rock to filter effective diffusion coefficients, and the ratio of the rock to borehole capacity.

A multi-species sorption model has been ported into the MCOTAC transport code and was successfully used to model the results of a Cs diffusion experiment in Opalinus Clay (break-through curve, out-diffusion curves, and mass balance). During 2010, this modelling approach will be applied to a series of Cs diffusion experiments in Opalinus Clay samples which were carried out under different experimental conditions in order to further check the applicability of the model.

The activities on colloid research are mainly confined to the “Colloid Formation and Migration” (CFM) work carried out at the Grimsel Test Site. The focus continues to remain on colloid generation, using single particle counting (SPC) as a characterisation technique. A co-operation with CIEMAT, Spain, was started in 2009 aimed at ways and means to optimise the radioanalytical work for measuring colloid breakthrough in the CFM experiment at the Grimsel Test Site. Labelling colloids with ^{64}Ge was decided as the best means of carrying out the proposed experiments.

Table 1.2: LES Organigram (December 2009)



2 GEOCHEMICAL MODELLING

W. Hummel, U. Berner, E. Curti, D. Kulik, T. Thoenen, L. Aimoz, K. Rozov

2.1 Overview

Work related to thermodynamic databases and codes was an important part of our activities.

- The update of the Nagra/PSI TDB 01/01 to the PSI/Nagra TDB 12/07 has been completed (documentation foreseen for 2010).
- “Default” SIT values were estimated based on a thorough statistical analysis of all published SIT interaction coefficients for NaCl and NaClO₄ media.
- The stand alone GEMS kernel program for use in coupled modelling codes has been documented and is currently under testing in several coupled codes.

Characterisation and modelling of solid solution systems was another important part of our activities.

- Ion exchange on montmorillonite has been modelled using a solid solution approach which can now be used in reactive transport modelling.
- Solubility data for hydroxalite – pyroaurite solid solutions have been interpreted using a Lippmann solubility diagram.
- Our modelling results for trace Sr incorporation into Ca carbonates demonstrated that atomistic simulation methods are mature enough to provide reliable predictions for carbonate solid solution phases incorporating cations with an accuracy comparable to that of the best experimental data.
- The first part of the joint JAEA – LES project on radium interaction with clays and minor minerals, focusing on the uptake of radium on barite, has now been completed. The Ra uptake data indicate the formation of non-ideal solid solutions between RaSO₄ and BaSO₄.
- The uptake of iodine (I) and selenium (SeO₃²⁻) onto pyrite has been studied using radiochemical assay, X-ray diffraction and X-ray spectroscopy techniques.

The teaching duties of W. Hummel as Privatdozent (PD) for “Nuclear Environmental Chemistry” at ETH Zurich, included lectures and exercises on nuclear waste management within the scope of the MSc courses “Nuclear Energy Systems” and “Landfilling, nuclear repositories and contaminated sites”.

2.2 Thermodynamic databases and software

2.2.1 PSI/Nagra Chemical Thermodynamic Database 12/07

The update of the Nagra/PSI TDB 01/01 to the PSI/Nagra TDB 12/07 has been completed. Changes in the data mostly arise from the OECD NEA reviews by GUILLAUMONT et al. (2003) for uranium, neptunium, plutonium, americium and technetium (update of previous NEA reviews), by BROWN et al. (2005) for zirconium, by OLIN et al. (2005) for selenium, by HUMMEL et al. (2005) for selected organic ligands, and by RAND et al. (2009) for thorium. An in-house review was performed for silicate complexes. Electronic versions of the PSI/Nagra TDB 12/07 have been prepared for PHREEQC and GEMS-PSI.

2.2.2 Estimations of SIT parameters by charge considerations only

Ionic solutions depart strongly from ideality, and this non-ideality is accounted for by the introduction of an activity coefficient γ_i relating the concentration, m_i , of species i with its “thermodynamic concentration” or activity $a_i = m_i \cdot \gamma_i$. There exists a number of different semi-empirical methods for the estimation of activity coefficients. One approach extending to high concentrations is the Specific Ion Interaction Theory (SIT)

$$\log_{10} \gamma_j = -A \cdot z_j^2 \cdot \sqrt{I_m} / (1 + 1.5 \cdot \sqrt{I_m}) + \sum \varepsilon(j,k) \cdot m_k$$

where A is a constant with a value of $0.509 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ at 298.15 K and 0.1 MPa, z_j is the ionic charge of species j , and I_m the ionic strength of the particular electrolyte and $\varepsilon(j,k)$ is an aqueous species interaction coefficient which describes the specific short-range interactions between aqueous species j and k .

The SIT equation has been used in the present TDB update for extrapolating laboratory data to zero ionic strength. The required $\varepsilon(j,k)$ coefficients were taken from RAND et al. (2009), or were derived from $\log_{10} K$ data at varying ionic strengths whenever possible. Note that the SIT equation is at present solely implemented in GEMS.

However, when SIT is applied in environmental

modelling, the formally correct implementation of SIT in a speciation code like GEMS is not sufficient. The remaining gaps in the SIT interaction coefficient matrix have to be filled with reasonably justified “default values”.

In the current version of our TDB we decided to restrict the application of SIT to environmental systems where the salinity is governed by NaCl. In addition, laboratory systems can be modelled for NaCl and NaClO₄ media. The nowadays rarely used background medium KNO₃ was not considered.

The method used to estimate “default” SIT values was a thorough statistical analysis of all published SIT interaction coefficients for NaCl and NaClO₄ media (HUMMEL, 2009). SIT $\epsilon(j,k)$ values were taken from RAND et al. (2009). Uncertainties in individual $\epsilon(j,k)$ values smaller than ± 0.05 have been increased to ± 0.05 . The results of the statistical analysis is shown in Fig. 2.1.

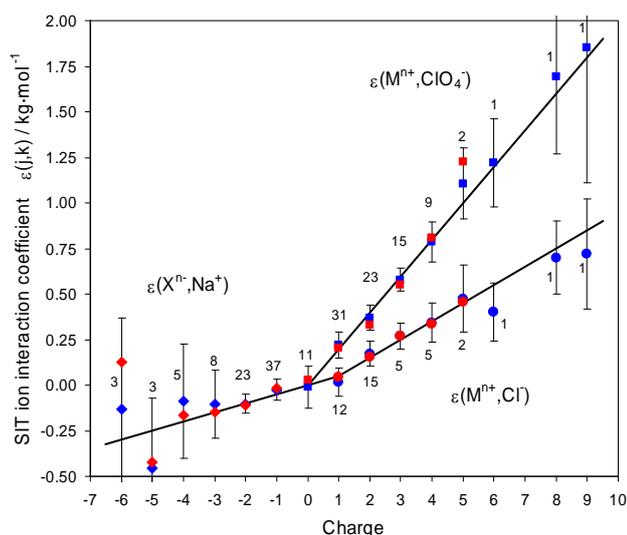


Fig. 2.1: Correlation of SIT interaction parameters with charge only. Blue symbols with error bars represent un-weighted means where the uncertainty is based on the dispersion of the data points. Red symbols represent weighted means, their uncertainties are always ± 0.02 or less, i.e. within the size of the red symbols. The number of data points used to calculate the means are given in the figure. In some cases there is only one measured data point, and the given experimental error is indicated. In all cases the uncertainty is estimated on the 95% confidence level. Black solid lines show the finally selected “default values” of SIT interaction parameters.

The finally selected “default values”, visualised in Fig. 2.1 as black lines, are based on these statistical results. However, they are expert choices which were guided by the idea of providing as simple as possible numbers which are still compatible with the statistical results. The “default values” can be calculated using the following equations:

$$\epsilon(M^{n+}, ClO_4^-) = \text{Charge} \times 0.2$$

$$\epsilon(M^{n+}, Cl^-) = -0.05 + \text{Charge} \times 0.1$$

$$\epsilon(X^{n-}, Na^+) = \text{Charge} \times 0.05$$

2.2.3 GEM-Selektor program package

GEMS-PSI v. 2.3.1 has been made available. A major upgrade to version 3.0.0 of GEM-Selektor (S. Dmytrieva), with a new graphical user interface has been performed and is currently being tested by LES/PSI and the IGMR/ETHZ team. It is expected to be released in March 2010. (Updates of the web site and online tutorials are pending.)

A GEMS wiki web site has been created (G. Kosakowski) to provide a platform for the exchange of data/ comments/ ideas/ examples between GEMS users and developers.

Contributions have been made by the IGMR/ETHZ team (T. Wagner) to the GEMS TSolMod framework with the aim of extending the range of the GEMS/GEMIPM2K applications as follows:

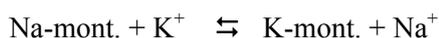
- Shvarov version of aqueous EDH (extended Debye-Hückel) model added;
- extended aqueous DH models with calculation of osmotic and water activity coefficient;
- extensions in aqueous DH based models (Davies, Limiting law, Debye-Hückel, Karpov, Helgeson, Shvarov) for consistent calculation of bulk phase excess;
- Peng-Robinson (PR78) fluid EoS model for pure fluids and mixtures added;
- option for combining fluid EoS models with different built-in mixing rules implemented;
- extensions in aqueous SIT model for temperature-dependent interaction parameters and calculation of bulk phase excess properties;
- Soave-Redlich-Kwong (SRK) fluid EoS model for pure nonelectrolyte fluids and mixtures added;
- extended Uniquac (EUNIQUAC) model for aqueous electrolyte solutions;
- built-in Pitzer aqueous model in TSolMod module completed (with F. Hingerl).

The development of the stand-alone GEMIPM2K kernel program for use in coupled modelling codes in connection with the CCES GEOTHERM project (D. Kulik, S. Dmytrieva, G. Kosakowski) was completed in July-August 2009. The GEMIPM2K kernel is currently under testing in several coupled codes (OpenGeoSys-GEM – G. Kosakowski, CSMP++-S. Fowler, IGMR ETHZ). Draft documentation files for GEMIPM2K have been prepared (available on the les-svn.psi.ch server) along with tests and numerous improvements in the code and will be finalized in a PSI TM (Technical Report). Part of this work on GEMIPM2K has been reported at the Migration'09 Conference (poster).

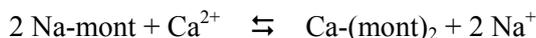
2.3 Solid solutions

2.3.1 Ion exchange on montmorillonite using a solid solution approach

In geochemical models the ion exchange of smectites is usually formulated with equilibria of the form



or, in the case of bi-valent cations



In such studies the basic framework of the smectite is, in principle, considered as a chemically non-reactive “Pin-board” where the structural negative charge is compensated by an ensemble of cations (Na, K, Ca, Mg, Fe, Sr....) which varies depending on the origin and the conditioning of the montmorillonite. Conventional geochemical models such as PHREEQC, MINEQL or EQ3/6 usually consider that all of the exchange sites are initially occupied e.g. with Na, and are treated as neutral, independent solution species with unit activity coefficients. In fact, exchange equilibria of the type shown in the equations given above then constitute an activity relationship among the exchangeable cations, determined by the ratio [montmorillonite-units]/ [exchangeable cations]. This setup correctly describes the cation exchange under the condition that the amount of exchangeable sites remains constant. It does not, however, take into account the chemistry of the montmorillonite, i.e. the fact that the montmorillonite may also participate in mineral transformation and dissolution processes e.g. as a result of interactions with high pH solutions from cementitious materials.

A new model concept was developed which is consistent with a model described by TARDY & FRITZ (1981). It assumes that the montmorillonite is an ideal solid solution with end members which solely differ in

the nature of the charge compensating cation.

The new ideal solid solution model for montmorillonite reproduces the results obtained by the “classical” exchange models. In addition, it offers several advantages: 1) extrapolation to systems with low porosities becomes simple. For example, the model easily describes the transition to low water content systems where the solution composition will be determined by the occupancy of the clay (including pH buffering by amphoteric sites). 2) The chemical reactivity of montmorillonite in aggressive media such as high-pH cement porewater solutions is fully taken into account. This feature additionally includes the potential reduction of specific sorbing sites through the dissolution of the montmorillonite structure or mineral transformations, e.g. illitisation by intruding potassium ions. 3) In coupled models (i.e. coupling transport with GEMS) the relevant sorbing phase can be treated as a common solid phase and the handling of difficult processes such as the release of interlayer water during mineral transformations in compacted systems, is simplified.

As a first application, the Opalinus Clay reference system, including the montmorillonite solid solution as a proxy for the smectites, a multitude of additional reactive phases, and about 5 % of a pore solution, has successfully been modelled.

2.3.2 Solubility of hydrotalcite – pyroaurite solid solutions

Experimental solubility products of hydrotalcite ($\text{Mg}_3\text{Al}(\text{OH})_8\text{CO}_3$) – pyroaurite ($\text{Mg}_3\text{Fe}(\text{OH})_8\text{CO}_3$) solid solutions have been represented in a so called Lippmann solubility diagram. In the Lippmann diagram each experimental point is represented twice: once as a function of the mole fraction of Fe in the solid (square symbols), and once as function of the mole fraction of $\text{Fe}(\text{OH})_4^-$ in solution (diamond symbols) on a single, common abscissa. Figure 2.2 combines both co-precipitation (filled symbols) and dissolution (empty symbols) experiments. The theoretical curves of an ideal solid solution are calculated from the solubility products of the pure end members where the mole fractions are zero (hydrotalcite) or unity (pyroaurite) by definition.

The concentration scale solubility products of hydrotalcite ($\log_{10}K = -33.9 \pm 1.2$) and pyroaurite ($\log_{10}K = -33.1 \pm 1.3$) at $\text{pH } 11.40 \pm 0.03$ are very similar.

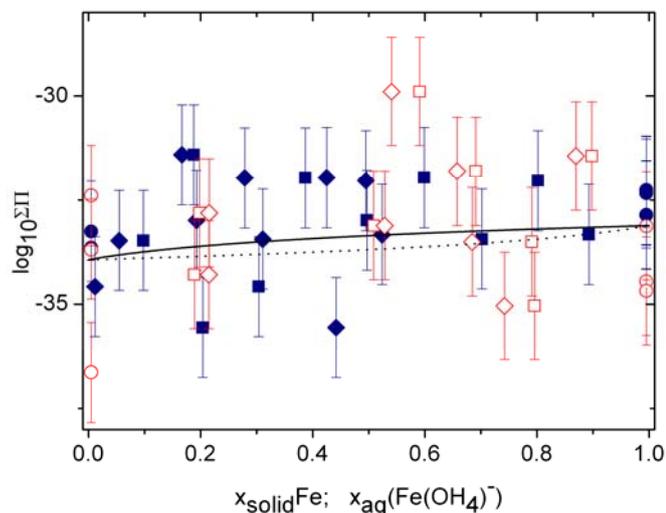


Fig. 2.2: Lippmann solubility diagram of the hydrotalcite – pyroaurite solid solution system at 25°C. The solid line represents the solidus, the mole fraction of Fe in the solid, whereas the dotted line represents the solutus, the corresponding mole fraction of Fe in the solution.

The tendency of the solutus points (diamond symbols) towards too low $\text{Fe}(\text{OH})_4^-$ mole fractions in solution probably indicates the presence of minor secondary phases (e.g. brucite, gibbsite, ferrihydrate) not detectable by XRD. Due to the substantial analytical uncertainties, the available data are not suitable to determine parameters for non-ideal solid solution models. Hence, the solid solution behaviour in the hydrotalcite - pyroaurite system is described, by default, as ideal.

2.3.3 From atomistic simulations to thermodynamic modelling: $(\text{Ca},\text{Sr})\text{CO}_3$ Aq-SS system

Solid-solution (SS) incorporation of strontium in calcium carbonates is a topic of sustained interest in (radio)geochemistry. Under ambient conditions, pure CaCO_3 and SrCO_3 (strontianite) end members have different structures (calcite and aragonite, respectively). Experimental data on SS mixing properties refer to the aragonite-strontianite system; the data on trace Sr uptake exist mainly for calcite (for details, see KULIK et al., 2009).

What is the right way to model this and similar Aq-SS systems where SS end members have different structures?

The available data on $(\text{Ca},\text{Sr})\text{CO}_3$ Aq-SS systems were reconciled using (1) DFT calculations and force-field modelling of thermodynamic properties of $(\text{Ca},\text{Sr})\text{CO}_3$ SS end members, including meta-stable pure SrCO_3 with the calcite structure; (2) force-field calculations using the double-defect method (VINOGRAD et al., 2009) to evaluate the excess properties of mixing in solid solutions with the aragonite and calcite structures; and (3) thermodynamic modelling of Aq-SS systems with SS phases of both structures using the GEMS code package. At step (3), Lippmann diagrams (and their analogues) were constructed using polynomial fits to free energies of mixing obtained at step (2) for calcite- and aragonite SS structures, as well as by applying the Darken's Quadratic Formulation (DQF) model (POWELL, 1987) to calcite - strontianite SS system. Within the same structure, the excess free energy of mixing is nearly symmetric, but the presence of two SS phases with different structures results in a quite asymmetric "miscibility gap" (Fig. 2.3) beginning on the calcite side at $x_{\text{SrCO}_3} = 0.003$, consistent with the experimental distribution coefficient of 0.021, a dimensionless value defined as $(x_{\text{SrCO}_3}/[\text{Sr}^{2+}]) / (x_{\text{CaCO}_3}/[\text{Ca}^{2+}])$ (TESORIERO & PANKOW, 1996).

Results predicted at step (2) for the aragonite-strontianite SS seem to be in a good agreement with calorimetric and electrochemical measurements (CASEY et al., 1996), but not with dissolution experiments (PLUMMER & BUSENBERG, 1987). Our modelling results for trace Sr incorporation in Ca carbonates demonstrate that atomistic simulation methods are mature enough to provide reliable predictions for carbonate SS phases incorporating (radio)toxic cations with an accuracy comparable to that of the best experimental data.

This work has been carried out within the Helmholtz Society Virtual Institute for Advanced Solid-Aqueous Radio-geochemistry, in collaboration with V. Vinograd and co-workers from the University of Frankfurt (Germany). Results were reported at the Migration'09 Conference and submitted to the proceedings.

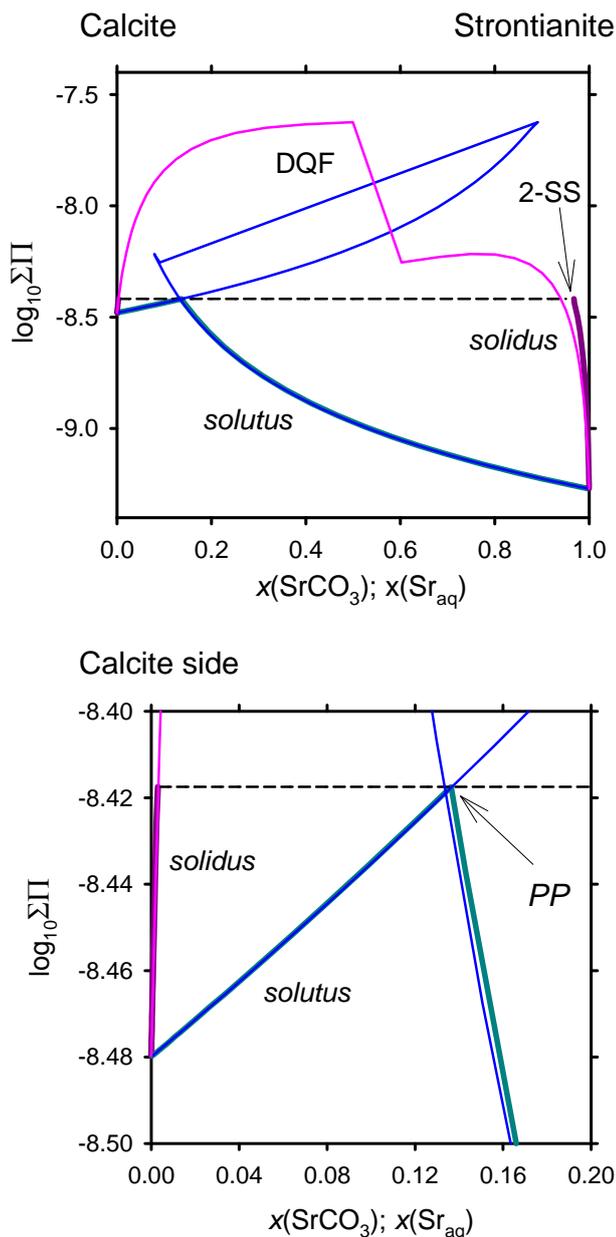


Fig. 2.3: Analogue of the Lippmann diagram for two $(Ca,Sr)CO_3$ phases, one with the calcite structure (left thick lines, calcite incorporating some Sr) and one with the aragonite structure (right thick lines, strontianite incorporating some Ca). The thick lines below the dashed horizontal line show the miscibility gap. PP is the peritectic point where the solution is in equilibrium with two solids. A superimposed Lippmann diagram (thin lines) shows the model calculations according to the DQF mixing model for one solid solution phase with calcite and strontianite end members. The thin lines above the dashed horizontal line represent metastable solid solutions. The step in the red line indicates the structural transition of the solid solution phase from the calcite to the aragonite structure.

2.3.4 Radium interaction with clays and minor minerals (JAEA-LES)

In close co-operation with the Japan Atomic Energy Agency (JAEA), LES is carrying out extensive investigations on the interaction of radium with selected minor minerals (barite, calcite and witherite) and clays (illite, montmorillonite). The first part of this project, focusing on the uptake of radium on barite, has now been completed, and a publication has been submitted (CURTI et al., 2009). The data obtained from ^{133}Ba and ^{226}Ra sorption experiments on synthetic barite, carried out in the pH range 4-8 and with different background electrolytes ($BaCl_2$, Na_2SO_4 , $NaHCO_3$, pure water) were combined and interpreted in terms of solid solution thermodynamics.

The results of the ^{133}Ba uptake experiments indicate that barite recrystallization was complete within the timescale of the experiments (up to 1.5 years), as an overall isotopic equilibrium between bulk solid and aqueous solution was reached in most cases (Fig. 2.4). Moreover, the tracer data are consistent with a homogeneous uptake mechanism, indicating that the tracer is uniformly distributed within the solid. The ^{133}Ba uptake data cannot be explained by local equilibrium with a thin layer at the barite surface (heterogeneous uptake, see Fig. 2.4), in which case compositional zoning would arise.

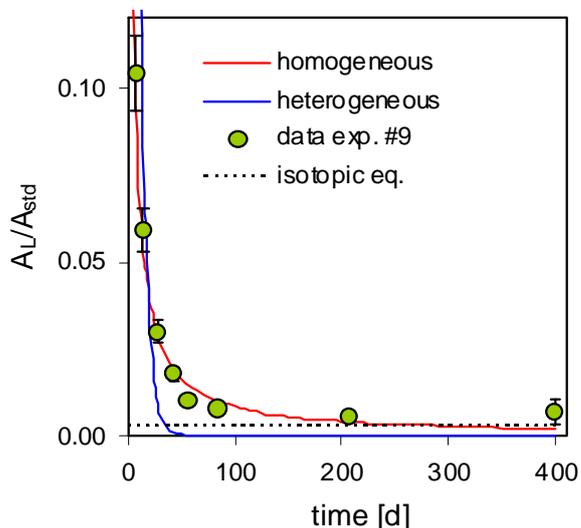


Fig. 2.4: Ratio of ^{133}Ba activity in solution (A_L) to total added activity (A_{std}) as a function of reaction time for barite in pure water, compared with model calculations for homogeneous (red continuous line) and heterogeneous incorporation (blue continuous line). The broken line indicates isotopic equilibrium between bulk solid and aqueous solution.

Our modelling indicates barite recrystallization rates ranging from $2 \mu\text{mol m}^{-2} \text{d}^{-1}$ (NaHCO_3 solutions at pH 8) to $50 \mu\text{mol m}^{-2} \text{d}^{-1}$ (pure water, pH ~ 5), depending on solution composition. Independent evidence for the recrystallization process is provided by SEM pictures taken before the start of the experiment and after 18 months reaction time in water (Fig. 2.5).

In spite of experimental difficulties and large experimental uncertainties, the Ra uptake data indicate the formation of non-ideal solid solutions between RaSO_4 and BaSO_4 with positive interaction parameters ($a_0=1.5-2.5$, $W_{AB} = 3720-6200 \text{ J/mol}$). The results are summarized in Fig. 2.6, showing the aqueous Ra concentrations in three different chemical systems as a function of the amount of barite recrystallized (n) as derived from the ^{133}Ba tests. In all cases, the Ra concentrations measured in the aqueous solution are higher than predicted for ideal solid solutions.

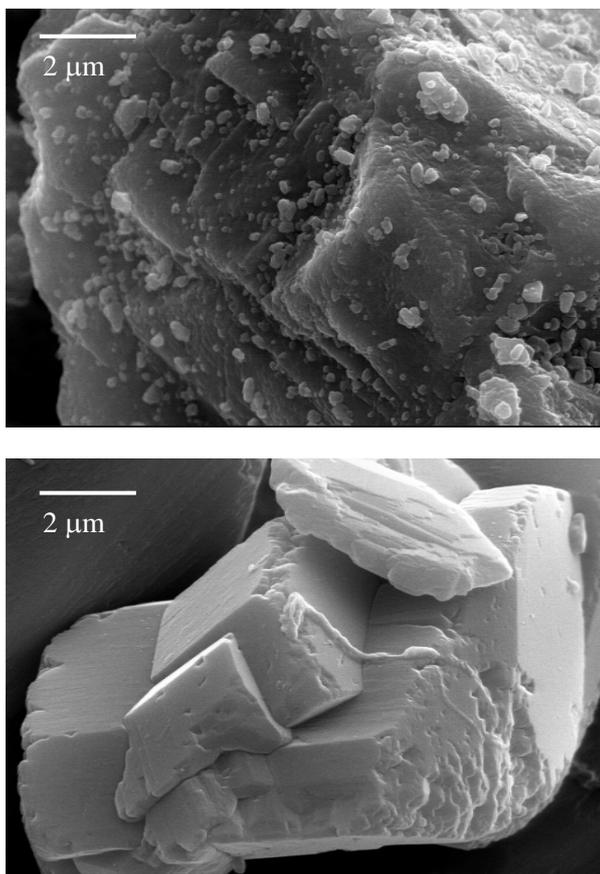


Fig. 2.5: SEM images of the barite used for the ^{133}Ba and ^{226}Ra tracer experiments before (top) and after 18 months reaction time in deionised water (bottom). The small nanometre-sized barite particles on top of the crystal surfaces of the pristine barite disappeared during the recrystallization process. In addition, surface roughness decreased and the crystal habitus became idiomorphic.

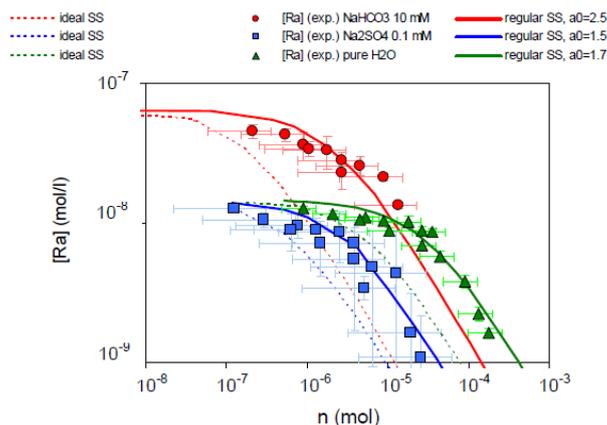


Fig. 2.6: Ra-barite solid solution data compared to GEMS-PSI model calculations. Broken lines: ideal solid solutions. Solid lines: best fits obtained by adjusting the non-ideality parameter a_0 .

Further data on the uptake of Ra by conditioned clays have been gathered recently by our Japanese colleagues and will be evaluated later. Currently, the activity related to this project has been delayed due to the high priority of studies required for the Swiss Sectoral Plan for deep geological repositories.

2.3.5 Uptake of anions by selected minerals

Pyrite and Layered Double Hydroxides (LDHs) have been proposed as minor mineral components which could act as potential sinks for some long-lived anionic radionuclides, particularly ^{129}I and ^{79}Se . In the context of an ongoing PhD project (L. Aimoz), the uptake of iodine (I^-) and selenium (SeO_3^{2-}) onto pyrite and LDHs is being studied using radiochemical assay, X-ray diffraction and X-ray spectroscopy techniques.

The uptake of iodine by natural pyrite samples from two different sources (Navajun, Spain and Huanzala, Peru) was investigated under anoxic conditions ($\text{O}_2(\text{g}) < 2 \text{ ppm}$). Distribution coefficients (R_d) of I^- onto pyrite were determined over a large concentration range from the decrease in ^{125}I tracer concentration after 7 days reaction time (Fig. 2.7). A strong reduction of R_d with increasing dissolved iodine concentration was observed, resulting in a highly non-linear isotherm. These data indicate that iodide uptake onto pyrite is weak and insufficient for pyrite to act as an effective iodine scavenger. Currently, a surface complexation model is under development to explain the observed sorption behaviour.

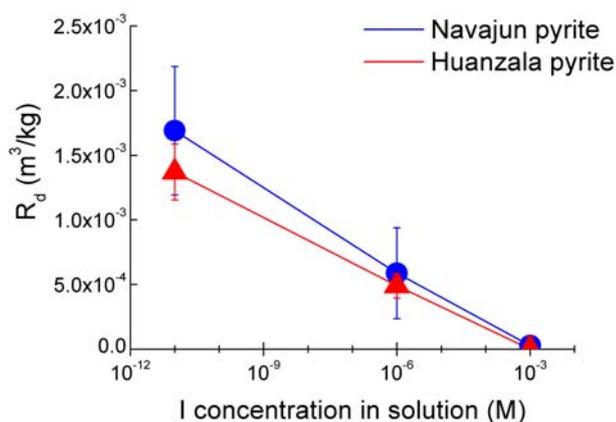


Fig. 2.7: R_d values of I sorption onto pyrite after 7 days reaction time.

The uptake of Se(IV) on pyrite, which is known from the literature to be significant (BRUGGEMANN et al., 2005), was investigated using μ -XRF and μ -XANES. The XRF maps and absorption spectra were acquired under an inert gas flux at the X05 beamline (SLS) on polished pyrite samples that had been previously exposed during 15 days - 2 months to 10^{-2} M Na_2SeO_3 solutions at 80 °C under strictly anoxic conditions. The uptake process was heterogeneous, since several micrometer-size Se-rich clusters were detected, surrounded by areas with low and uniform Se-level distribution (Fig. 2.8). The XANES data revealed that most of the adsorbed Se was reduced to Se(0). However, at least part of the dissolved selenium was first adsorbed as Se(IV) on the pyrite surface before being reduced to Se(0) (see the spectrum of spot 4 in Fig. 2.9, which indicates the presence of both Se(IV) and Se(0) in the same cluster).

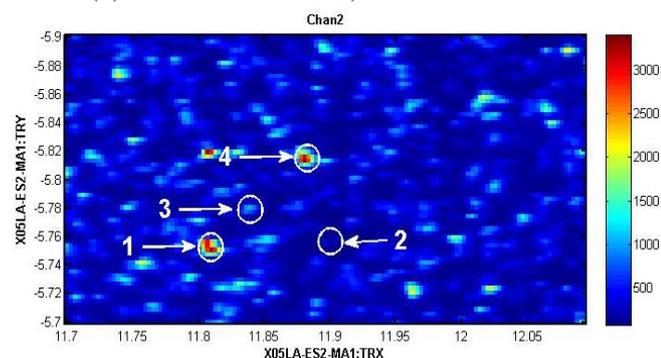


Fig. 2.8: Color coded micro-XRF map of the Se-K α signal for a polished pyrite chip reacted during two months with Na_2SeO_3 under anoxic conditions. Selected analyzed μ -XANES spots are labelled 1 to 4.

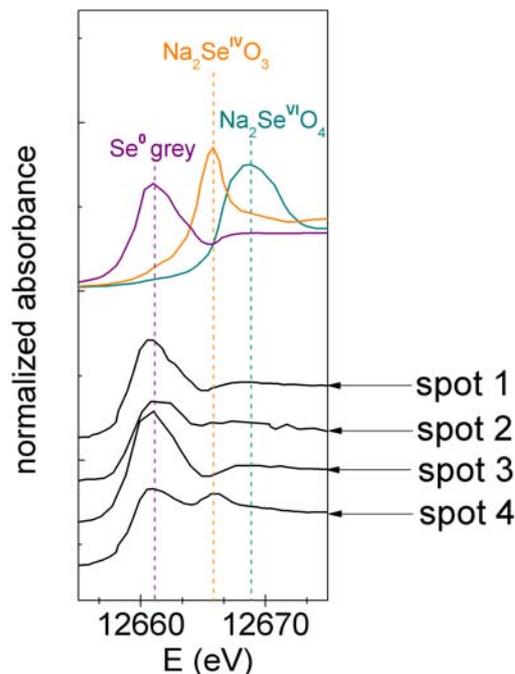


Fig. 2.9: Se K-edge μ -XANES of the selected spots, compared to the white line positions for the oxidation states 0, IV and VI as defined by reference compounds.

2.4 References

- BROWN P.L., CURTI E., GRAMBOW B. (2005) Chemical Thermodynamics of Zirconium. Elsevier, Amsterdam, 512p.
- BRUGGEMANN C., MAES A., VANCLUYSEN J., VANDEMUSSELE P. (2005) Selenite reduction in Boom clay: Effect of FeS_2 , clay minerals and dissolved organic matter. Environ. Pollut. 137, 209-221.
- CASEY W.H., CHAI L., NAVROTSKY A., ROCK P.A. (1996) Thermochemistry of mixing strontianite [$SrCO_3(s)$] and aragonite [$CaCO_3(s)$] to form $Ca_xSr_{1-x}CO_3(s)$ solid solutions. Geochim. Cosmochim. Acta 60, 933-940.
- CURTI E., FUJIWARA K., IJIMA K., TITS J., CUESTA C., KITAMURA A., GLAUS M.A., MÜLLER W. (2009) Radium uptake during barite recrystallization at $23 \pm 2^\circ C$ as a function of solution composition: An experimental ^{133}Ba and ^{226}Ra tracer study. Submitted to Geochim. Cosmochim. Acta.

- GUILLAUMONT R., FANGHÄNEL T., FUGER J., GRENTHE I., NECK V., PALMER D.A., RAND M.A. (2003)
Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier, Amsterdam, 763pp.
- HUMMEL W. (2009)
Ionic strength corrections and estimation of SIT ion interaction coefficients. PSI Technical Report, TM-44-09-01, 15 p.
- HUMMEL W., ANDEREGG G., PUIGDOMÈNECH I., RAO L., TOCHIYAMA O. (2005)
Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands. Elsevier, Amsterdam, 1088p.
- KULIK D.A., VINOGRAD V.L., PAULSEN N., WINKLER B. (2009)
(Ca,Sr)CO₃ aqueous- solid solution systems: From atomistic simulations to thermodynamic modeling. Phys. Chem. Earth, submitted.
- OLIN Å., NOLÄNG G., OSADCHII E., ÖHMAN L.-O., ROSÉN E. (2005)
Chemical Thermodynamics of Selenium. Elsevier, Amsterdam, 851p.
- PLUMMER L.N., BUSENBERG E. (1987)
Thermodynamics of aragonite-strontianite solid solutions: Results from stoichiometric solubility at 25 and 76 °C. Geochim. Cosmochim. Acta 51, 1393-1411.
- POWELL R. (1987)
Darken's quadratic formalism and the thermodynamics of minerals. Am. Mineral. 72, 1-11.
- RAND M., FUGER J., GRENTHE I., NECK V., RAI D. (2009)
Chemical Thermodynamics of Thorium. OECD NEA, Issy-les-Moulineaux, France, 900 p.
- TARDY Y., FRITZ B. (1981)
An ideal solid solution model for calculating solubility of clay minerals. Clay Minerals 16, 361-373.
- TESORIERO A.J., PANKOW J.F. (1996)
Solid solution partitioning of Sr²⁺, Ba²⁺ and Cd²⁺ to calcite. Geochim. Cosmochim. Acta 60, 1053-1063.
- VINOGRAD V.L., SLUITER M.H.F., WINKLER B. (2009)
Subsolidus phase relations in the CaCO₃-MgCO₃ system predicted from the excess enthalpies of supercell structures with single and double defects. Phys. Rev. B 79, 10421-1 - 10421-9.

3 TRANSPORT MECHANISMS

S. Churakov, T. Gimmi, M. Hayek, F. Hingerl, A. Jakob, G. Kosakowski, W. Pfingsten

3.1 Overview

Transport modelling at the LES is based on an interdisciplinary approach which merges experimental knowledge on the field and laboratory scales, state-of-the-art geochemical modelling and mechanistic understanding of transport phenomena. The modelling helps us to understand diffusion processes and to derive transport parameters for clay rich rocks on the field and laboratory scales (section 3.2). We apply advanced geochemical models coupled to reactive transport codes to predict the geochemical evolution in the near field of HAA and SMA repositories as an input to performance assessment studies (section 3.3). To understand the nature and mechanisms of radionuclide migration and retention in clay rich rocks, we setup advanced transport models, which take into account information on microscopic mineral and porosity distributions as well as molecular diffusion mechanisms (section 3.4). Such simulations help us to test the validity of, and assumptions in, the large scale models used in performance assessment. By supervising PhD students, holding courses and organizing conferences and workshop (section 3.5) we are maintaining our connections with universities and furthering knowledge transfer.

3.2 Data acquisition from experiments on the field and laboratory scales

3.2.1 Field experiments in the Mont Terri Rock Laboratory

In order to perform sensitivity analyses for the diffusion-retention (DR) experiment in the Mont Terri Rock Laboratory, we have developed a simplified semi-analytical model describing the diffusive transport of aqueous species. This model allows us to calculate the sensitivity of the simulations, i.e. the change of simulated concentrations per unit change of the parameter with respect to three lumped parameters. These parameters are the apparent rock diffusion rate (apparent rock diffusion coefficient divided by b^2 , where b is the radius of the filter-rock interface), the weighted ratio of the rock to filter effective diffusion coefficients (the weighting coefficient is equal to $\log[b/a]$, where a is the radius of the borehole-filter interface), and the weighted ratio of the rock to borehole capacities for a given solute

(weighting coefficient is equal to $2*b^2/a^2$). Capacities are defined as the total concentration of a compound per porewater concentration, and thus depend on sorption.

Typical calculations for HTO and Cs tracers are shown in Fig. 3.1. The calculations indicate that for a Cs tracer the early borehole measurements (Fig. 3.1, left) are sensitive to all three lumped parameters, whereas at the later stages of the experiment the dependence on the filter diffusion coefficient is weak. The similar shape of the curves for the Cs borehole concentrations indicates strong correlations between the three lumped parameters. The HTO tracer is insensitive to the effect of the filter, and becomes sensitive to the rock diffusion and sorption parameters only in the later stages of the experiment.

The situation is different for the porewater concentrations in the rock (Fig. 3.1, right). There, the sensitivity to the apparent rock diffusion rate changes sign with increasing radial distance for both Cs and HTO, in contrast to the sensitivities to the other two parameters. Note that the sensitivity to the filter is very small at such late times anyway. The different shapes of the curves indicate a weak correlation between the three lumped parameters. Accordingly, profile data are better suited than borehole data to discriminate between the effects of the different lumped parameters or also between the individual sorption and diffusion parameters.

In April 2009, a new tracer injection took place which included ^{18}O (in both upper and lower intervals of the DR experiments) and ^{75}Se (in the upper interval of the DR experiment only). The latter was added in form of SeO_4^{2-} , which seems to be stable under the conditions of the experiment. All newly acquired tracer data (HTO, HDO, ^{18}O , I, Br, ^{75}Se , ^{22}Na , ^{133}Ba , ^{60}Co , stable Cs and ^{137}Cs , stable Eu and ^{152}Eu ; ^{85}Sr is below detection limit) were compiled, and distributed to the different modelling groups. The overcoring of the injection intervals is planned for the end of 2009. To assist the project planning and the experiment setup, the tracer concentration profiles at the time of the overcoring were simulated (Figs. 3.2 and 3.3).

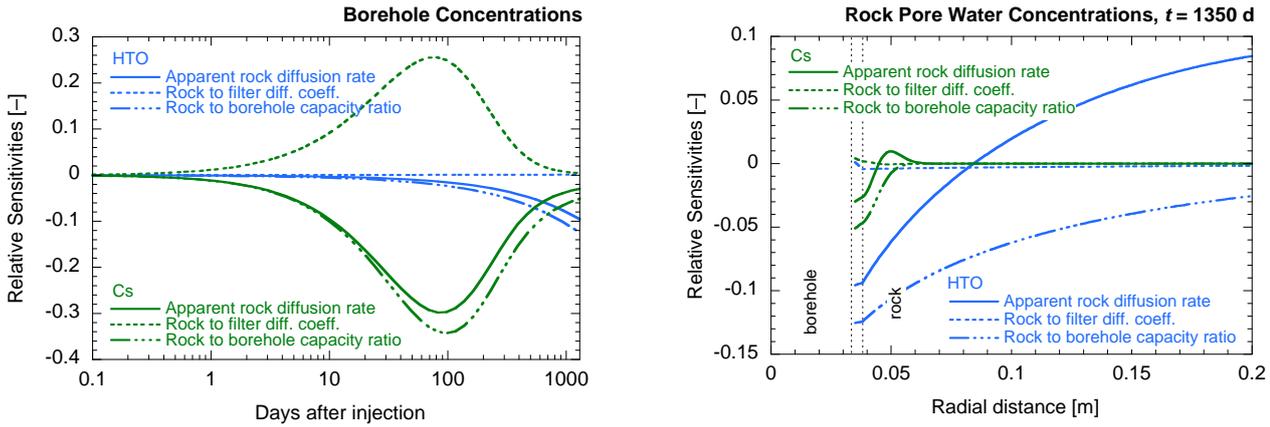


Fig. 3.1: Relative sensitivities of HTO and Cs concentrations in the borehole (left) and in the porewater (right) to three lumped parameters (apparent diffusion ratio in the rock, ratio of rock to filter effective diffusion coefficient, and ratio of rock to borehole capacity).

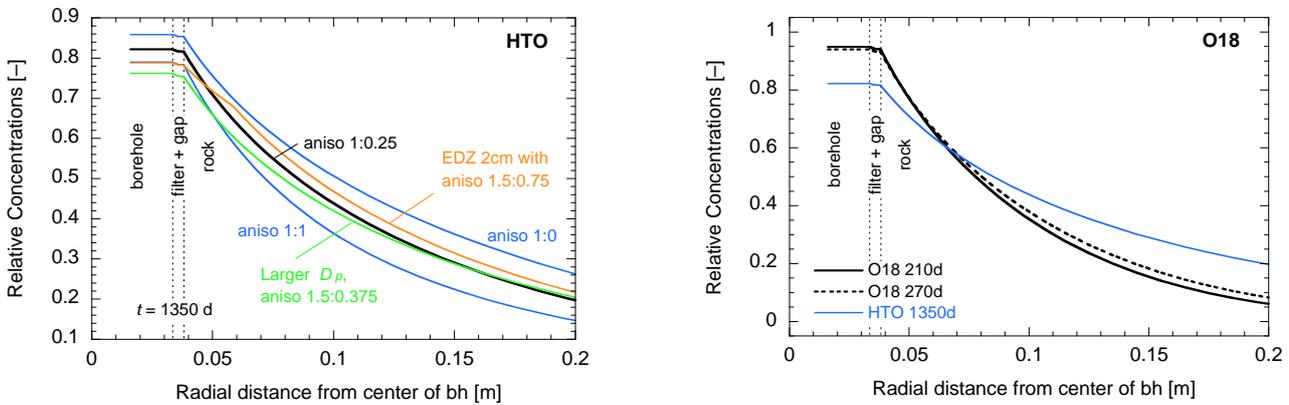


Fig. 3.2: Left: Predicted porewater concentration profiles for HTO tracer after 1350 d (i.e., the end of 2009). The black lines represent the reference case (anisotropy ratio of 1:0.25 and other parameters estimated from earlier experiments). The coloured lines represent the results for alternative model parameters (different anisotropy ratio, larger pore diffusion coefficient, presence of a disturbed zone). Right: Predicted porewater concentration profiles for ^{18}O after 210 d and 270 d (i.e., for the originally foreseen time span for the over-coring, at 1.11.2009 and 31.12.2009, respectively), using parameters from previous experiments. The predicted profile for HTO tracer is shown for comparison.

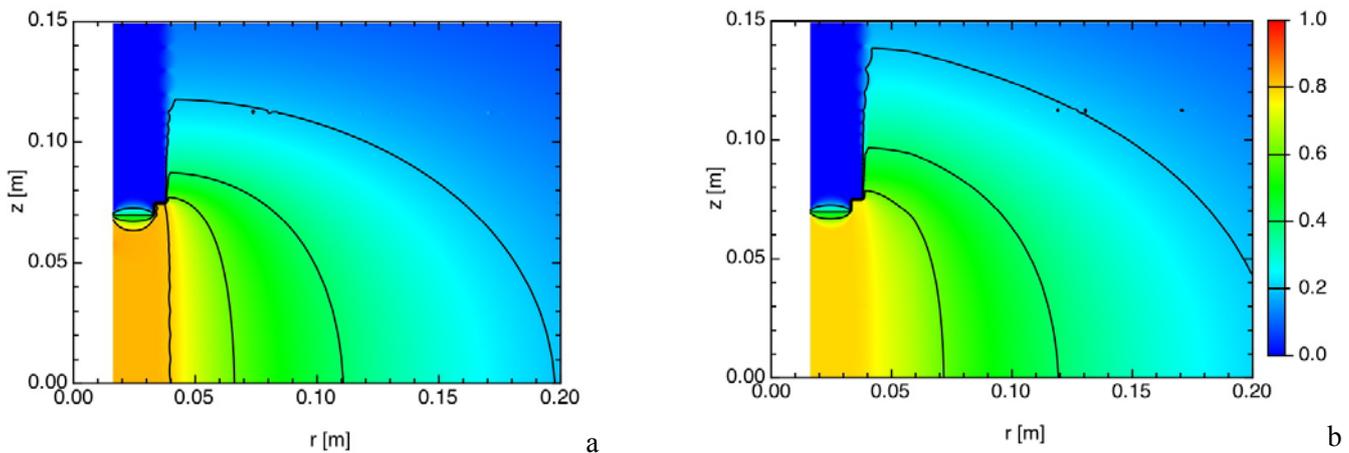


Fig. 3.3: Contour plots of the simulated porewater concentrations for HTO tracer (relative units) after 1350 d (i.e. at the end of 2009). (a) Reference case (anisotropy ratio of 1:0.25, parameters estimated from earlier experiments), (b) case with a 2-cm borehole disturbed zone (EDZ) with larger diffusion coefficients.

3.2.2 Reactive transport modelling of laboratory Cs diffusion experiments

In 2008 a multi-species sorption model was ported into the MCOTAC transport code and was successfully used to model the results of a Cs diffusion experiment in Opalinus Clay (break-through curve, out-diffusion curves, and mass-balance). In order to further check the model, it is being applied to a series of Cs diffusion experiments in Opalinus Clay samples which were carried out under different experimental conditions e.g. variable porewater chemistry and different confining pressures.

3.3 Predictive modelling of in-situ repository evolution

3.3.1 Reactive transport modelling of geochemical evolution of SMA repository near field

In the present concepts for a SMA repository, large quantities of cementitious materials are present in the argillaceous host rocks. Upon re-saturation of the repository, mineral alteration processes at the cement/host-rock and cement/backfill interfaces are expected. This may influence the transport and retention properties of the barrier system. In particular, the repository design must ensure the release of gas produced as the result of anaerobic iron corrosion and the degradation of organics.

In order to assess the geochemical evolution of the barrier system in the repository near field we have incorporated state-of-the-art geochemical models for cementitious and argillaceous rocks into the reactive transport code OPENGEO-SYS-GEMS. This model was developed in the Geochemical Modelling Group. It allows us to account for major geochemical processes in the system such as dissolution/precipitation of mineral phases, formation of solid solutions, cation exchange and surface complexation processes on mineral phases. To verify and test the model we simulated the results from laboratory experiments on cement degradation in contact with bentonite provided by Prof. K. Nakarai (Gunma University, Japan). These simulations confirm that our model accurately reproduces the experimentally observed geochemical evolution of the interfaces between concrete and clays. We are now using this model to predict the geochemical evolution of a cementitious SMA repository near field in contact with different host rocks as an input to performance assessment studies (Fig. 3.4).

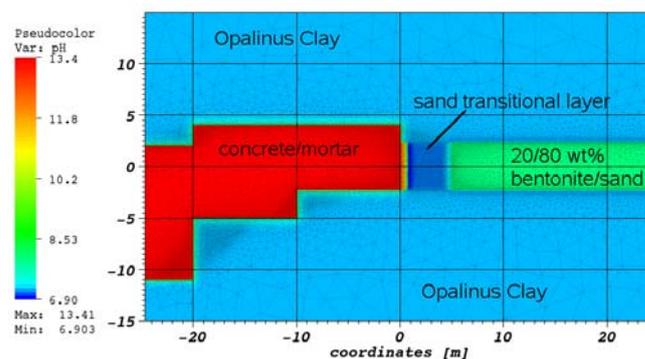


Fig. 3.4: Migration of a high pH-plume in the near field of a fully saturated LLW-repository after 25 years. Preliminary calculations for a diffusive transport scenario. Colour scheme indicates pH distribution.

3.3.2 Reactive transport modelling of Ni diffusion through bentonite

In 2008 we ported the 2SPNE SC/CE mechanistic sorption model into the MCOTAC transport code and applied it to investigate the influence of Fe, Mn and Zn sorption-competition on Ni diffusion through bentonite. The 2SPNE SC/CE model applied was taken one to one from that used to describe the experimental results on dispersed systems (solid to liquid (SL) ratio ~ 1 g/L). This model did not include charge neutrality constraints, which are essentially negligible for such dispersed systems. We recognized that when dealing with transport calculations at high solid to liquid ratios (100's of g/L), the lack of a charge balance constraint results in a significant charge accumulation and influences the speciation of the migrating species. We re-formulated the 2SPNE SC/CE model introducing the charge balanced equations using Na^+ and Cl^- . The surface complexation constants given in BRADBURY & BAEYENS (2005) were modified by the aqueous activity coefficients of either Na^+ or Cl^- as appropriate. With such a re-formulation of the surface complexation reactions, the reactive transport calculations became intrinsically charge balanced even for systems with a high solid to liquid ratio.

We applied the improved sorption model to further investigate the influence of different Fe(II) background concentrations in the bentonite porewater on the diffusive transport of Ni through bentonite.

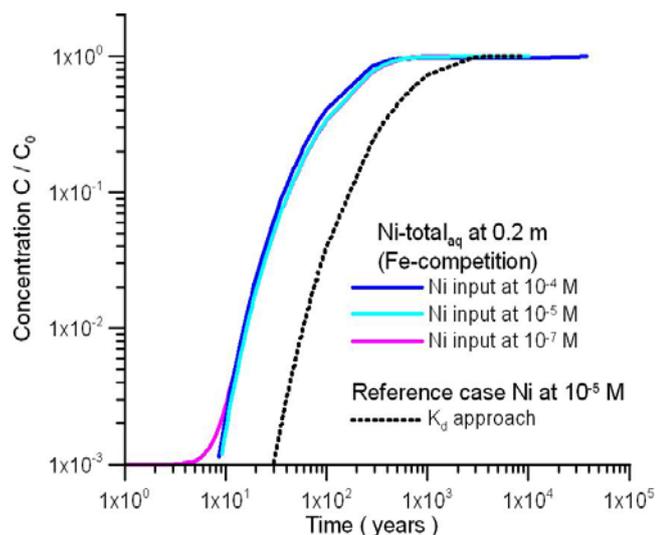


Fig. 3.5: Ni breakthrough at $x=0.2$ m from the source in the bentonite calculated for different input Ni concentration levels ($C_0=10^{-4}$ M, 10^{-5} M, and 10^{-7} M) using the mechanistic sorption model and the numerical K_d approach. The Fe(II) concentration in porewater is given by the siderite solubility.

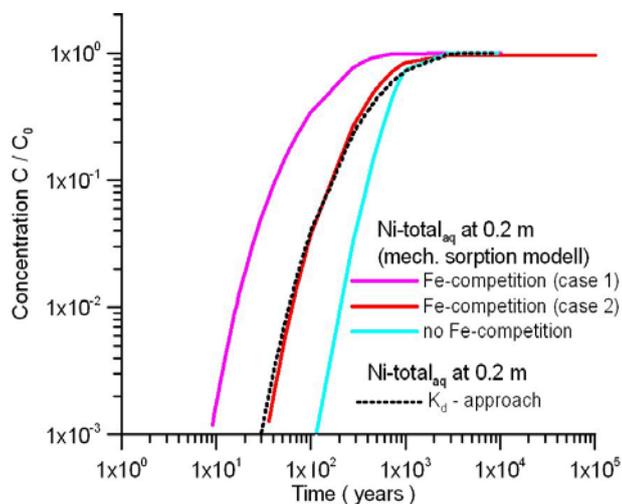


Fig. 3.6: Ni breakthrough curves at $x=0.2$ m from the source in the bentonite calculated for different Fe solubility limits and different sorption model setups (sorption competition vs. no-competition) compared to the breakthroughs predicted by a K_d approach. Ni boundary concentration (C_0) was 10^{-5} M, initial Ni background was assumed to be 10^{-10} M. Case 1: Fe(II) concentration in the porewater was limited by the solubility of siderite. Case 2: the equilibrium Fe(II) concentration in the porewater was set to be 10 times lower than the solubility of siderite.

The modelling of the Ni sorption was performed using two different procedures (a) an approach based on a numerical constant K_d , taking into account the initial background concentration of Ni in the bentonite porewater (PFINGSTEN et. al., in prep.), and (b) a mechanistic sorption model approach that includes surface protonation, surface complexation and cation exchange reactions. The simulations were conducted for one-dimensional spatial geometry using the reactive transport code MCOTAC (PFINGSTEN, 2002). Charge balance was explicitly formulated for the surface complexation reactions. Selectivity coefficients and surface complexation data were taken from BRADBURY & BAEYENS (1997). The surface complexation constants for Fe were derived from the Linear Free Energy Relationship (BRADBURY & BAEYENS, 2005).

For the realisations using the mechanistic sorption model approach, Ni breakthrough curves in the bentonite were calculated for different Ni concentration levels both including and excluding Ni-Fe sorption-competition effects on the exchange and surface sites for different Fe background concentrations in the bentonite porewater. In a simulation scenario where the background Fe concentration in the bentonite porewater was buffered by the solubility of siderite, the model with Ni-Fe sorption competition predicted identical Ni-breakthrough curves for different input concentrations of Ni (C_0) in the range from 10^{-4} to 10^{-7} M (Fig. 3.5, concentrations normalised by C_0). The numerical constant K_d approach led to an order of magnitude later breakthrough for an input concentration of 10^{-5} M (Fig. 3.5, Fe(II) concentration buffered by the siderite solubility limit as generally assumed for the bentonite porewater). Since the Fe concentration in the near field of a high-level nuclear waste repository may change with time due to canister corrosion processes and mineral precipitation/dissolution reactions, Ni, and more generally, bivalent transition metal ion diffusion should be modelled using mechanistic sorption models which takes into account properly the ion sorption-competition processes, Fig. 3.6.

3.3.3 Reactive transport modelling of Ra retardation in bentonite

During the past year we have used the OPENGEO-SYS-GEMS coupled code to investigate the role of Ra-Sr-Ba solid solutions in the retardation of Ra in Opalinus Clay. As a next step in the model development process we investigated the competitive effect of cation exchange and Ra incorporation in Ba/Sr-carbonate and -sulphate solid solutions on the

retardation of aqueous Ra in the near field of a SMA repository. In our idealized geochemical model (SHAO et al., 2009), numerical simulations showed that Ba, Sr, and Ra, which form sulphate solid solutions, also partition to the cation exchange sites of montmorillonite, which is the major mineral constituent of bentonite. At high montmorillonite contents, most of the Ra partitions to montmorillonite, while incorporation of Ra in sulphate solid solutions is more important at low montmorillonite contents. It was found that a decrease in Ra fixation due to low montmorillonite contents - which may occur in sand-bentonite mixtures - is compensated by the formation of solid solutions, and so the migration distance of aqueous Ra is similar at different montmorillonite/water ratios (Fig. 3.7).

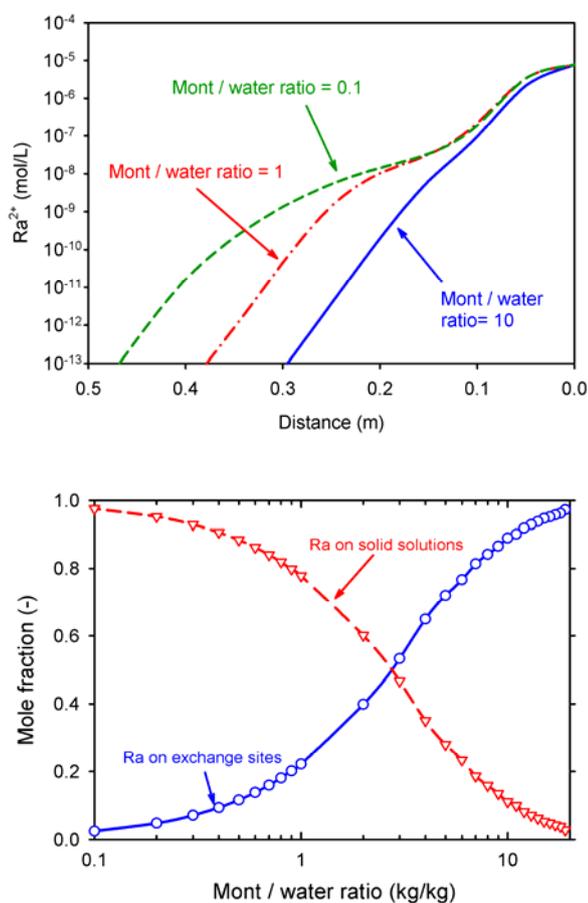


Fig. 3.7: Top: Aqueous phase Ra profile after 1000 years for different Clay water ratios. Bottom: Partitioning of Ra between sulphate solid solutions and Clay cation exchange sorption sites in montmorillonite as function of the montmorillonite-water ratio. Montmorillonite-water mass ratios 1.0 and 10 kg/kg correspond to sand-bentonite mixtures and highly compacted bentonite, respectively.

3.3.4 Diffusion report

We have prepared a report on diffusion in argillaceous rocks and compacted clays. This report is currently under review.

3.4 Understanding the radionuclide transport mechanisms

3.4.1 Effects of heterogeneous mineral distributions on solute transport

Transport properties in argillaceous rocks and compacted clays have been, and still are, studied mainly in small-scale laboratory experiments. In some cases results from larger-scale field tracer tests are available, but to a lesser extent. In all the laboratory experiments, the mass flow through, into, or out of a sample is measured as a function of time. The analysis of diffusion experiments is commonly based on (1) classical Fickian laws and (2) on the assumption that the transport properties of the media are homogeneous (not space dependent) and isotropic (not dependent on the direction).

Natural porous media are – as a rule – far from being homogeneous and isotropic and are, instead, a mixture of different minerals and interstitial porosity forming a complex three dimensional entity. In addition, sedimentary rocks have a layered structure, thereby offering preferential pathways for solute diffusion. Each interconnected mineral phase represents, in principle, an individual transport pathway. Also, the solute mobility at grain interfaces is probably much higher than in the interior of minerals. Carefully performed diffusion experiments in argillaceous rocks have confirmed that solutes do not migrate uniformly through such materials and have revealed the limits of simple homogeneous, isotropic transport models. In some diffusion experiments the temporal evolution of the diffusive tracer flux or spatial tracer profile shows a bi-modal behaviour which cannot be explained on the basis of a single porosity model (Figs. 3.8 and 3.9).

To assess the influence of spatial heterogeneities in clay samples on solute diffusion we perform transport simulations explicitly taking into account the mineral distribution in the sample. A 3D clay fraction distribution in the Opalinus Clay was reconstructed based on a set of 2D tomograms, obtained at the PSI-TOMCAT beam line, Fig. 3.10.

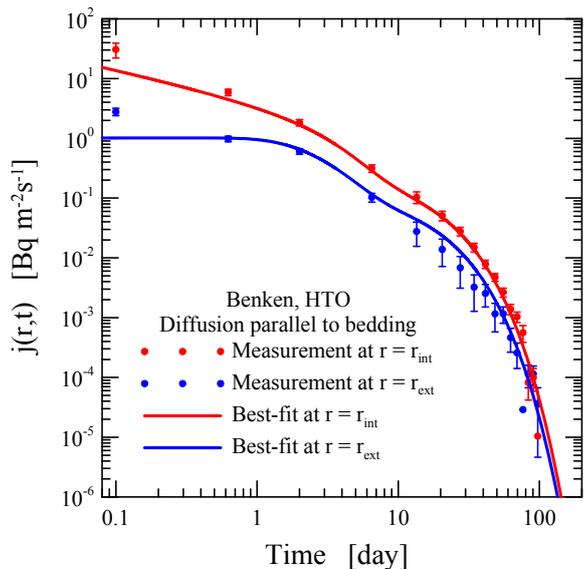


Fig. 3.8: Measured diffusive flux data versus time for tritiated water (HTO) using a hollow cylinder of Opalinus Clay from Benken (Switzerland). Transport of the tracer takes place parallel to the fabric. A second preferential transport pathway accessible for HTO is evident from the bi-modal tracer breakthrough, which cannot be explained by a single porosity model. The best fit was obtained using a dual porosity model. (Figure taken from VAN LOON & JAKOB, 2005).

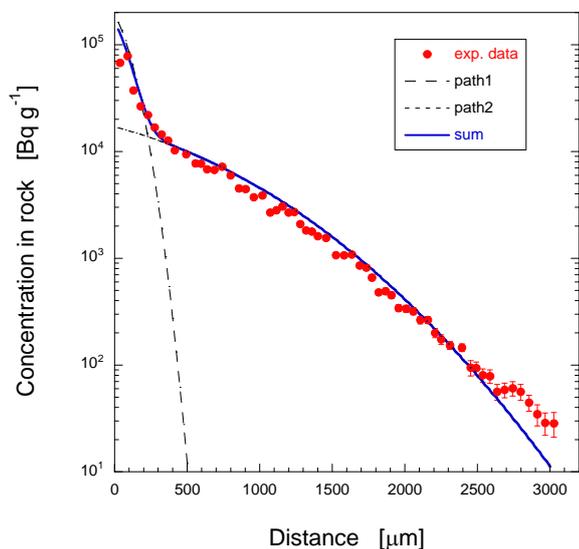


Fig. 3.9: Measured ^{60}Co distribution in Opalinus Clay from the Mont Terri test site after 50 days of indiffusion. Such a distribution cannot be explained by a single porous medium transport model. The best fit shown in the figure was obtained using a dual porosity concept. (Figure taken from VAN LOON & MÜLLER, in prep.).

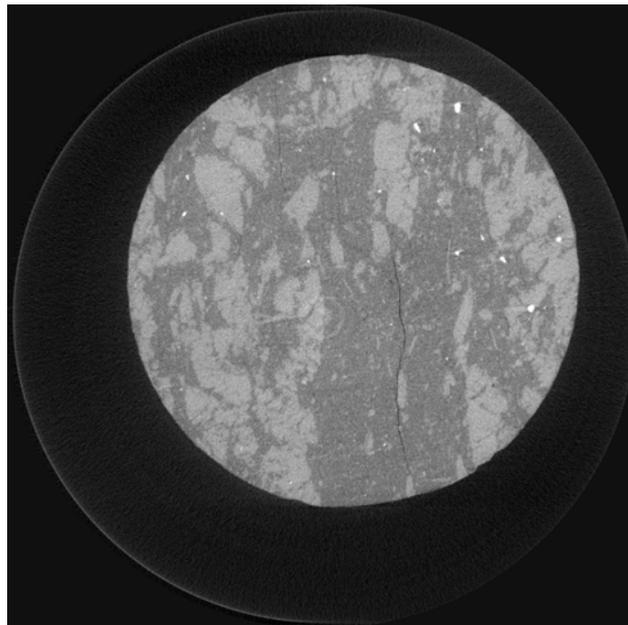


Fig. 3.10a: Horizontal slice through a cylindrical sample of Opalinus Clay from Mont Terri (sample diameter: 3 mm). The measurements were performed at the PSI TOMCAT beam line. Two major mineral domains, and some small-scale impurities, are clearly resolved. Light-grey is clay matrix. Dark-grey is calcite (CaCO_3). Bright spots are high density inclusions of Fe-oxides (to be confirmed).

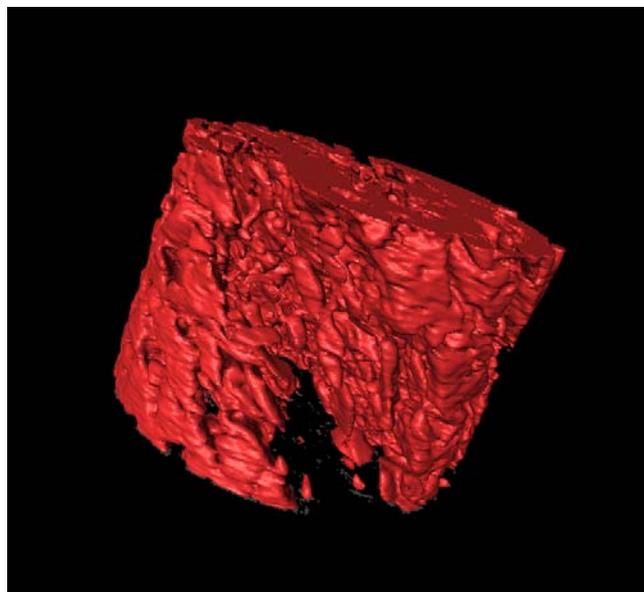


Fig. 3.10b: Reconstructed 3D clay domain of the Opalinus Clay sample based on individual 2D-slices. The extracted clay mineral distributions were used in the subsequent transport modelling.

A corresponding tracer distribution profile assuming diffusion only through the clay mineral fraction was calculated using the COMSOL-Multiphysics code, Fig. 3.11. The micro-XRF beam line at the Swiss Light Source offers a unique opportunity to measure non-destructively time resolved 3D tracer distributions in clay samples which can be directly compared with the results of the simulations. Such investigations are being planned.

In the near future new, and refined, diffusion tests using different argillaceous rock samples and various weakly, as well as strongly, interacting radionuclides will be carried out. In subsequent inverse modelling studies, where a time series of measured tracer distributions will be analysed, we expect to be able to increase our understanding of solute/rock interaction processes and deduce high-precision values for the transport parameters. This will be done by fine-tuning the transport parameters of the individual mineral phases of the rock. Supplementary data on sorption and diffusion in each of the most relevant minerals phases will help to reduce the numbers of adjustable parameters. We will subsequently compare our results with those obtained with the models based on homogeneous, isotropic transport media to resolve open issues regarding the up-scaling of transport parameters.

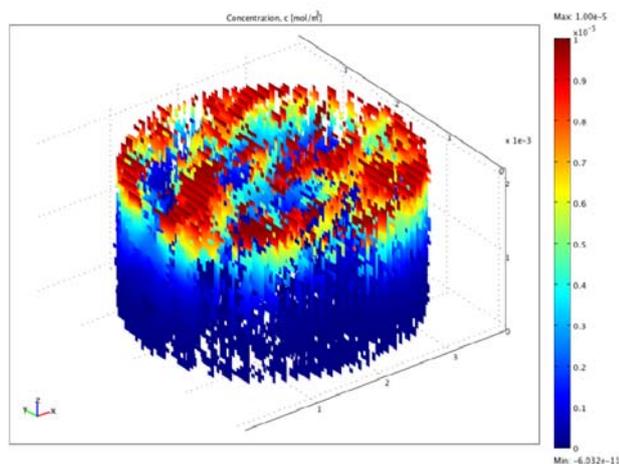


Fig. 3.11: Computed solute concentration distribution profile through the clay fraction of an Opalinus Clay sample from Mont Terri (sample diameter is 3 mm, see Fig. 3.10). The red to blue colour map indicates high and low solute concentrations, respectively. Non-uniform tracer migration through the sample is a consequence of the microscopic heterogeneities in the rock. Interstitial “void space” corresponds to the mineral phases impermeable for the solute transport.

3.4.2 Influence of clay particle arrangement on molecular diffusion coefficients in clays

Molecular dynamics (MD) technique have been widely used to predict and understand the diffusive transport of ions and molecules in the interlayers of clay minerals.

MD simulations provide the dependence of local diffusion coefficients of ions and molecules on water content, degree of compaction and chemical composition of clay particles. The major limitation of such simulations is the system size, which effectively limits the studied geometry to a single interlayer. Even though successful attempts have been undertaken to model the structure of water near the edges of clay minerals (CHURAKOV, 2007) and cation exchange between interlayer and external pore solutions (ROTENBERG et al., 2007), it is currently not feasible to model realistic ensembles of clay particles using a full atomistic description of the system. On the other hand, the macroscopic continuum models are not able to capture the essence of the transport along the mineral-fluid interfaces. Therefore, we are developing a model which links the nano-scale diffusion coefficients, as they were obtained from molecular modelling, and sample-scale diffusion coefficients obtained from the solute transport based on an explicit model for pore structure. A set of simulations have been performed for an assumed specific clay structure, from which laboratory-scale diffusion coefficients and anisotropy ratios of water tracers were derived.

3.4.3 Molecular modelling of hydronium transport in the interlayer of montmorillonite

The crystal chemistry and surface reactivity of phyllosilicate minerals is a key issue for modelling ion mobility and retardation in clay rich rocks. We used the Car-Parrinello molecular dynamics simulation technique to predict the structure and dynamics of hydronium solvation in mono-, bi- and tri-hydrated Na-montmorillonite (CHURAKOV & KOSAKOWSKI, 2010).

In mono-hydrated montmorillonite, hydronium ions are located within the hexagonal rings of the basal clay plane. Oxygen sites of hydronium ions point towards the clay surface and hydrogen atoms towards water layer (Fig. 3.12). In bi- and tri-hydrated montmorillonite, the hydronium ions form water solvated outer-sphere complexes.

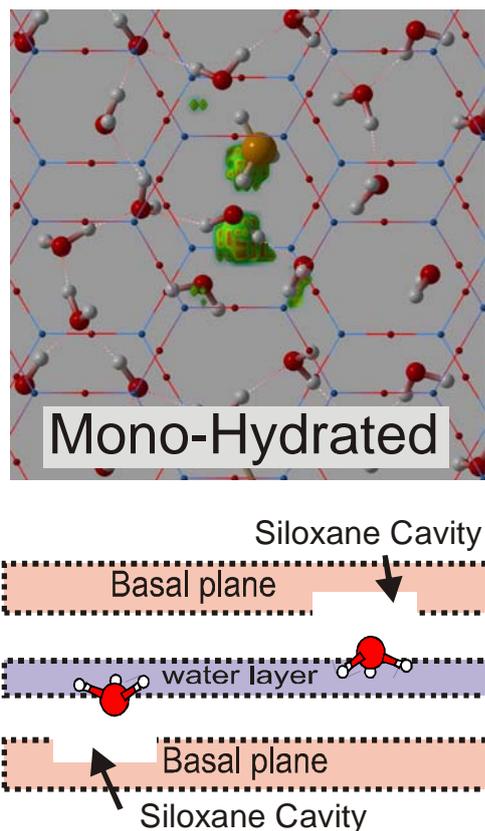


Fig. 3.12: Top: Probability density distribution (green to grey shaded area) of H_3O^+ ion in the interlayer of monohydrated montmorillonite seen in the [001] direction. An instantaneous configuration of the H_3O^+ ion is shown as a large brown sphere. Water molecules are shown as red spheres (oxygen sites) attached to two small gray spheres (hydrogen sites). Upper and lower tetrahedral layers of clay sheet are shown as tiny red (oxygen) and blue (silica) spheres attached in a typical pseudo-hexagonal framework. Bottom: a schematic view of a preferential orientation of H_3O^+ in a monohydrated montmorillonite.

Similar to the solvation mechanism in bulk water, hydronium ions donate three hydrogen bonds to interlayer water molecules. In all of the studied hydration states, hydronium ions do not form hydrogen bonds with the basal oxygen sites. Again similar to bulk water, the free energy barrier for a classical proton transfer between interlayer water molecules is comparable with the thermal kinetic energy of molecular motion and is therefore not a limiting factor for proton diffusion. The diffusivity of hydrogen in the interlayer is controlled by the structural rearrangements of the solvating water molecules.

3.5 Know-how transfer, connections with universities, benchmarking of coupled codes and networking

3.5.1 Fluid-rock interaction modelling

In November 2008 a joint PhD project on simulations of geochemical processes in Enhanced Geothermal Systems (EGS) was started between LES and the Institut für Isotopengeologie und Mineralische Rohstoffe of the ETH Zürich, as a contribution to understanding and developing an alternative sustainable energy source free of CO_2 -emission. The project is fully funded by the Competence Centre for Environment and Sustainability of the ETH-Department.

Predictions of fluid-rock interaction in EGS (Fig. 3.13) still face several major challenges. Recent benchmarking studies (ANDRÉ et al., 2006) demonstrated that slight differences in thermodynamic equilibrium constants, activity coefficients and kinetic models, can result in significant differences in predicted mineral precipitation behavior. Therefore, uncertainties in these factors directly affect the predictions for reservoir porosity evolution and scaling behavior in technical installations. In order to perform reasonably realistic modelling of EGS, thermodynamic databases and activity models must be tailored to geothermal conditions.

Owing to the high salinity (ionic strength: ≤ 2 molal) and elevated temperature and pressure ($\sim 200^\circ C$, ~ 450 bar) of an EGS, the standard Debye-Hückel activity models are not applicable for the calculation of aqueous speciation.

We therefore implemented the Pitzer (HARVIE et al., 1984) and the EUNQUAC (THOMSEN & RASMUSSEN, 1999) aqueous activity models, either of which is applicable to mixed electrolyte systems at high ionic strengths. In order to apply the implemented electrolyte solution models, we are currently compiling a thermodynamic database and extending it with the relevant Pitzer and EUNQUAC parameters for calculating mineral solubilities at a wide range of temperatures, pressures and ionic strengths. We have also implemented the Soave-Redlich-Kwong and Peng-Robinson equations of state for non-ideal gas mixtures, which will enable the simultaneous calculation of gas solubilities and boiling processes.

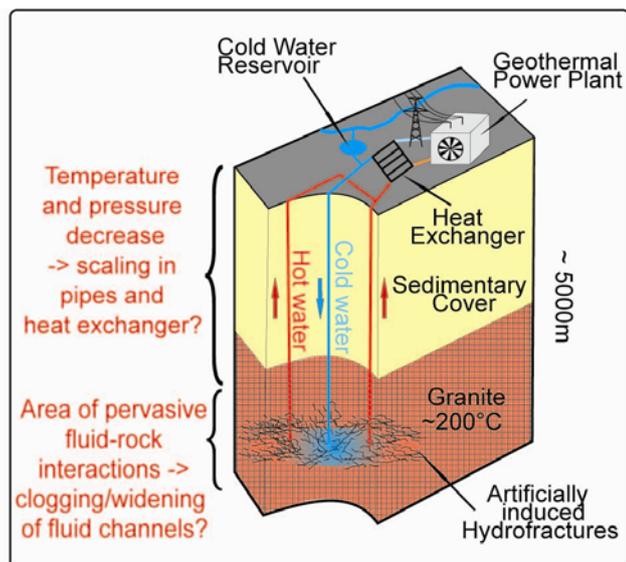


Fig. 3.13: A simplified sketch of a typical Hot-Dry-Rock-EGS. Cold water from a reservoir is pumped into the crystalline basement which is used as a heat source. Heated water is transported upwards to the heat exchanger used for house-heating or for electricity generation in a geothermal power plant. To optimize the power yield efficiency, and prevent scaling of mineral phases in the technical installations, the operating conditions are tuned based on the results of the thermodynamic modelling.

The activity models used for the speciation calculations are implemented in the GEMS package, which is coupled to the OPENGEOYSYS and MCOTAC codes used for reactive transport modelling. Therefore, the advanced geochemical models developed in the GEOTHERM project will equip us to contribute to future performance assessment studies in which geochemical modelling at elevated temperatures and/or elevated porewater salinities is required.

3.5.2 Benchmarking of coupled codes

The benchmarking of the modelling codes is an essential activity in the group, and is aimed at ensuring the validity of the simulation results. In co-operation with ENSI, earlier simulations of radionuclide transport performed with Frac3D were benchmarked against COMSOLE and Tough2-EOS9nT (ENSI-AN-6877). Several codes are benchmarked in the Mont Terri field diffusion experiments.

Within a joint PhD project with the Department of Environmental Informatics at the Helmholtz Centre for Environmental Research – UFZ Halle-Leipzig, Germany (Prof. O. Kolditz) we ensure the necessary

development, support and benchmarking of the reactive transport code OPENGEOYSYS (<http://www.ufz.de/index.php?en=18345>), being developed at the UFZ. The OPENGEOYSYS is a new name for the next generation of the previously used ROCKFLOW/GEOSYS transport code.

3.5.3 Forthcoming projects

We have received full financial support from the NES department for a 2-year postdoc project “Two dimensional investigations of reactive transport processes at heterogeneous interfaces”. The position was filled on November 1, 2009 by Dr. M. Hayek who will develop a model for the correct numerical and conceptual treatment of porosity changes due to mineral dissociation/precipitation reactions at cement-clay interfaces in reactive transport codes.

A 2 year postdoc project entitled “A multi-scale modelling approach to diffusion in clays” has received the full financial support by PSI-research committee. The search for an appropriate candidate to fill the position has started.

In co-operation with Prof. Hutter, from the Physical Chemistry Institute, University of Zurich, we have submitted SNF-PhD proposal on joint experimental-theoretical investigations of ion diffusion mechanisms in compacted clays.

Within the European Cement Research Network, NANOCEM, we are co-proposers on several submitted PhD and postdoc research proposals focused on water transport in cement (“Water dynamics in cement”, lead: P. McDonald Univ. Surrey, UK) and the thermodynamics of amorphous Calcium-Aluminum-Silicate-Hydrate phases (“Stable phase composition in cementitious systems: C-A-S-H”, lead: Dr. B. Lothenbach, Empa).

3.6 References

- ANDRÉ L., SPYCHER N., XU T., PRUESS K., VUATAZ F.D. (2006)
Comparing FRACHEM and TOUGHREACT for reactive transport modelling of brine-rock interaction in Enhanced Geothermal Systems (EGS). Proceedings 31. Workshop on Geothermal Reservoir Engineering, Stanford University, 2006. SGP-TR-179
- BRADBURY M.H., BAEYENS B. (1997)
A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part II: Modelling. J. Contam. Hydrol. 27, 223-248

- BRADBURY M.H., BAEYENS B. (2005)
Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides. *Geochim Cosmochim. Acta* 69(4), 875-892
- CHURAKOV S.V. (2007)
Structure and dynamics of water films confined between edges of pyrophyllite. A first principle study. *Geochim. Cosmochim. Acta* 71(5), 1130-1144
- CHURAKOV S.V., KOSAKOWSKI G. (2010)
An ab initio molecular dynamics study of hydronium complexation in Na-Montmorillonite. *Philosophical Magazine* (in press)
- HARVIE E.H., MOLLER N., WEARE J.H. (1984)
The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to high ionic strengths at 25°C. *Geochim. Cosmochim. Acta* 48, 723-751
- PFINGSTEN W. (2002)
Experimental and modelling indications for self-sealing of a cementitious L&ILW repository by calcite precipitation. *Nucl. Technol.* 140, 63-82
- PFINGSTEN W., BRADBURY M.H., BAEYENS B.
Modelling in-diffusion in bentonite using different sorption models. (in prep.)
- ROTENBERG B., MARRY V., VUILLEUMIER R., MALIKOVA N., SIMON CH., TURQ P. (2007).
Water and ions in clays: Unraveling the interlayer/micropore exchange using molecular dynamics. *Geochim. Cosmochim. Acta* 71, 5089-5101
- SENTÍS M.L., ALTORFER F., HERFORT M. (2009)
Benchmarkberechnungen für die Simulation der Ausbreitung ausgewählter Nuklide innerhalb von Bentonite und Opalinustonschichten mit den Rechenprogrammen Tough2[®] EOS9nT und COMSOL. ENSI-AN-6877
- SHAO H., KULIK D.A., BERNER U., KOSAKOWSKI G., KOLDITZ O. (2009)
Modeling the competition between solid solution formation and cation exchange on the retardation of aqueous radium in an idealized bentonite column. *Geochem. J.* 43, 37-42
- THOMSEN K., RASMUSSEN P. (1999)
Modelling of Vapor-Liquid-Solid Equilibria in Gas – Aqueous Electrolyte Systems. *Chem. Eng. Sci.* 54, 1787-1802
- VAN LOON L.R., JAKOB A. (2005)
Evidence for a second transport porosity for the diffusion of tritiated water (HTO) in a sedimentary rock (Opalinus Clay – OPA): Application for through- and out-diffusion techniques. *Transport in Porous Media* 61, 193 – 214
- VAN LOON L.R., MÜLLER W.
Diffusion and retention behaviour of ⁶⁰Co(II) in Opalinus Clay: first results from an in-diffusion experiment combined with a μ-abrasive technique for profile analysis (in prep.)

4 CLAY SORPTION MECHANISMS

B. Baeyens, M. Bradbury, R. Dähn, M. Marques-Fernandes, V. Kalbermatter, A. Schaible

4.1 Overview

Within the framework of the Sectoral Plan (Sachplan Geologische Tiefenlagerung), the work on the development of generic sorption databases (SDBs) for argillaceous, crystalline and calcareous rocks for groundwater compositions covering the ranges measured in the corresponding systems in Switzerland has been documented as a Nagra NTB. The validity of the approach for deriving SDBs for argillaceous rocks based on the proposed procedures described in this report was successfully tested against the existing Opalinus Clay SDB. The approach was further supported by a blind modelling exercise of sorption isotherms for Co(II), Eu(III), Th(IV) and U(VI) measured on Opalinus Clay in a realistic porewater composition. A report summarising the physico-chemical characteristics of MX-80 bentonite and sorption measurements for Cs(I), Sr(II)/Ca(II), Ni(II), Eu(III), Th(IV), U(VI), Cl(-I), I(-I) and Se(IV) has been prepared as a Nagra NTB.

A series of experiments with MX-80 bentonite were carried out to check the buffer capacity of the amphoteric surface hydroxyl groups and the previous predictions made for the initial pH of the porewater in the compacted material. Model calculations agreed well with the experimental data and confirmed the extremely high buffer capacity of MX-80.

The influence of temperature and kinetics on the sorption behaviour of Cs on illite at very low (FES sites) to low (type II sites) loadings was investigated. The results indicated that the Cs sorption on these two site types decreased by a factor of ~ 4 at 90 °C compared to measurements carried out at room temperature.

EXAFS investigations demonstrated that the amphoteric strong sorption sites of montmorillonite are selective for Ni(II), Th(IV) and U(VI), confirming the non-competitive sorption behaviour of these radionuclides as previously measured in batch sorption tests.

A PhD proposal entitled “The influence of Fe(II) on clay properties, the sorption of Fe(II) on clays and competitive sorption investigations: a combined macroscopic and microscopic study” has been prepared, and approved by the PSI Forschungskommission (FoKo).

4.2 Performance assessment

Within the framework of the Sectoral Planning numerous sorption databases (SDBs) for various potential host rocks for SMA, LMA and HAA repositories are required in the near future. The methodology for providing SDBs is continuously under development in LES (BRADBURY & BAEYENS, 2003, BRADBURY et al., 2009). The aim is to produce robust sorption values in a clear, transparent, and traceable manner. The ultimate goal is to set up a thermodynamic SDB (TD-SDB) based on a mechanistic understanding of the sorption processes, and use the associated sorption models and parameters to calculate distribution ratios (R_d values) under any given conditions (mineralogy, water chemistry). Although this endeavour is being pursued energetically (BRADBURY & BAEYENS, 2005, 2009a,b), the realisation of a TD-SDB is still some way off. However, a significant part of the measured data and knowledge gained in this activity is applied in many different ways in the SDB work for performance assessment, as will be amply illustrated in the following sections.

4.2.1 Generic sorption databases

Within the framework of the Sectoral Plan, generic sorption databases for the main host rock types in Switzerland (crystalline, argillaceous and calcareous) have been developed and published (BRADBURY et al., 2008). The groundwater compositions used in this study covered the ranges of experimental data measured for the corresponding rocks. These SDBs provided part of the information required to enable a transparent, defensible and robust selection of the regions in Switzerland suitable for siting radioactive waste repositories (NAGRA, 2008). An updated and improved version of this work has now been prepared as a Nagra NTB (BRADBURY et al., 2009).

4.2.2 Comparison of the current Opalinus Clay sorption database with one predicted from illite sorption data

In the development of the generic SDBs, the basic premise was that the clay mineral fraction (2:1 type clays) is predominantly responsible for the uptake of radionuclides (BRADBURY et al., 2009). In the case of

argillaceous rocks, where the clay mineral component contains a significant weight fraction of 2:1 type clay minerals (illite, smectite and illite-smectite mixed layers), the further assumption is made that the sorption values are principally determined by this clay fraction. Such an approach is conservative, since any contributions to the overall sorption from the other clay minerals present is ignored. The above assumption was tested in an exercise in which the R_d values for Opalinus Clay (OPA) were calculated (predominantly) from illite source data using the methodology described in BRADBURY et al. (2009), and compared with the values in the OPA-SDB generated for, and used in, the performance assessment carried out for the Entsorgungsnachweis (NAGRA, 2002). A comparison of the sorption values derived by the illite \Rightarrow OPA approach, and those given in the OPA SDB (BRADBURY & BAEYENS, 2003), indicated that in $\sim 90\%$ of the cases the R_d values were within a factor of 2 of one another. Instances where the compared values were outside this range were discussed on a case by case basis. The results of this comparative exercise (BRADBURY & BAEYENS, 2009c) illustrated clearly that the illite \Rightarrow OPA methodology, coupled with up-to-date knowledge, produced a SDB which was at the very least as good as, and in certain instances certainly better than, the SDB for OPA produced in the past by a different approach. This work provides a very strong indication that the same basic approach described here can be applied with confidence to other argillaceous rock systems where the necessary information is available (mineralogy, water chemistry), but where direct sorption data measurements may be missing.

4.2.3 Bottom-up approach (blind predictions)

The general strategy followed within LES in sorption modelling is that by understanding the mechanistic uptake processes on single clay minerals, and developing models to describe them, this knowledge can be used to understand and quantitatively predict the uptake of radionuclides in complex mineral-/groundwater systems, the so called "bottom-up" approach. However, in order to use the sorption model to predict radionuclide uptake in natural systems, the influence of complexation with the most abundant anions (chloride, inorganic carbon, sulphate) has to be quantified. This in turn requires that the aqueous phase stability constants are "correct" and that the sorption characteristics of the complexes are quantified, sorbing or non-sorbing. In some cases the simplifying assumption that only free cations, positively charged and neutral hydrolysed species are sorbing works e.g. Ni(II), and in other cases it does

not e.g. Eu(III) (MARQUES et al., 2008). The modelling results for the sorption of radionuclides (Ni(II), Co(II), Eu(III), Th(IV), U(VI)) on montmorillonite and illite have been used to predict sorption isotherms measured on the MX-80 and Opalinus Clay systems, respectively. The scaling in both cases was over the respective wt. % of the 2:1 type clay minerals in the "real system". Examples of the results of modelling the isotherms of Ni(II) on MX-80, and Co(II) on OPA, are shown in Figs. 4.1 and 4.2 respectively. The results of these two cases together with examples for other radionuclides (Eu(III), Th(IV), U(VI)) will be presented at the Clay Conference in Nantes in Spring 2010.

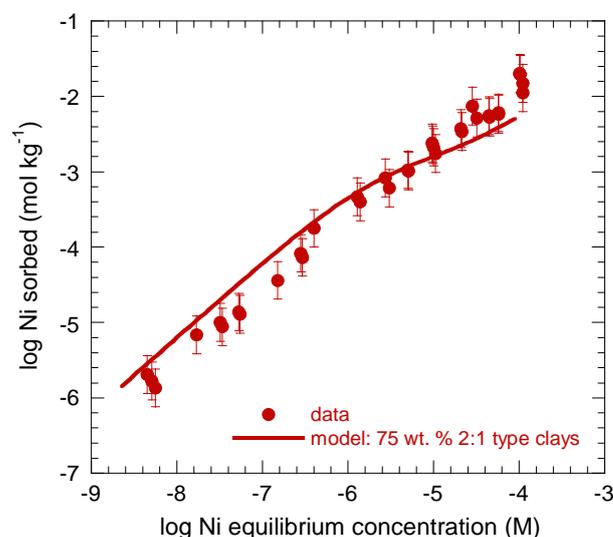


Fig. 4.1: Sorption of Ni(II) on MX-80 bentonite: the symbols are measured data, the solid line is the model prediction using the "bottom up" approach.

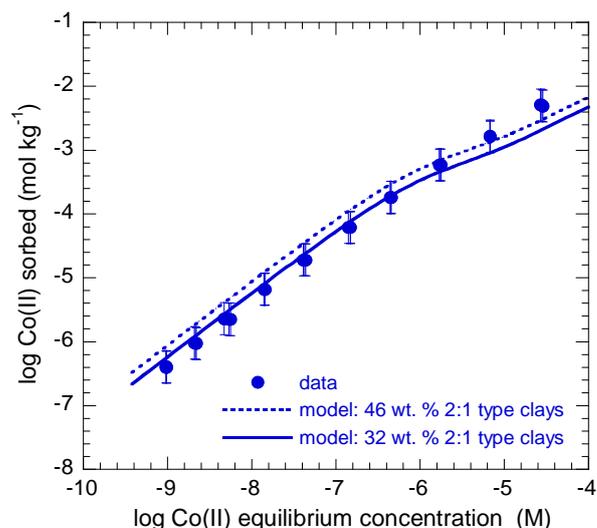


Fig. 4.2: Sorption of Co(II) on Opalinus Clay: the symbols are measured data, the lines are the model prediction using the "bottom up" approach.

4.3 Other activities

4.3.1 MX-80 bentonite physico-chemical characteristics and sorption

A report describing the work carried out in LES on MX-80 bentonite in support of Swiss radioactive waste performance assessment studies has been produced. With particular regard to Part 2, Stage 2 of the Sectoral Plan for deep geological disposal, it was considered to be important to bring together, in one document, the information and results that have accrued over the years from both “in house” studies and associated relevant literature data. The report gives a brief overview of the physico-chemical characteristics and porewater chemistry determined for MX-80 bentonite followed by the results of an extensive experimental sorption programme on the uptake of Cs(I), Sr(II)/Ca(II), Ni(II), Eu(III), Th(IV), U(VI), Cl(-I), I(-I) and Se(IV) on the same material (BRADBURY & BAEYENS, 2009d).

4.3.2 MX-80 pH buffering

Almost invariably the compositions of porewaters given for highly compacted bentonite are calculated values, because reliable water samples from compacted material are virtually impossible to obtain, even by squeezing under very high pressures. Assumptions and simplifications are made in the geochemical models used to perform such calculations and the predictions are seldom if ever tested. One of the main hypotheses in a recently proposed model for calculating the porewater in compacted bentonite was that the initial pH is determined by the initial “as received” state of the amphoteric surface hydroxyl groups, $\equiv\text{SOH}$ type sites, on the montmorillonite component. The calculations indicated that the initial pH of the porewater is close to 8. The aims of the work performed here were to check the predictions of the model in terms of the pH, which is one of the most important parameters for any porewater, and the predicted strong buffering effect of the $\equiv\text{SOH}$ type sites. The concept behind the tests was to take a powdered bentonite and a background electrolyte (0.2 M CaCl_2) containing known quantities of acid or base (pH values between 1.5 and 12), mix them together at a high solid to liquid ratio (312 g L^{-1}) and then allow them to react in the absence of air in a closed system. If the model concepts and parameter values are valid, then the model should be able to predict the pH measured in such experiments. The model calculations agreed well with the measured pH values and confirmed that it is highly likely that the $\equiv\text{SOH}$ type sites determine the initial pH of the

porewater in compacted bentonite systems. Further, these amphoteric surface hydroxyl groups at the edges of montmorillonite provide an extremely high buffer capacity in the compacted system for maintaining the bentonite porewater pH at a value of ~ 8 (BRADBURY & BAEYENS, 2009e).

4.3.3 Effect of temperature on the sorption of Cs onto illite

The sorption of Cs was measured on Illite du Puy (IdP) as a function of time and at 3 different Cs concentrations at pH ~ 7 at 25 °C as well as 90 °C. Experimental results of the sorption kinetics and the isotherm of Cs on Na-IdP are shown in Figs. 4.3a,b. A decrease in Cs sorption ($\log R_d$ decreased by 0.6 log units) was observed with increasing temperature. The experimental data were fitted with the Cs sorption model (frayed edge sites (FES), Type II sites) (BRADBURY & BAEYENS, 2000). The modelling results are shown as solid lines in Fig. 4.3b and the parameters are summarized in Table 4.1.

Table 4.1: Summary of the parameters derived from the modelling of Cs sorption on Na-Illite at 25 °C and 90 °C. CEC: 225 meq·kg⁻¹.

Site type	Site capacity (meq kg ⁻¹)	$\log \frac{C_s}{Na} K_c$	
		at 25 °C	at 90 °C
FES	0.56	6.5	5.9
Type II sites	45	3.4	2.8

4.4 Surface analysis investigations

One of the main pillars on which the disposal concept in performance assessment for future Swiss radioactive waste repositories rests, is the high affinity of clay minerals for radionuclides. Most of the sorption studies carried out to date investigated the uptake of only one radionuclide at a time. The sorption behaviour onto clay minerals was quantified from such batch experiments (e.g. BRADBURY & BAEYENS, 1997; BRADBURY & BAEYENS, 1999; BRADBURY & BAEYENS, 2005a). However this approach ignores the potential effect of competitive sorption. A recent study investigated the competitive sorption behaviour of radionuclides with different valence states (BRADBURY & BAEYENS, 2005b). The main conclusion was that radionuclides such as Ni(II), Th(IV) and U(VI) are not competitive, and that a multiple set of sorption sites at clay mineral surfaces must exist. Extended X-ray absorption fine structure (EXAFS) measurements were performed to

unequivocally identify the nature of sorption complexes of Ni(II), Th(IV) and U(VI) on montmorillonite.

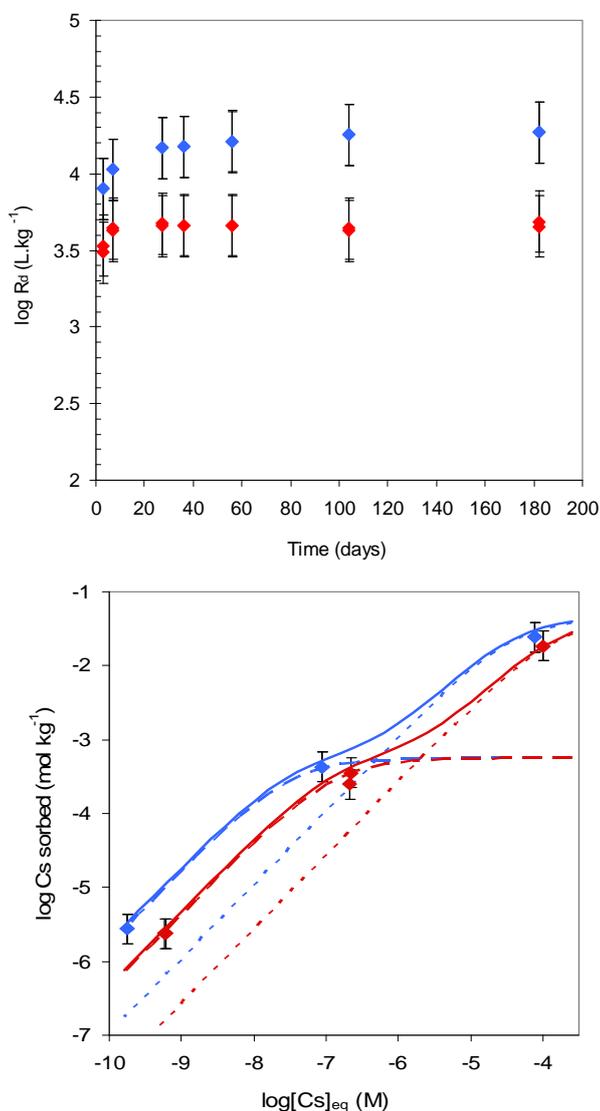


Fig. 4.3: **a)** Cs sorption kinetics for conditioned Na-IdP (pH ~7, 0.1 M NaClO₄) on the FES sites at 25 °C (♦) and 90 °C (♦). **b)** Cs sorption isotherm after 182 days at 25 °C (♦) and 90 °C (♦). The solid lines are the fit to the data using the parameter values given in Table 4.1. The dashed and dotted lines are the contributions made by FES and type II sites to the overall sorption of Cs, respectively.

The EXAFS study of the sorption of Ni(II) on montmorillonite demonstrated that the Ni(II) surface complexes are located at the edges of montmorillonite platelets (Fig. 4.4) in the continuity of the Al-octahedral layers (DÄHN et al., 2003). Th(IV) complexes, however, are only bound to silanol sites of montmorillonite, Fig. 4.4 (DÄHN et al., 2002). In the case of U(VI) uptake by montmorillonite, it was found

that the Fe(III) content (isomorphous substitutions in the octahedral sheets) strongly influenced the sorption behaviour. CATALANO & BROWN (2005) and MARQUES et al. (2009) showed that U(VI) is bound to one Si from the silanol and one Fe from the octahedral sites.

The EXAFS investigations showed clearly that the sorption sites of montmorillonite are selective for radionuclides of different valence states and supported the general conclusion of the wet chemistry experiments that radionuclides of like valence compete, whereas radionuclides of different valencies do not.

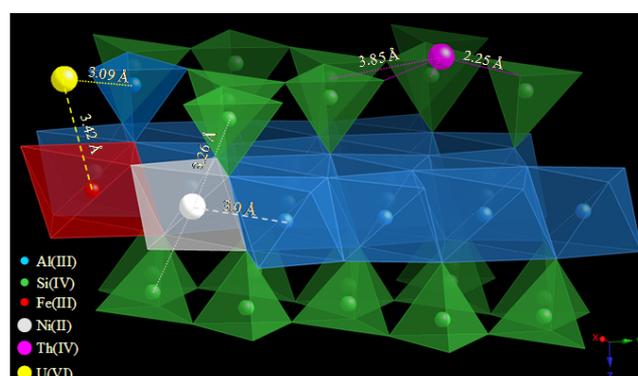


Fig. 4.4: Specific strong sorption site types for Ni(II), Th(IV) and U(VI) on montmorillonite as determined by EXAFS.

4.5 PhD Project

A PhD proposal entitled “The influence of Fe(II) on clay properties, the sorption of Fe(II) on clays and competitive sorption investigations: a combined macroscopic and microscopic study” has been prepared, and was approved by the PSI Research Committee. The project is now under evaluation by the Swiss National Science Foundation. The overall objective is to investigate, in a combined macroscopic (wet chemistry) and microscopic (surface analysis) approach, the influence of reducing conditions on the characteristics of representative clay materials, particularly with respect to radionuclide retention in the presence of high aqueous Fe(II) concentrations.

One of the key questions regarding strongly reducing conditions is whether the state of the structural Fe(III) changes and whether this influences the characteristics (especially sorption) of the clay mineral. Subsequently, the sorption behaviour of Fe(II) on clay minerals will be studied with the aim of elucidating the uptake mechanism. This is particularly relevant to predict quantitatively the influence of high Fe(II)

concentrations on the retention behaviour of other radionuclides in the system, since this is currently unclear. The competitiveness of Fe(II) on the sorption of radionuclides with valence states between (II) and (IV) will be investigated. Quantifying the competitive effect of Fe(II) is of importance in repository safety analyses and for the prediction of the fate of metals in the environment. X-ray absorption spectroscopy (EXAFS, XANES) will be applied at low metal loadings to determine the nature of surface complexes located at clay edges sites and to study the formation of newly formed phases, such as Fe-phyllsilicates, at elevated metal concentrations. The sorption of metals onto clay mineral surface, and the possible formation of neoformed phyllsilicates, can significantly decrease their ability to migrate into the geosphere, and thus influences the long-term behaviour of radionuclides.

4.6 References

- BRADBURY M.H., BAEYENS B. (1997)
A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part II: Modelling. *J. Contam. Hydrol.* 27, 223-248.
- BRADBURY M.H., BAEYENS B. (1999)
Modelling the sorption of Zn and Ni on Ca-montmorillonite. *Geochim. Cosmochim. Acta* 63, 325-336.
- BRADBURY M.H., BAEYENS B. (2000)
A generalised sorption model for the concentration dependent uptake of Cs by argillaceous rock. *J. Contam. Hydrol.* 42, 141-163.
- BRADBURY M.H., BAEYENS B. (2002)
Sorption of Eu on Na- and Ca-montmorillonites: Experimental investigations and modelling with cation exchange and surface complexation. *Geochim. Cosmochim. Acta* 66, 2325-2334.
- BRADBURY M.H., BAEYENS B. (2003)
Far field sorption databases for performance assessment of a HLW repository in an undisturbed Opalinus Clay host rock. PSI Bericht Nr. 03-08 and Nagra NTB 02-19.
- BRADBURY M. H., BAEYENS B. (2005a)
Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides. *Geochim. Cosmochim. Acta* 69, 875-892.
- BRADBURY M.H., BAEYENS B. (2005b)
Experimental measurements and modelling of sorption competition on montmorillonite. *Geochim. Cosmochim. Acta* 69, 4187-4197.
- BRADBURY M.H., BAEYENS B. (2009a)
Sorption modelling on illite. Part I: Titration measurements and the sorption of Ni, Co, Eu and Sn. *Geochim. Cosmochim. Acta* 73, 990-1003.
- BRADBURY M.H. & BAEYENS B. (2009b)
Sorption modelling on illite. Part II Actinide sorption and linear free energy relationships. *Geochim. Cosmochim. Acta* 73, 1004-1013.
- BRADBURY M.H., BAEYENS B. (2009c)
Comparison of the current Opalinus Clay sorption database with one predicted from illite sorption data. Nagra NTB 09-07, (in review).
- BRADBURY M.H., BAEYENS B. (2009d)
Physico-chemical characterisation data and sorption measurements of Cs, Ni, Eu, Th, U, Cl, I and Se on MX-80 bentonite. Nagra NTB 09-xx, (in review).
- BRADBURY M.H., BAEYENS B. (2009e)
Experimental and modelling studies on the pH buffering of MX-80 bentonite porewater. *Appl. Geochem.* 24, 419-425.
- BRADBURY M.H., BAEYENS B., THOENEN T. (2008)
Sorption Databases for Generic Swiss Argillaceous, Crystalline and Calcareous Rock Systems, Nagra NAB 08-50.
- BRADBURY M.H., BAEYENS B., THOENEN T. (2009)
Sorption Databases for Generic Swiss Argillaceous, Crystalline and Calcareous Rock Systems, Nagra NTB 09-03 (in review).
- CATALANO J.G., BROWN JR. G.E. (2005)
Uranyl adsorption onto montmorillonite: Evaluation of binding sites and carbonate complexation *Geochim. Cosmochim. Acta* 69, 2995-3005.
- DÄHN R., SCHEIDEGGER A.M., MANCEAU A., CURTI E., BAEYENS B., BRADBURY M. H., CHATEIGNER D. (2002)
Th uptake on montmorillonite: A powder and polarized extended x-ray absorption fine structure (EXAFS) study. *J. Colloid Interface Sci.* 249, 8-21.
- DÄHN R., SCHEIDEGGER A.M., MANCEAU A., SCHLEGEL M. L., BAEYENS B., BRADBURY M. H., AND CHATEIGNER D. (2003)
Structural evidence for the sorption of Ni(II) atoms on the edges of montmorillonite Clay minerals. A polarized X-ray absorption fine structure study. *Geochim. Cosmochim. Acta* 67, 1-15.

MARQUES FERNANDES M., BAEYENS B., BRADBURY M.H. (2008)

The influence of carbonate complexation on lanthanide/actinide sorption on montmorillonite. *Radiochim. Acta* 96, 691–697.

MARQUES FERNANDES M., DÄHN R., BAEYENS B., GEIPEL G., BRADBURY M.H. (2009)

Influence of carbonate on the sorption of U(VI) on clay minerals: A macroscopic and microscopic approach. (to be submitted to *Geochim. Cosmochim. Acta*).

NAGRA (2002)

Project Opalinus Clay: Safety Report. Demonstration of disposal feasibility (Entsorgungsnachweis) for spent fuel, vitrified high-level waste and long-lived intermediate-level waste. Nagra NTB 02-05.

NAGRA (2008)

Vorschlag geologischer Standortgebiete für das SMA- und das HAA-Lager: Darlegung der Anforderungen, des Vorgehens und der Ergebnisse. Nagra NTB 08-03.

5 CEMENT SYSTEMS

E. Wieland, J. Tits, J. Gaona, D. Kunz, A. Laube, N. Macé, D. Popov, B. Dilnesa (Empa)

5.1 Overview

The long-term goal of the group “Cement Systems” is to develop mechanistic models for the interaction of safety relevant radionuclides with cementitious materials. The aim is to improve current knowledge on the chemical processes in the near field of the planned Swiss SMA and LMA repositories, providing better source term descriptions and strengthening the credibility of the sorption values used in performance assessment (PA) studies. The cement used for the experimental studies is a sulphate-resisting Portland cement CEM I 52.5 N HTS (Lafarge, France), which is currently in use for the conditioning of radioactive waste in Switzerland. Calcium silicate hydrate (C-S-H) phases are considered to be the most important constituent of HCP for cation and anion binding, which is why complementary studies using C-S-H phases have been carried out.

The main lines in our research activities in 2009 were:

- Sorption studies with the dose-determining radionuclides ^{14}C , ^{129}I and ^{36}Cl on cement;
- Sorption studies and spectroscopic investigations on the interaction of Np(IV/V) and U(VI) with cement and C-S-H phases;
- Development of a methodology for phase identification at the clay-cement interface using micro-diffraction.

The sorption and spectroscopic studies on Np(IV/V) uptake processes by cementitious materials are carried out within the 7th EU Framework Programme collaborative project “RECOZY” (REdox phenomena COntrolling SYstems).

The MISUC project, which was fully financed by the EU in the framework of a Marie-Curie Fellowship, and focused on spectroscopic studies on U(VI) uptake by cement, was finished on 31st August, 2009.

D. Popov (post doctoral fellow) joined the “XAFS” sub-programme in 2008. His research activities in 2009 will be summarized in this Chapter of the LES progress report.

5.2 Sorption studies with dose-determining radionuclides

The long-term activity release rate (mSv per year) from the cementitious near field into the far field is dominated by iodide (^{129}I), chloride (^{36}Cl), selenium

(^{79}Se) and ^{14}C species (NAGRA 2002). Investigations into the interaction of these dose-determining radionuclides aim at i) determining robust sorption values for such weakly sorbing radionuclides, ii) resolving apparent inconsistencies reported between the sorption values on dispersed and intact cementitious systems (up-scaling), and iii) identifying the cement minerals and chemical processes responsible for retention of the radionuclides. Previous studies have suggested that knowledge of the total concentration of chloride in cementitious systems is the key to understanding the currently existing inconsistencies in the sorption values of chloride and iodide (Progress Report, 2008). In 2009, studies on the uptake of iodide (^{125}I) and chloride (^{36}Cl) by HCP were carried out at varying solid-to-liquid (S/L) ratios. Further, ^{125}I and ^{36}Cl uptake was investigated on cement which had been altered to the portlandite-controlled stage of cement degradation (pH = 12.5). In all of these systems the total concentration of chloride was monitored in the aqueous phase using high-performance anion exchange chromatography. The influence of the total chloride concentration on ^{36}Cl and ^{125}I uptake could be verified. Future studies will focus on identifying the cement minerals and the underlying chemical mechanism responsible for anion binding in the cement matrix.

Investigations on the chemical speciation of ^{14}C and the fate of small organic molecules under the alkaline conditions of a cementitious near field are new topics being dealt with in the “Cement Systems” group. Hydrocarbons, such as methane, ethane etc., or oxygenated hydrocarbons, such as alcohols, aldehydes, or carboxylic acids, are expected to form during anaerobic corrosion of carbon steel (DENG et al., 1997; SASOH, 2004). For PA studies it is important to quantify exactly the uptake of these weakly sorbing compounds by cement since even very low sorption may have a beneficial effect on the retention of ^{14}C release from the cementitious near field, e.g. ^{14}C decay reduces the long-term release rates.

The uptake of small organic molecules was determined in compact cement samples (0.5 L volume) doped with methanol, ethanol, formaldehyde, acetaldehyde, formic acid and acetic acid. After ageing for 28 days, cement porewater was squeezed from the hardened samples using the steel die method at pressures up to 530 N mm⁻². Total organic carbon was determined in the extracted and filtered pore

solutions. Distribution ratios (R_d) were calculated from mass balance considerations based on the initial concentrations added, and the solution concentrations determined in the aged samples. These values can be compared with those obtained from short-term equilibration experiments for which solutions containing the organics were equilibrated with unhydrated cement for one hour (Table 5.1). Sorption by compact hydrating cement was found to be very weak. Nevertheless, the approach developed in this study allowed the low sorption values to be quantified accurately. Retention was not dependent on time in the case of methanol, ethanol, formaldehyde and acetaldehyde. A significant increase in sorption with time was, however, observed for the carboxylic acids. The reason is presently unclear. This study was carried out in co-operation with the Laboratory for Concrete and Construction Chemistry at Empa, Dübendorf, Switzerland.

Table 5.1: Uptake of selected small organic molecules by cement.

Organics	R_d ($\text{m}^3 \text{kg}^{-1}$)	
	1 hour	28 days
Methanol	$(9\pm 3)\cdot 10^{-5}$	$(1\pm 0.3)\cdot 10^{-4}$
Ethanol	$(2\pm 0.7)\cdot 10^{-4}$	$(1\pm 0.3)\cdot 10^{-4}$
Formaldehyde	$(6\pm 2)\cdot 10^{-5}$	$(8\pm 3)\cdot 10^{-5}$
Acetaldehyde	$(4\pm 1)\cdot 10^{-4}$	$(4\pm 1)\cdot 10^{-4}$
Formic acid	$(6\pm 2)\cdot 10^{-5}$	$(1\pm 0.3)\cdot 10^{-3}$
Acetic acid	$(5\pm 2)\cdot 10^{-5}$	$(5\pm 2)\cdot 10^{-4}$

5.3 Uptake of neptunium by cementitious materials

The sorption behaviour of redox sensitive actinides under the reducing conditions of a cementitious near field is poorly known (WIELAND & VAN LOON, 2002). In most sorption databases used in PA studies it is assumed that the sorption behavior of tetravalent actinides, such as Np(IV) and Pu(IV), is similar to that of Th(IV). Measurements with Np(V) on cementitious materials are completely lacking. In the latter case chemical analogy with bivalent metal cations was assumed based on its effective charge of +2.3 (CHOPPIN, 1982; WIELAND & VAN LOON, 2002). To verify the above assumptions, the uptake of Np(IV) and Np(V) by HCP and C-S-H phases under reducing and oxidizing conditions is being investigated within the framework of the RECOSY project.

5.3.1 Macroscopic studies

Sorption studies carried out in previous years indicated a strong uptake of Np(V) by C-S-H phases ($R_d = 10^2 \text{ m}^3 \text{kg}^{-1} - 2\cdot 10^3 \text{ m}^3 \text{kg}^{-1}$) although the sorption behaviour was expected to be similar to that of bivalent metal cations ($R_d \sim 10 \text{ m}^3 \text{kg}^{-1}$). Furthermore, Np(V) uptake by C-S-H phases was found to be linear in a loading range between $10^{-4} \text{ mol kg}^{-1}$ and 0.1 mol kg^{-1} , and not dependent on the Ca:Si (C:S) ratio of the C-S-H phases. Sorption studies on fresh HCP further supported the strong uptake of Np(V) ($R_d = (3\pm 1)\cdot 10^2 \text{ m}^3 \text{kg}^{-1}$), suggesting that C-S-H phases could be the uptake controlling cement component for Np(V).

In 2009 kinetic studies on the Np(V) uptake by C-S-H phases were carried out and included the monitoring of the redox potential in these systems (Fig. 5.1). The experiments showed that Np(V) sorption is a two-step process: a fast initial sorption process occurring within a few hours ($R_d = (8\pm 2)\cdot 10^1 \text{ m}^3 \text{kg}^{-1}$), which is followed by a slower step. The latter process reached steady state after ~ 25 days equilibration ($R_d \leq (6\pm 2)\cdot 10^2 \text{ m}^3 \text{kg}^{-1}$) (Fig. 5.1a). Furthermore, it was observed that the E_h gradually decreased as a function of the reaction time to a value $< 0.1 \text{ V}$ (Fig. 5.1b). Np(IV)/Np(V) were the only redox sensitive species in the C-S-H systems which could cause such a change. Thermodynamic calculations revealed that a reduction of E_h from +0.1 V to -0.3 V, controlled by the Np(IV)/Np(V) redox couple, could significantly change the Np speciation in solution from 100% Np(V) to almost 100% Np(IV). Hence, the observed decrease in the redox potential suggests that Np(V) was reduced to Np(IV) during the uptake of Np(V) by C-S-H. The only source of e^- available for reduction is the electrolysis of H_2O , thus resulting in the formation of O_2 .

The coupled sorption-reduction process for Np(V) would explain the unexpectedly high R_d values observed in the batch sorption experiments (Fig. 5.1a). The high amount of Np taken up by the solid, together with the very low Np concentration in solution and the reducing conditions were taken as evidence that sorbed Np was predominantly in the +IV state. The driving force for the reduction of Np(V) to Np(IV) is the higher affinity of C-S-H for Np(IV) (effective charge +4) than Np(V) (effective charge +2.3). Based on the above assumptions, a thermodynamic model for the Np(V) uptake by C-S-H is being developed with the aim of assessing the influence of changes in the redox conditions on Np(V) sorption using reported thermodynamic data for Np(IV/V) (HUMMEL et al., 2002; GUILLAUMONT et al., 2003).

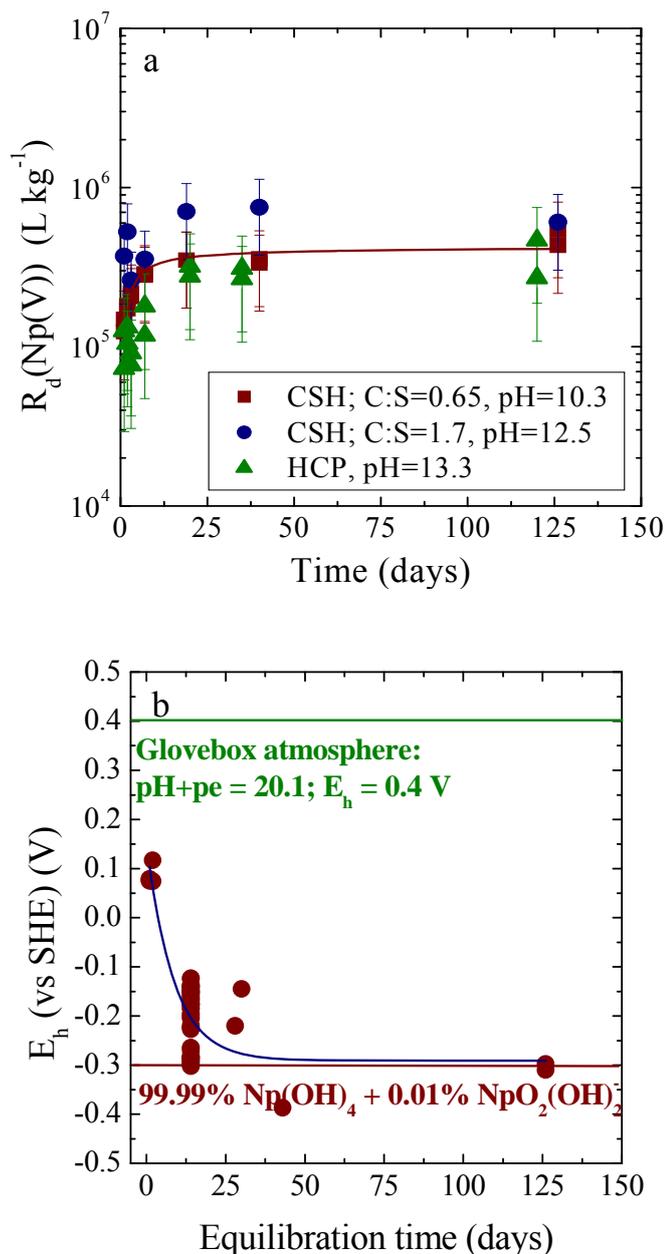


Fig. 5.1: Np(V) sorption kinetics on C-S-H phases with different C:S ratios under alkali ion free conditions and in artificial cement porewater (ACW) at pH = 13.3. a) R_d values for Np(V) sorption onto two C-S-H phases and on HCP. b) Changes in the redox potentials of Np(V) – C-S-H suspensions in ACW at pH 13.3 with increasing equilibration time.

The model is tending to suggest thermodynamic equilibrium between the aqueous Np(IV/V) and the Np(IV/V) surface species in the E_h range $-0.4 \text{ V} < E_h < +0.4 \text{ V}$.

Complementary speciation calculations for the Np redox systems were carried out in the pH range 10 – 14. These latter calculations further revealed a strong

dependence of the Np(V) stability field on the choice of the Np species. For example, including the Np(VI) hydroxy-complexes, $\text{NpO}_2(\text{OH})_3^-$ and $\text{NpO}_2(\text{OH})_4^{2-}$, based on chemical analogy with the corresponding U(VI) complexes in the oxidizing domain (HUMMEL et al., 2002), significantly reduced the Np(V) stability field. The Np(V) stability field became even smaller when the Np(IV/V) solid phases were taken into account. In this case, the Np(V) stability field strongly depended on the total Np concentration. In contrast, the existence of ternary Np(V) hydroxides, such as $\text{Ca}_{0.5}\text{NpO}_2(\text{OH})_2(\text{s,hyd})$ (ALTMAIER et al., 2008), could result in the stabilisation of the Np(V) redox state. The thermodynamic calculations clearly revealed that our current understanding of Np speciation under hyper-alkaline remains insufficient. A better knowledge of the Np speciation under reducing, alkaline conditions, however, is a prerequisite for a sufficiently detailed mechanistic interpretation of Np(IV)/Np(V) sorption onto cementitious materials. Determination of the key data will be the subject of a future collaboration with the Institut für Nukleare Entsorgung (INE) at the Karlsruhe Institute of Technology-Research Center Karlsruhe (KIT/FZK, Karlsruhe, Germany) in the framework of RECOSY.

5.3.2 Synchrotron-based studies

During the past year, a first series of EXAFS measurements were carried out at the ROBL (Rossendorf beamline, ESRF) with the aim of assessing the applicability of bulk-EXAFS measurements at the Np L_{III} edge (17610 eV) to Np redox speciation studies in cementitious materials. Np doped C-S-H and HCP samples (Np loading ~ 1000 – 1500 ppm) were prepared by adding either Np(IV), Np(V) or Np(VI) solutions, respectively, to C-S-H and HCP materials.

The Np(IV) tracer was stabilized in $\text{Na}_2\text{S}_2\text{O}_4$; while Np(VI) was produced by oxidizing Np(V) with NaOCl. The main difference appearing in the Np(IV) and Np(V) EXAFS spectra was caused by the split shell of neighboring oxygen atoms observed in the coordination environment of Np(V), which can be attributed to the neptunyl ($[\text{O}=\text{Np}=\text{O}][+]$) structure. The split oxygen shell was not observed for Np(IV). Axial (O_{ax}) and equatorial (O_{eq}) oxygen atoms had to be considered in the fitting of the spectra from all bulk samples (Fig. 5.2). In particular, acceptable fits for the Np(IV) and Np(V) samples could only be achieved by including both O_{ax} - and O_{eq} -shells, and either fixing the number of axial oxygens ($N_{\text{Oax}} = 2$) or the Debye Waller factor (σ_{Oax}^2). These observations indicate the

presence of Np(IV/V) mixtures in these samples rather than the presence of pure Np(IV) or Np(V) species, respectively, in accord with the study of DENECKE et al. (2005). Under oxidizing conditions in the presence of NaOCl, short Np-O_{ax} and Np-O_{eq} distances were observed, indicating the formation of sorbed Np(VI) species. These test measurements showed that EXAFS spectroscopy can be used to distinguish Np redox states in cementitious materials. However, they further revealed that transfer of Np(IV) samples to the beamline has to be carried out under strictly anoxic conditions to avoid partial re-oxidation. This is presumably the reason why both Np(IV) and Np(V) species were observed in those samples initially doped with either Np(IV) or Np(V), respectively. Note that the appearance of Np(IV) in the latter samples further indicates Np(V) reduction to Np(IV) during uptake by C-S-H and HCP. It is foreseen to perform additional EXAFS studies in 2010 with the aim of further elucidating the formation of Np(IV) surface species (>Np(OH)₄(ads)) in Np(V) doped cementitious materials.

5.4 Uptake of U(VI) by cementitious materials

5.4.1 Spectroscopic investigations of U(VI) uptake processes

The U(VI) surface speciation studies in cement were aimed at developing a mechanistic model of U(VI) retention in cementitious materials. The chemical nature of the U(VI) sorbed species, and the solubility-limiting phase of U(VI) under hyper-alkaline conditions, are poorly known. In 2009, micro-X-ray fluorescence (XRF) and micro-X-ray absorption spectroscopy (XAS) measurements were carried out with the aim of determining the distribution and chemical coordination environment of U(VI) in compact HCP at “low” (2500 ppm) and “high” U(VI) loadings (25000 ppm). Micro-XRF studies were performed on the microXAS beamline at the Swiss Light Source (SLS), while a combined micro-XRF/XAS study was carried out on beamline BL-2.3 at the Stanford Synchrotron Radiation Lightsource (SSRL, Menlo Park, USA). Uncovered polished thin sections embedded in epoxy resin, and mounted on glass supports, were prepared for these measurements. Micro-XRF provided information on the distribution of U(VI) in the compact HCP (Fig. 5.3), while micro-XAS allowed the structural arrangement of U(VI) in the U(VI)-enriched regions to be determined (Fig. 5.4).

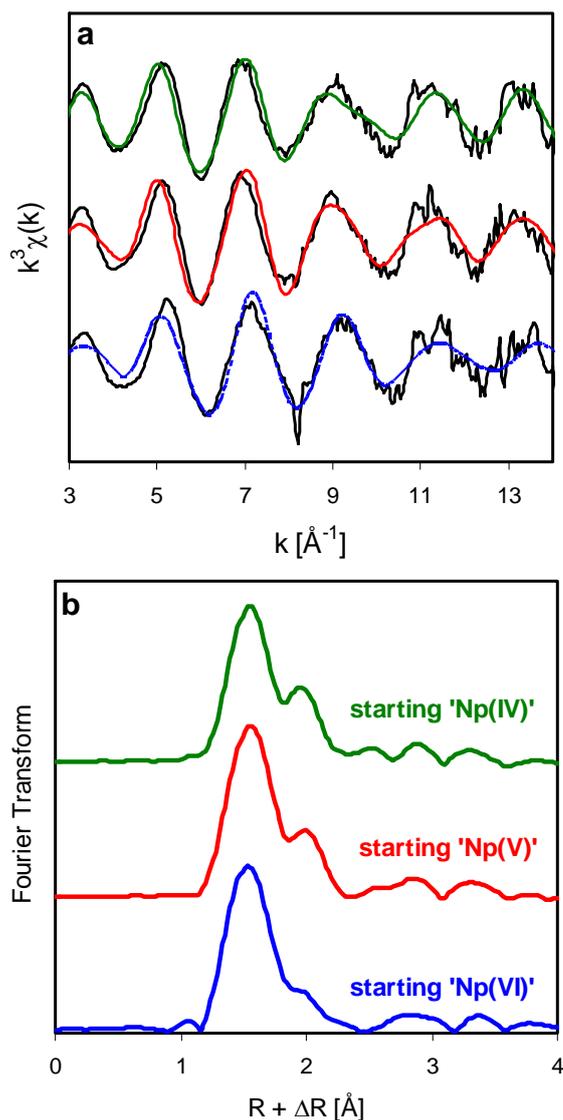


Fig. 5.2: a) EXAFS spectra (experimental and modelled) and b) Fourier-transformed EXAFS for Np(IV), Np(V) and Np(VI) starting valencies sorbed on C-S-H (C:S = 1.0).

U(VI) was found to be distributed heterogeneously in the cement matrix (Fig. 5.3). U(VI) “hot spots” were mainly located adjacent to reacting clinker minerals. EXAFS measurements at the U L_{III} edge (17166 eV) were performed on several U(VI) spots on each sample. Principal component analysis (PCA) revealed that the U(VI) EXAFS spectra were composite spectra with contributions from one (low loading, LL) or two (high loading, HL) species.

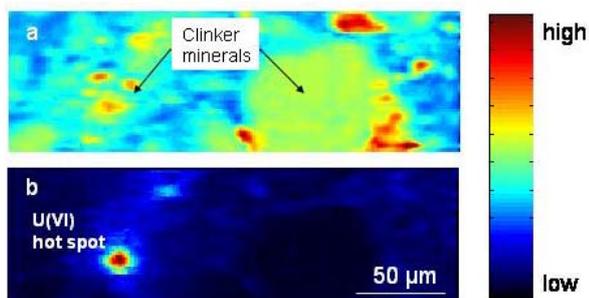


Fig. 5.3: XRF map recorded at the microXAS beamline, a) Ca and b) U distribution in U(VI) doped compact hardened cement paste (U loading = 2500 ppm).

Target transformation further enabled us to identify the reference compounds appropriate for reconstructing the composite spectra. The spectra of the latter compounds were available from bulk-EXAFS measurements carried out earlier at the ROBL (Progress report, 2008). Data analysis revealed that all spectra collected on the sample with 2500 ppm U(VI) corresponded to the spectrum of one U(VI) species (LL). In the samples with the higher U(VI) loadings, however, two species with very different spectra appeared (HL_1 and HL_2) (Fig. 5.4). The HL_1 EXAFS spectrum was identical to that of the U(VI) species detected at the lower U(VI) loading (LL). Comparison with reference spectra finally revealed that the LL and HL_1 species corresponded to U(VI) bound to C-S-H phases, while the HL_2 species had a coordination environment similar to that of U(VI) in Ca-uranate.

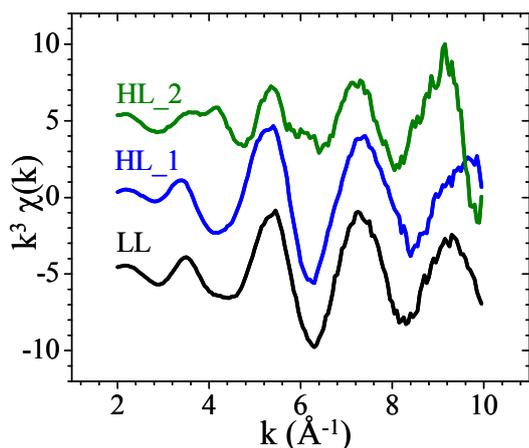


Fig. 5.4: k^3 -weighed EXAFS spectra of the main components obtained with PCA. At low U(VI) loading (LL) all spectra correspond to the spectrum of one U(VI) species. At high U(VI) loading all composite spectra collected at the different U(VI) spots contained two U(VI) species designated as HL_1 and HL_2 species. K-range for data analysis was taken between 2 and 10 Å.

In 2009, time resolved laser fluorescence spectroscopy (TRLFS) investigations were also carried out in collaboration with the Institut für Nukleare Entsorgung at KIT/FZK. The aim of the TRLFS study was to identify the coordination environment of U(VI) bound to C-S-H phases. Previous EXAFS investigations suggested that the coordination environment of U(VI) in C-S-H and HCP resembled that of U(VI) bound in uranyl-silicate minerals, such as soddyite or uranophane.

Nevertheless, the local structure of U(VI) could not be fully resolved by EXAFS due to the close similarity in the structural arrangements of the neighboring atoms in soddyite and uranophane (Progress report, 2008). Thus, TRLFS measurements at 4 K provided complementary information on the speciation at low U(VI) concentrations. U(VI) was added to suspensions of C-S-H and HCP, which were equilibrated with alkali-rich ACW (TITS et al., 2008).

Fig. 5.5 shows that the emission spectra of U(VI) taken up by C-S-H and HCP are very similar and further correspond to the spectrum determined for soddyite. The latter finding suggests a structural arrangement of the nearest neighboring atoms similar to that of U(VI) in soddyite rather than uranophane. The TRLFS study shows that C-S-H is the uptake-controlling cement phase for U(VI) in cement and further confirms that U(VI) is bound in an uranyl-silicate-like coordination environment in C-S-H and HCP. C-S-H phases will be present in the cementitious near field over a very long period of time. This ensures that U(VI) will be bound over equally long time scale.

5.4.2 Aqueous-solid solution thermodynamic model of U(VI) uptake by C-S-H phases

Thermodynamic modelling allows the interaction of radionuclides with cementitious materials to be predicted for varying repository conditions, and therefore, it proves a versatile tool for use in PA studies. In the past years thermodynamic models for the interaction of Sr and Ra with cementitious materials were developed (TITS et al., 2006a/b; WIELAND et al., 2008). The currently available wet chemistry data and spectroscopic information allowed an aqueous-solid solution model of U(VI) uptake by C-S-H to be developed. The model is based on results from U(VI) sorption isotherm measurements on C-S-H phases with different C:S ratios and complementary structural information from EXAFS and TRLFS. C-S-H-U(VI) solid solution modelling uses the sublattice CSH3T solid solution model for C-S-H (KULIK, in prep.).

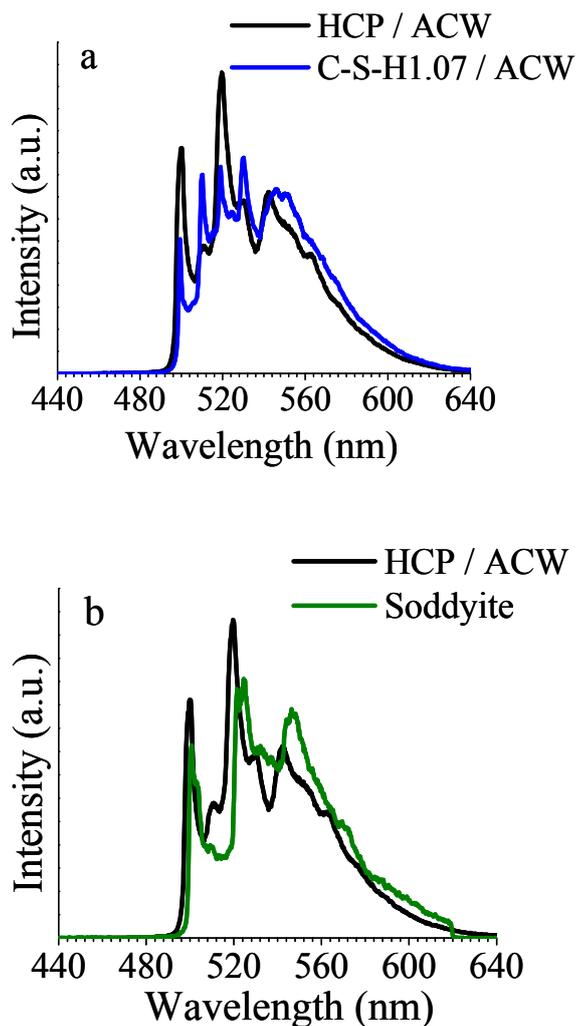


Fig. 5.5: Emission spectra a) for U(VI) sorbed onto HCP in ACW and U(VI) sorbed onto C-S-H (C:S = 1.07) in ACW and b) U(VI) sorbed onto HCP in ACW and sodydite. Measurements: (M)OPO laser system at excitation wavelength of 500 nm and samples at 4 K.

The latter model has been extended with uranyl-containing species and end members, which were selected in agreement with spectroscopic evidences and crystallographic considerations (Fig. 5.6).

The uranyl species were attributed to BTI (bridging tetrahedra – interlayer) sites in the C-S-H structure, resulting in 9 possible end member stoichiometries. Three end-members $[(\text{CaO})_2(\text{UO}_3)(\text{SiO}_2)_{2.5}(\text{H}_2\text{O})_5]$, $(\text{CaO})_2(\text{UO}_3)_{1.5}(\text{SiO}_2)_2(\text{H}_2\text{O})_5$ and $(\text{CaO})_3(\text{UO}_3)_{1.5}(\text{SiO}_2)_2(\text{H}_2\text{O})_{5.5}$ were selected for the extended C-S-H3T-U solid solution model based on forward and inverse modelling of U(VI) sorption isotherms in GEMS. With provisional thermodynamic data, this model describes sorption isotherms of U(VI) onto C-S-H phases of C:S = 0.6, 1.0 and 1.6 well. The project, which started in 2009, is ongoing.

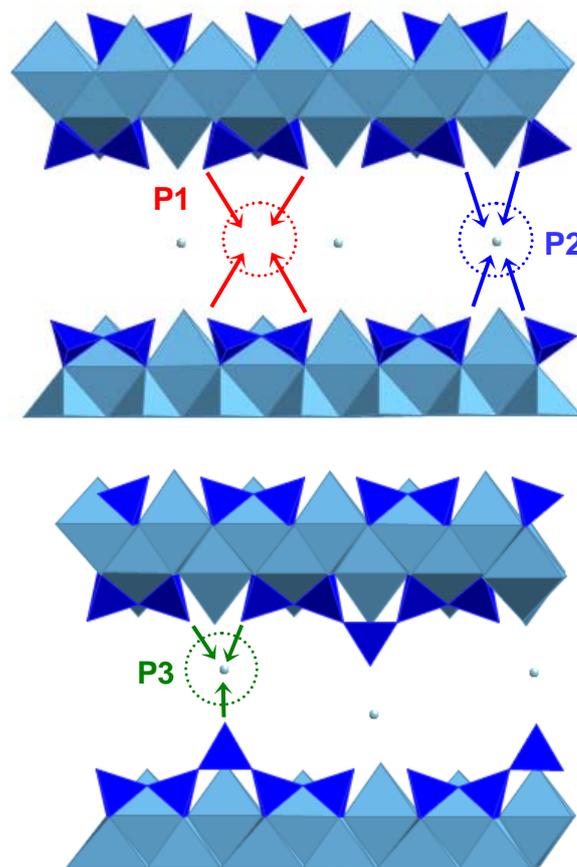


Fig. 5.6: Three possible positions of U(VI) in the interlayer of two different C-S-H structures providing uranophane-like (P1 and P2) and sodydite-like (P3) molecular environments. These structural arrangements represent three out of nine end member stoichiometries.

5.5 CI project

LES is contributing to the laboratory programme associated with the Mont Terri field experiment on cement-Opalinus Clay interaction (CI project). In 2009 the X-ray micro-diffraction (micro-XRD) technique for characterizing reaction products at clay-cement interfaces with micro-scale resolution was further developed and applied in a first case study on Maqarin samples. The natural analogue site at Maqarin (Jordan) is the only known natural hyper-alkaline system and has been studied for more than a decade (MÄDER et al., 2001; MIŁODOWSKI et al., 2001). High temperature and low pressure conditions led to the formation of clinker minerals, and subsequent re-hydration led to the formation of natural cement. U-Th disequilibrium series dating suggests an age of the cement mineralization of ~100000 years. Continuous leaching along fracture-bound groundwater flow-paths formed cementitious in-fills, interfaces to the adjacent bio-micritic and

clay-bearing limestone, and caused diffusion-controlled wall-rock alteration. Thin sections were prepared from Maqarin samples and studied using optical microscopy, scanning electron microscopy coupled with microanalysis (SEM/EDS) and micro-XRD (Fig. 5.7). The diffraction measurements were performed at the microXAS beamline at the SLS using a beam size focused down to $\sim 1 \times 1 \mu\text{m}^2$ and at the CRISTAL beamline of SOLEIL (Saclay, France) using a larger beam (50-200 μm). In both cases a total of 90 XRD patterns were collected and integrated into a composite image in order to identify the predominant phases present in the interface by performing a search in a database.

SEM imaging revealed the needle-like morphology of the C-S-H phases with thickness in the micron and sub-micron range (Figs. 5.7 and 5.8). Ettringite and tobermorite were the major crystalline components identified at the interface using the $\sim 10 \times 10 \mu\text{m}^2$ micro-beam. The measurements carried out at the CRISTAL beamline with the unfocused beam (50-200 μm) showed powder rings of tobermorite and almost no reflections of ettringite due to the large amounts of amorphous material. Using the smaller beam at the microXAS beamline, however, revealed a wealth of XRD information on ettringite. The findings show that the phase was crystalline in the smaller beam, while it was clearly XRD amorphous using the larger beam. Therefore, micro- to nano-diffraction is a very promising tool, well suited to identify and characterize samples which are considered to be amorphous based on powder diffraction studies.

Structure refinement of tobermorite is currently being performed using the XRD data collected at the microXAS beamline at the SLS (beam size $\sim 1 \times 1 \mu\text{m}^2$). Indexation of the diffraction spots from the tobermorite crystals was performed using the CrysAlis program (Fig. 5.8b). The refined unit cell corresponded to 11 Å tobermorite (MERLINO et al., 2001). Further data analysis revealed difficulties in data interpretation caused by the poor crystallinity of some phases. Software was developed which allows the quality of the diffraction data of as many crystals as possible to be checked. It was found that only two out of ~ 30 crystals probed yielded the data quality required for structure refinement. To the best of our knowledge, this is the first structure refinement of 11 Å tobermorite using XRD data recorded from micro-diffraction measurements. The project is continuing into 2010.

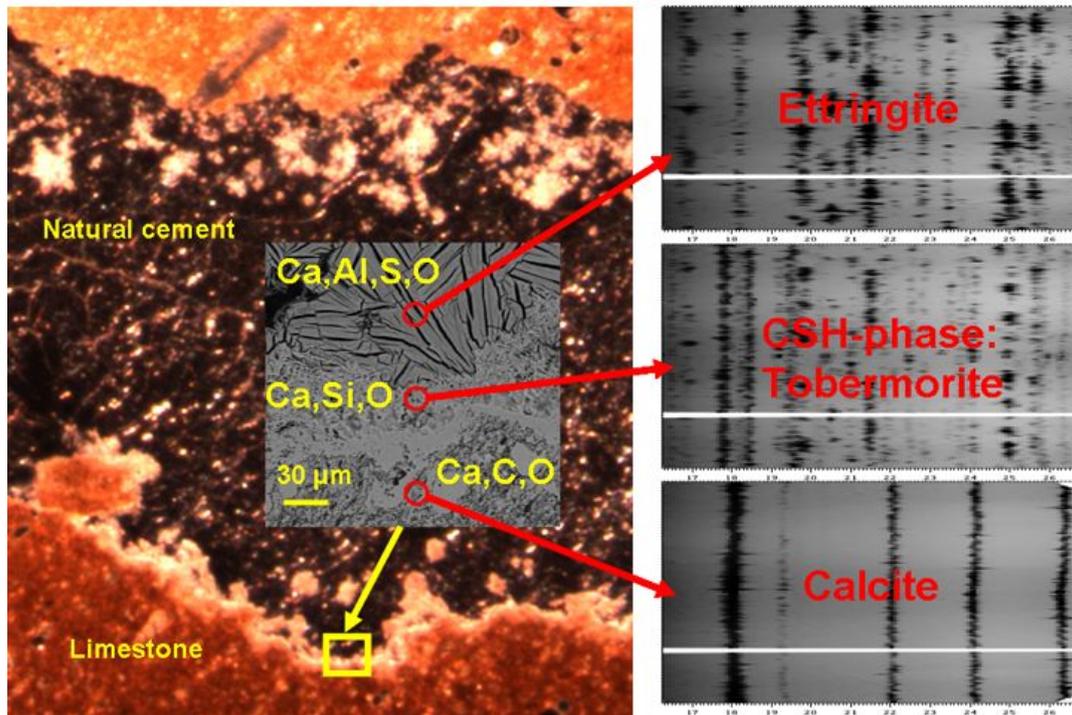


Fig. 5.7: Identification of major crystalline components (right) across the interface between the cementitious in-fill (natural cement) and surrounding limestone (left; $\lambda = 0.9537\text{\AA}$).

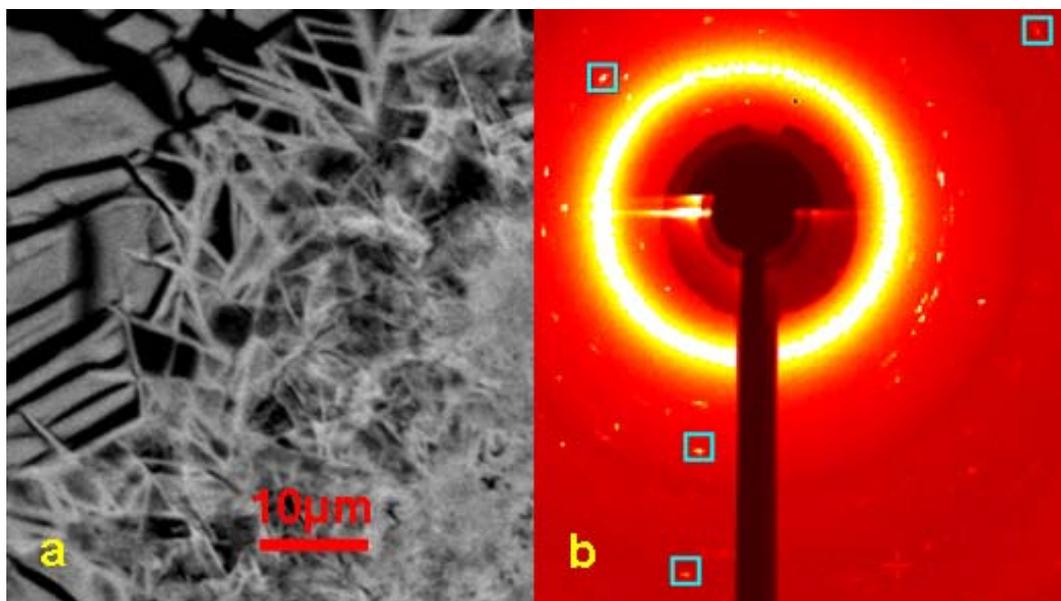


Fig. 5.8: SEM image of a) micro-crystals of tobermorite and b) diffraction pattern from the selected single-crystals with characteristic reflections (squares).

5.6 References

- ALTMAYER M., BANIK N.L., HAUSER W., KLENZE R., LINDQVIST P., MARQUARDT C., NECK V., PANAK P.J., RABUNG TH., RUNKE J., SKERENCAK A., FANGHÄNEL TH. (2008)
Annual Report 2007, Institut für Nukleare Entsorgung, Karlsruhe, Institute of Technology, Karlsruhe, Germany.
- CHOPPIN G.R. (1982)
Solution chemistry of actinides. *Radiochim. Acta* 32, 43–53.
- DENG B. L., CAMPBELL T. J., BURRIS D. R. (1997)
Hydrocarbon formation in metallic iron/water systems. *Environ. Sci. Technol.* 31, 1185-1190.
- DENECKE M.A., DARDENNE K., MARQUARDT C.M. (2005)
Np(IV)/Np(V) valence determinations from Np L3 edge XANES/EXAFS. *Talanta* 65, 1008-1014.
- GUILLAUMONT R., FANGHÄNEL T., FUGER J., GREINER I., NECK V., PALMER D.A., RAND M.H. (2003)
Chemical thermodynamics Vol. 5. Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium, Elsevier, Amsterdam.
- HUMMEL W., BERNER U., CURTI E., PEARSON F.J., THOENEN T. (2002)
Nagra/PSI chemical thermodynamic database 01/01. Universal Publishers, Florida, USA.
- KULIK D.A.
Calcium silicate hydrates (C-S-H): Matching thermodynamic aqueous solid solution model with structural and spectroscopic information. PSI Bericht (in prep.).
- MÄDER U.K., ADLER M., LANGER V., DEGNAN P., MILODOWSKI A.E., SMELLIE J.A.T., SALAMEH E., KHOURY H.N., GRIFFAULT L.Y., TROTIGNON L. (2001)
The Maqarin natural analogue study of a cement-buffered hyperalkaline groundwater plume: structural model and flow system. In: R. Cidu (ed.), *Proceedings WRI-10*. Balkema, 185-188.
- MERLINO S., BONACCORSI E., ARMBRUSTER T. (2001)
The real structure of tobermorite 11 Å: normal and anomalous forms, OD character and polytypic modifications. *Eur. J. Mineral.* 13, 577-590.
- MILODOWSKI A.E., HYSLOP E.K., KHOURY H.N., HUGHES C.R., MÄDER U., GRIFFAULT L.Y., TROTIGNON L. (2001)
Mineralogical alteration of hyperalkaline groundwater in northern Jordan. In: R. Cidu (ed.), *Proceedings WRI-10*. Balkema, 1347-1350.
- NAGRA (2002)
Project Opalinus Clay – safety report. Demonstration of disposal feasibility for spent fuel, vitrified high-level waste and long-lived intermediate-level waste (Entsorgungsnachweis). Nagra Technical Report NTB 02-05, Nagra, Wettingen, Switzerland.
- SASOH M. (2004)
The study for the chemical forms of C-14 released from activated metals. In: L.H. Johnson and B. Schwyn (eds), *Proceedings of a workshop on the release and transport of C-14 in repository environments*. Nagra Internal Report NIB 04-03, Nagra, Wettingen, Switzerland.
- TITS J., WIELAND E., MÜLLER C.J., LANDESMAN C., BRADBURY M.H. (2006)
A wet chemistry study of the strontium binding by calcium silicate hydrates. *J. Colloid Interface Sci.* 300, 78-87.
- TITS J., IJIMA K., WIELAND E., KAMEI G. (2006)
Radium binding by calcium silicate hydrates and hardened cement paste. *Radiochim. Acta* 94, 637-643.
- TITS J., FUJITA T., TSUKAMOTO M., WIELAND E. (2008)
Uranium(VI) uptake by synthetic calcium silicate hydrates. In: W.E. Lee, J.W. Roberts, N.C. Hyatt, R.W. Grimes (eds.), *Scientific Basis for Nuclear Waste Management XXXI*. Mat. Res. Soc. Symp. Proc. 1107, 467-474.
- WIELAND E., VAN LOON L.R. (2002)
Cementitious near field sorption database for performance assessment of an ILW repository in Opalinus Clay. PSI Bericht 03-06, Paul Scherrer Institut, Villigen, Switzerland, 2003, and Nagra Technical Report NTB 02-20, Wettingen, Switzerland.
- WIELAND E., TITS J., D. KUNZ D., DÄHN R. (2008)
Strontium uptake by cementitious materials: A combined wet chemistry and EXAFS study. *Environ. Sci. Technol.* 42, 403-409.

6 COLLOID CHEMISTRY

C. Degueldre, S. Garcia Garcia, S. Frick*

** KTH, Stockholm, Sweden*

6.1 General

The aim of the colloid sub-program is to understand the role of colloids in the migration of radionuclides in the geosphere. The colloid properties studied are concentration, size distribution and behaviour under safety relevant conditions. This report summarises our activities over the past year within the framework of the Grimsel colloid project: "Colloid Formation and Migration", (CFM). The focus continues to remain on colloid generation, using single particle counting (SPC) as a characterisation technique. The colloid generation approach followed is a "first" in this area and has the possibility of evaluating clay colloid size distributions, not only in batch systems, but also under the quasi-stagnant conditions of the CFM system.

The knowledge and understanding in groundwater colloid science gained over the last decade allows well founded judgements to be made concerning the potential role played by colloids in the transport of radionuclides in the argillaceous rock formations proposed by Nagra in the frame of the Sectoral Plan (Sachplan Geologische Tiefenlagerung, SGT).

6.2 Activities in the CFM project

The Colloid Formation and Migration (CFM) project is conducted in the framework of Phase VI of the research program of the Grimsel Test Site (GTS). GTS Phase VI runs from 2004 to 2013 and is dedicated to repository-relevant (i.e. large-scale, long-term) in-situ experiments.

The CFM project is the latest project in a series of experiments conducted within the Radionuclide Retardation Program (RRP) of the GTS over the past years. It is divided into 2 Phases. Phase I began in 2004 and lasted for 3 years. The main tasks were related to preparatory studies concerning in-situ boundary conditions, predictive modelling and to carrying out supporting laboratory experiments. Phase II of the CFM project will run for 4 to 6 years, from 2008 to 2011/13, with the aim of studying the in-situ generation and migration of colloids in the Grimsel migration zone environment. The main goal of this project is to understand the generation of colloids in quasi-stagnant water at a bentonite block/groundwater flow interface. The LES task is

sub-divided into two parts: participation in the in-situ colloid measurement campaigns and studying colloid generation mechanisms.

In the laboratory, both generation and sedimentation processes of bentonite colloids in NaCl solutions were examined using the single particle counting (SPC) technique. Na-type (Wyoming, purified) and Ca-type (Wyoming, treated) bentonite pellets were used in batch type tests, and colloid populations were observed to form quickly (within one hour). This process may be attributed to the detachment of colloids accompanied by structural changes of the hydrated clay pellet and colloid self-diffusion. After the initial particle creation period, colloid size-distributions varied over several hundreds of hours in the batch tests. Spontaneous diffusion into the bulk liquid after detachment (mostly small colloids) from the colloid-bed was followed by aggregation of these small colloids in the suspension. Colloid generation from the bentonite pellets was reduced in higher salinity solutions (Fig. 6.1) since the tendency to agglomerate increased. The sedimentation process was highly dependent on particle size. Whether the starting point was a clay pellet or a concentrated clay suspension, the colloid size-distributions reached similar pseudo-equilibrium states (see Fig. 6.1). A pseudo-equilibrium concentration was reached in generation and sedimentation experiments. The colloid concentration initially decreased with distance (elevation) from the colloid source at the bottom of the container. At a distance of ~ 7 cm from the colloid source, the pseudo-equilibrium Na-montmorillonite colloid mass concentrations (for sizes ranging from 50 to 1000 nm) were 4.0, 0.4 and 0.2 (± 0.1) mg L⁻¹ in 0.001, 0.01 and 0.1 M NaCl respectively, for an assumed density of 1.2 g cm⁻³ (corresponding to gel like aggregates). For Ca-montmorillonite, the mass concentration in 0.001 M NaCl was 0.3 mg L⁻¹ for sizes ranging from 50-1000 nm for an assumed density of 1.2 g cm⁻³.

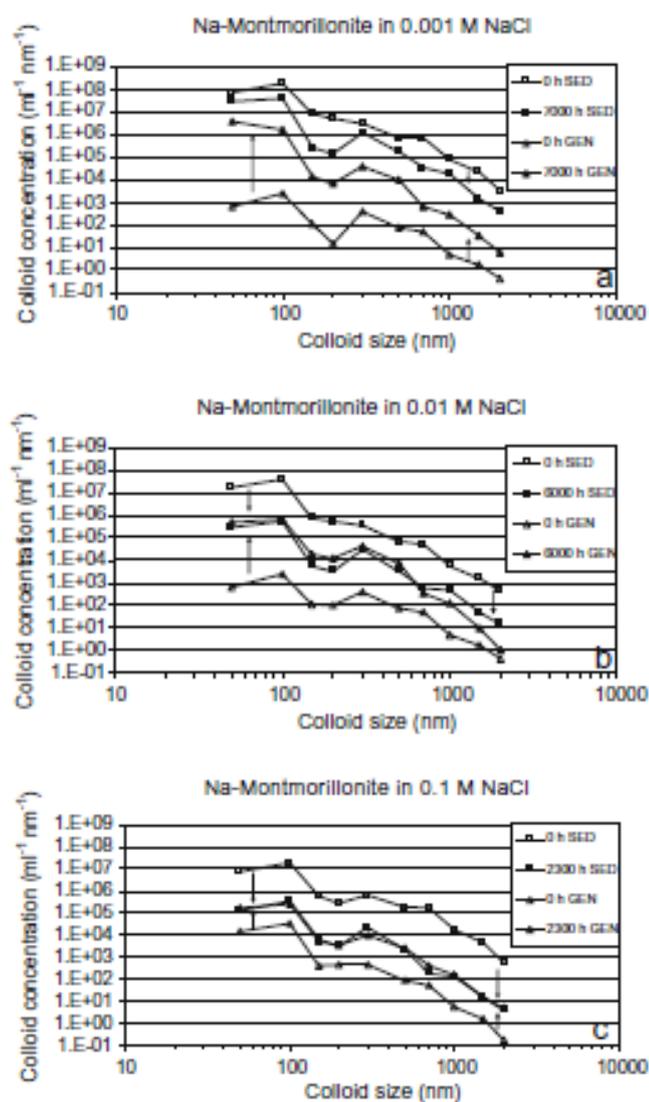


Fig. 6.1: Normalised size distribution of Na-montmorillonite (Wyoming) colloids for the initial (0 h) and final recorded stages in the colloid generation and sedimentation experiments toward pseudo-equilibrium profile. (a) 0.001 M NaCl for 7000 h, (b) 0.01 M NaCl for 6000 h, (c) 0.1 M NaCl for 2200 h (see GARCIA GARCIA et al. (2009)).

6.3 Other colloid activities

The environmental behaviour of colloidal clay in aquatic systems is linked to the properties of their aggregates. Earlier investigations of clay colloids were performed with electron microscope techniques which caused dehydration of the particles. These images are not representative of clay colloids occurring in aqueous systems because of this. Information on the structure of clay colloid aggregates is needed to understand their sedimentation behaviour, as well as colloid contaminant transport in natural systems. By using scanning transmission X-ray

microspectroscopy, images of montmorillonite colloid aggregates in a pseudo equilibrium state in a mM NaCl suspension after more than one year have been successfully produced (see Fig. 6.2).

These clay aggregates were revealed at photon energies below the oxygen absorption edges of clay and water. They were spherical or ellipsoidal in shape with sizes of ~100 to ~800 nm in diameter or axis (for ellipses the major axis ratio was a maximum of approximately 2). The aggregates looked porous, with densities lower than the clay mineral. Aggregates with cores of higher density material surrounded by a lower density gel like material were observed. These investigations are important for colloid generation modelling of clay aggregates in aqueous environments because colloids with sizes larger than 50 nm would readily sediment if they had a density of 2 g cm^{-3}

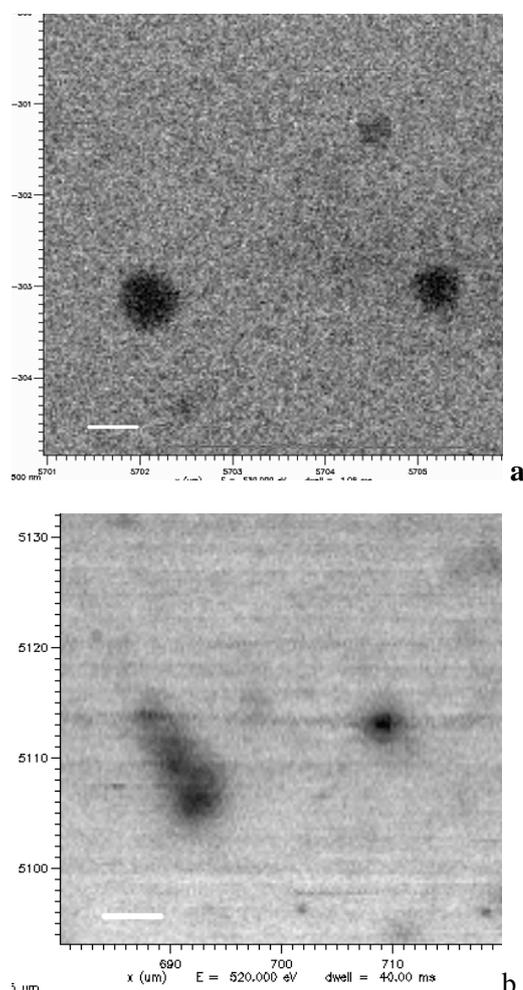


Fig. 6.2: X-ray micrograph of montmorillonite clay aggregate in 0.001 M (a), and in 0.1 M (b) NaCl. Conditions: bar scale 500 nm (a), 1000 nm (b). Note the heterogeneous aggregate structure in the NaCl concentrated suspension.

A co-operation with CIEMAT has started this year. The main aim is to optimise the radioanalytical work for measuring colloid breakthrough in the CFM experiment at the Grimsel Test Site. Colloid labeling was discussed, and it was decided that ^{68}Ge could be used. Since ^{68}Ge is a β^+ emitter, it can be used for breakthrough tests (in the lab and in-situ), and be detected by liquid scintillation and by PET during core breakthrough tests allowing a 3D reconstruction of the colloid pathway in laboratory experiments. The PET analysis is foreseen to be carried out at CIEMAT. A Spanish student will carry out the work of characterizing the colloids prior to, and after, ^{68}Ge labeling using the SPC units at LES.

6.4 Future work

CFM homologue tests are foreseen in early 2010, and SPC will be used together with other techniques to characterize the colloids during breakthrough in in situ experiments. During these tests the flow rate will be varied from one experiment to the next. For the CFM project, the generation of colloids at a bentonite bloc / groundwater flow interface with quasi-stagnant water is being studied from a mechanistic point of view. The LES in house colloid generation model will be used to systematically describe the colloid

generation during the main experiment which is in the process of being designed. Colloid size distributions from the bentonite source (obtained by direct re-suspension) will be compared with those from the groundwater system sampled during the experiment directly contacting FEBEX bentonite in the Grimsel Test Site.

The application of the advances made in groundwater colloid sciences over the last decade will allow colloid data to be derived for the hydrogeochemical systems in the argillaceous rock formations proposed by Nagra in the frame of the Sectoral Plan. A report/publication is foreseen which will include: groundwater colloid concentration results from field experiments from dilute to relatively salty groundwaters, comparison of concentration results with laboratory batch experiments, and the results of colloid adhesion tests (attachment factor values). The study will be completed by calculations of colloid concentrations in the relevant systems using the suspension pseudo-equilibrium model derived recently (DEGUELDRE et al. 2009). This field/lab and modelling study will provide the required colloid data for the new formations being investigated at NAGRA.

7 DIFFUSION PROCESSES

L.R. Van Loon, M.A. Glaus, W. Müller, S. Frick, N. Diaz

7.1 General

The focus of the activities in the “Diffusion Processes” group lies in i) understanding the diffusion of radionuclides in compacted argillaceous materials and ii) measuring diffusion parameters (effective diffusion coefficients and rock capacity values) that can be used in Performance Assessment studies. The clay systems currently under investigation are Opalinus Clay (OPA), and compacted clay minerals such as montmorillonite, illite and kaolinite.

The supporting laboratory diffusion studies for the long-term field diffusion experiment (DR) in Mont Terri were completed at the end of 2009. The modelling of the diffusion data is foreseen for 2010.

Members of the Diffusion Processes Group are co-proposers of two new PhD projects which started on September 1, 2009. Hao Wang (China) began a project on “Quantitative analysis of micro heterogeneous systems: A joint employment of complementary micro beam techniques“, in co-operation with Dr. D. Grolimund (Swiss Light Source, SLS) and Prof. D. Günther (Laboratory for Inorganic Chemistry, ETHZ). The project deals with the application of micro beam techniques for studying the diffusive behaviour of strongly sorbing tracers in heterogeneous systems. Martina Bestel (Germany) started a project on "Water dynamics in clays", in co-operation with Dr. F. Juranyi (Laboratory for Neutron Scattering, PSI) and Prof. L. Diamond (Uni Bern). The latter project deals with the study of the properties of confined water using neutron scattering techniques. Both projects are financed by the Swiss National Science Foundation (SNF).

A proposal for a new EU project (CatClay) was submitted and accepted by the European Commission. The project focuses on the diffusion of strongly sorbing radionuclides in argillaceous rocks.

On April 1, 2009 Dr. N. Diaz (France) joined the Laboratory for Waste Management as a post doc to work on a project to study micro-scale heterogeneities in clays and to implement such structures in a 3D transport model for compacted argillaceous materials. The project is jointly financed by PSI and CEA and is being carried out in co-operation with the Transport Mechanisms Group.

The work on pure clay minerals (TRAPHICCS) was continued. Extensive diffusion data sets for ^{85}Sr , ^{22}Na , ^{134}Cs , $^{36}\text{Cl}^-$ and $^{35}\text{SO}_4^{2-}$ in Na-montmorillonite, Na-illite and kaolinite under different chemical conditions are now available and are making a contribution to a better understanding of diffusion mechanisms/processes in clays.

7.2 Diffusion in Opalinus Clay

In the framework of the long-term diffusion/retention experiment (DR) in Mont Terri, supporting diffusion experiments are performed in LES. Diffusion measurements in Opalinus Clay of ^{85}Sr , ^{133}Ba and $^{75}\text{SeO}_4^{2-}$ were completed in 2009. The diffusion of ^{134}Cs is still ongoing and will be continued for at least one more year. Since 2007 we have studied the diffusion of HTO, D_2O , H_2^{18}O , $^{36}\text{Cl}^-$, Br^- , I^- , ^{22}Na , ^{85}Sr , ^{133}Ba and ^{134}Cs , for example see Fig. 7.1. Modelling the diffusion experiments with PHREEQC in combination with PEST, a model-independent parameter estimation and uncertainty analysis code (DOHERTY, 1994), was recently started and will be finished in the first quarter of 2010.

The diffusion of ^{134}Cs and ^{60}Co were studied using a gradient free diffusion set up in which the confining filters were advectively flushed.

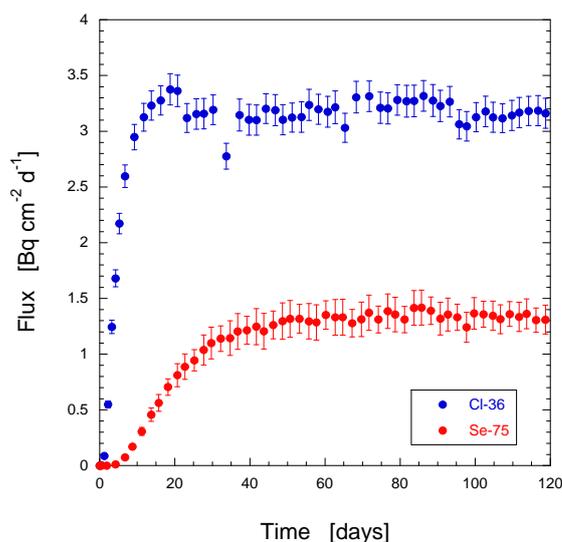
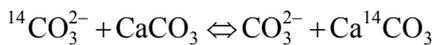
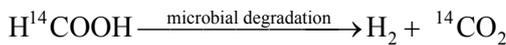


Fig. 7.1: Diffusion (flux vs. time) of $^{36}\text{Cl}^-$ and $^{75}\text{SeO}_4^{2-}$ in Opalinus Clay. Diffusion of $^{75}\text{SeO}_4^{2-}$ is slower than $^{36}\text{Cl}^-$ and can be explained by the factor of two lower diffusion coefficient of $^{75}\text{SeO}_4^{2-}$ in water (LI & GREGORY, 1974; $D_{w,\text{Cl}} = 2.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $D_{w,\text{Se}} = 9.46 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).

This set up reduces the strong effects of filters on the overall diffusion behaviour of the system (filter-clay-filter sandwich) and allows a more accurate determination of the diffusion properties of the clay. The dual porosity like behaviour observed in earlier experiments with ^{60}Co was confirmed, and the data indicated a faster than expected diffusion of ^{60}Co .

Through-diffusion measurements of ^{14}C labelled formate ($^{14}\text{CHOO}^-$: a potential product from the anaerobic corrosion of carbon steels) showed that formate was not stable in the OPA porewater under anaerobic conditions. Although the ^{14}C activity continuously decreased in the source reservoir, no break-through could be observed in the target reservoir after 150 days. Because sorption of formate on OPA is unlikely, a microbial transformation of formate to CO_3^{2-} and H_2 (SCHLEGEL, 1976), followed by an isotopic exchange of $^{14}\text{CO}_3^{2-}$ with the CO_3^{2-} present in calcite, is hypothesized:



Prevention of this microbial transformation by adding different antibacterial agents such as azide or chromate to the OPA/water system is currently being tried.

Compilation of diffusion data measured on different sedimentary rocks showed a relationship between the diffusion accessible porosity and the effective diffusion coefficient (Fig. 7.2). For a porosity value larger than 0.1, this relationship is known as Archie's Law. Below a porosity of 0.1, a deviation from Archie's Law is observed. An extended version of Archie's Law is needed to describe the relationship over the whole range:

$$D_e = D_w \cdot \varepsilon^m + A \cdot \varepsilon^n$$

with: D_w = diffusion coefficient in bulk water

$$m = 2.5 \text{ (min. value} = 2; \text{max. value} = 3.5)$$

$$A = 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ (min. value} = 5 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}; \text{max. value} = 2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1})$$

$$n = 0.85 \text{ (min. value} = 0.8; \text{max. value} = 0.9)$$

This extended relationship can be used to estimate the effective diffusion coefficient of radionuclides in sedimentary rocks without performing diffusion experiments. The only parameter required is the physical porosity. A more detailed study of this extended Archie's Law relationship and its predicting potential is currently under investigation.

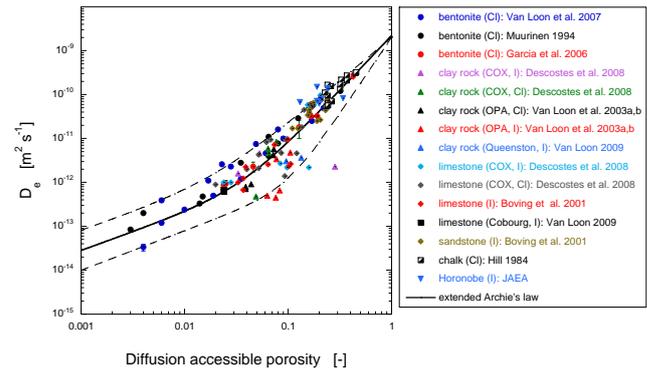


Fig. 7.2: Extended Archie's Law (solid line) describing the relationship between the diffusion accessible porosity and the effective diffusion coefficient for anions.

7.3 Use of micro-beam techniques for studying the diffusion of strongly sorbing tracers

The diffusive behaviour of strongly sorbing tracers in porous media may be (significantly) influenced by their micro-heterogeneity (spatial distribution of minerals and their nature). In order to improve our understanding on the behaviour of strongly sorbing radionuclides in heterogeneous porous systems, high-resolution techniques for measuring the spatial distribution of elements on a micrometer scale have to be used. This allows us to study the assembly structure and its chemical reactivity. On September 1, 2009, Hao Wang started a PhD on this topic. He will use laser-ablation/mass spectroscopy and micro-XRF to measure the elemental distribution in Opalinus Clay. The project is a co-operation between LES, Prof. D. Günther (ETHZ) and Dr. D. Grolimund (Swiss Light Source, SLS).

7.4 Assessment of heterogeneities (Amicam)

Since April 2009, a postdoc project on the assessment of heterogeneities on the microscopic scale and the implementation of such structures in a 3D transport model for compacted argillaceous materials has been running. The project is performed in close co-operation with the Transport Modelling Group. More details on the project can be found in Chapter 3 of this report.

7.5 Water dynamics in water-clay systems

Because diffusion takes mainly place in the aqueous phase (porewater) of the porous medium, it is very important to know the properties of confined water. On September 1, Martina Bestel started a PhD on this topic. The project is a continuation of a previous PhD

project (GONZÁLEZ, 2007) and will focus on the 2D water diffusion in the interlayer space of montmorillonite and on the effect of temperature, bulk dry density and cations on water diffusion by using neutron scattering techniques. The study will be performed in close co-operation with Prof. L. Diamond (University of Bern) and Dr. F. Juranyi (Laboratory for Neutron Scattering and SINQ).

7.6 Transport phenomena in compacted clay systems (TRAPHICCS)

A large part of the work carried out in the present year was dedicated to consolidating the diffusion data measured on Na-montmorillonite compacted to dry-bulk densities of 1300 and 1600 kg m⁻³. A substantial reduction of the uncertainties in the data could be achieved by the use of equipment with gradient-free advectively flushed confining filter plates, and by using filter plates with smaller pore sizes. In addition to this activity, diffusion experiments using bivalent anions, viz. SO₄²⁻ and SeO₄²⁻, were almost completed. No reliable experimental diffusion data are, as yet, available for Cs. It has now been definitely established that the through-diffusion technique using thin clay samples with thicknesses of ~1 mm is not suitable. A series of new experiments with Cs and Na-montmorillonite has been recently started. In these experiments the combined information of the decrease of the tracer in the source reservoir and its distribution across the clay sample will be analysed to obtain independent information on the effective diffusion coefficient and the rock capacity factor.

In the past years a large number of effective diffusion coefficients¹ (D_e) for differently charged tracers have been measured under various experimental conditions, i.e. variation of the degree of compaction and external salt concentration. Differences of up to four orders of magnitude between the D_e values for ³⁶Cl⁻ and ²²Na were observed in extreme cases. Such observations are not compatible with a simple pore diffusion model in which it is assumed that the D_e values in the porous medium are directly proportional to the respective diffusion coefficients in bulk water, D_w (2.0×10^{-9} m² s⁻¹ for Cl⁻ and 1.3×10^{-9} m² s⁻¹ for Na). It is therefore necessary to assume that the diffusion of charged species in expanding clays, such as montmorillonite, may be influenced by different pathways and controlled by different driving forces.

We have proposed a concept based on a volumetric tracer concentration gradient of "sorbed" cations in the interlayer as the driving force for cation diffusion (GLAUS et al., 2007) with the total porosity (interlayer and free water) being available for diffusion. For anions we assume that the tracer concentration in the external aqueous phase to be the driving force with a reduced porosity due to anion exclusion (VAN LOON et al., 2007). In some work submitted for publication (GLAUS et al., 2010) it has been shown that the diffusion coefficients obtained on the above approach can be related to the diffusion coefficients in bulk water (D_w) by a normalisation procedure taking into account the dependence of the pore diffusion coefficients (D_p) on the accessible porosity according to Archie's law:

$$D_p = A \cdot \varepsilon_{acc}^{m-1}$$

where A and m are material-specific constants and ε_{acc} is the accessible porosity. Details of this normalisation procedure can be found elsewhere (GLAUS et al., 2010). Fig. 7.3 shows the results obtained for the diffusion coefficients of HTO, ³⁶Cl⁻ and ²²Na in Na-conditioned illite and montmorillonite.

Although relatively large uncertainties are introduced by the normalisation procedure, the data are consistent, and show reasonable agreement of the D_p values for the three tracers with the order of their respective D_w values. Thus, it seems that the diffusion coefficients obtained from the different approaches given above for expanding clays can be re-expressed through a normalisation procedure in terms of the respective diffusion coefficients in bulk water.

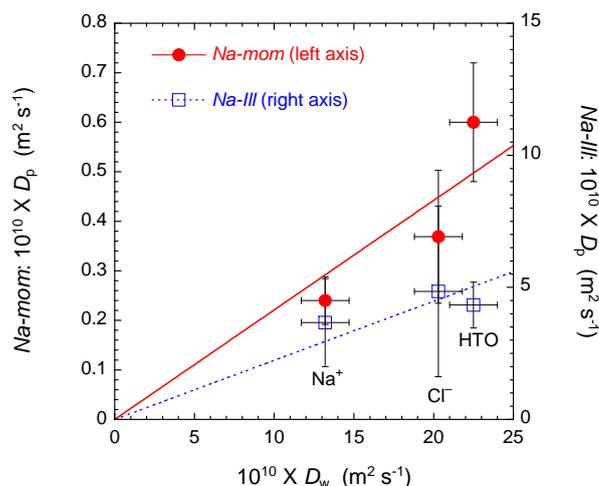


Fig. 7.3: Normalised pore diffusion coefficients (D_p) for the diffusion of HTO, ²²Na and ³⁶Cl⁻ in Na-montmorillonite (Na-mom) and Na-illite (Na-III) in comparison with the respective D_w values.

¹ defined in the present context as a proportionality between the tracer concentration gradient in the external electrolyte solution and the observed mass transfer rate

7.7 References

- BOVING T.B., GRATHWOHL P. (2001)
Tracer diffusion coefficients in sedimentary rocks: correlation to porosity and hydraulic conductivity. *J. Contam. Hydrol.* 53, 85-100
- DESCOSTES M., BLIN V., BAZER-BACHI F., MEIER P., GRENUT B., RADWAN J., SCHLEGEL M.L., BUSCHAERT S., COELHO D., TEVISSSEN E. (2008)
Diffusion of anionic species in Callovo-Oxfordian argillites and Oxfordian limestones (Meuse/Haute-Marne, France). *Appl. Geochem.* 23, 655-677
- DOHERTY J. (1994)
PEST, Model-independent parameter estimation. <http://www.sspa.com/pest/download.html> 808
- GARCÍA-GUTIÉRREZ M., CORMENZANA J.L., MISSANA T., MINGARRO M., MOLINERO J. (2006)
Overview of laboratory methods employed for obtaining diffusion coefficients in FEBEX compacted bentonite. *J. Iberian Geol.* 32, 37-53
- GLAUS M., BAEYENS B., BRADBURY M.H., JAKOB A., VAN LOON L.R., YAROSHCHUK A. (2007)
Diffusion of ^{22}Na and ^{85}Sr in montmorillonite: Evidence of interlayer diffusion being the dominant pathway at high compaction. *Environ. Sci. Technol.* 41, 478-485
- GLAUS M., FRICK S., ROSSÉ R., VAN LOON L.R.
Comparative study of tracer diffusion of HTO, $^{22}\text{Na}^+$ and $^{36}\text{Cl}^-$ in compacted kaolinite, illite and montmorillonite. *Geochim. Cosmochim. Acta* (in press).
- GONZÁLEZ F. (2007).
Water diffusion through compacted clays analyzed by neutron scattering and tracer experiments. PhD. Thesis, University of Bern, Switzerland
- HILL D. (1984).
Diffusion coefficients of nitrate, chloride, sulphate and water in cracked and uncracked Chalk. *J. Soil Sci.* 35, 27-33
- LI Y.-H, GREGORY S. (1974)
Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta* 38, 703-714
- MADSEN F.T., KAHR G. (1993)
Diffusion of ions in compacted bentonite. *Proc. Int. Conf. Nuclear Waste Management and Environmental Remediation*, 239-246
- MUURINEN A., RANTANEN J., PENTTILÄ-HILTUNEN P. (1985)
Diffusion mechanisms of strontium, cesium and cobalt in compacted sodium bentonite. *Mater. Res. Soc. Symp. Proc.* 50, 617-624
- SCHLEGEL H.G. (1976)
Allgemeine Mikrobiologie, 4. Edition, Georg Thieme Verlag, Stuttgart
- VAN LOON L.R., SOLER J.M., BRADBURY M.H. (2003a)
Diffusion of HTO, $^{36}\text{Cl}^-$ and $^{125}\text{I}^-$ in Opalinus Clay samples from Mont Terri. Effect of confining pressure. *J. Contam. Hydrol.* 61, 73-83
- VAN LOON L.R., SOLER J.M., JAKOB A., BRADBURY M.H. (2003b)
Effect of confining pressure on the diffusion of HTO, $^{36}\text{Cl}^-$ and $^{125}\text{I}^-$ in a layered argillaceous rock (Opalinus Clay): diffusion perpendicular to the fabric. *Appl. Geochem.* 18, 1653-1662
- VAN LOON L.R., MUELLER W., GLAUS M. (2007)
Anion exclusion effects in compacted bentonites: towards a better understanding of anion diffusion. *Appl. Geochem.* 22, 2536-2552

8 PUBLICATIONS

8.1 Peer reviewed journals and reports

BESSHO K., DEGUELDRE C. (2009)

Generation and sedimentation of colloidal bentonite particles in water. *Appl. Clay Sci.* 43, 253-259

BRADBURY M.H., BAEYENS B. (2009)

Sorption modelling on illite. Part I: Titration measurements and the sorption of Ni, Co, Eu and Sn. *Geochim. Cosmochim. Acta* 73, 990-1003

BRADBURY M.H., BAEYENS B. (2009)

Sorption modelling on illite. Part II Actinide sorption and linear free energy relationships. *Geochim. Cosmochim. Acta* 73, 1004-1013

BRADBURY M.H., BAEYENS B. (2009)

Experimental and modelling studies on the pH buffering of MX-80 bentonite porewater. *Appl. Geochem.* 24, 419-425

CHURAKOV S.V. (2009)

Structural position of H₂O molecules and hydrogen bonding in anomalous 11 Å tobermorite. *Amer. Mineral.* 94, 156-166

CHURAKOV S.V. (2009)

Structure of the interlayer in normal 11 Å tobermorite from an ab initio study. *Eur. J. Mineral.* 21, 261-271

CURTI E., DÄHN R., FARGE S.F.^{1,2}, VESPA M. (2009)

Na, Mg, Ni and Ca distribution and speciation after long-term alteration of simulated nuclear waste glass: A micro-XAS/XRF/XRF and wet chemical study. *Geochim. Cosmochim. Acta* 73, 2283-2298

¹ Museum Natl Hist Nat, Paris, France

² Stanford University, Stanford, USA

DEGUELDRE C., BOLEK M.¹ (2009)

Modelling plutonium association onto model colloids: the effect of pH and redox potential. *Appl. Geochem.* 24, 310-318

¹ EPFL, Lausanne, Switzerland

DEGUELDRE C., AEBERHARD P., KUNZE P., BESSHO K. (2009)

Colloid generation/elimination dynamic processes: toward a pseudo-equilibrium. *Coll. Surf. A* 33, 117-126

DEGUELDRE C., RAABE J., WOLD S.¹ (2009)

Morphologic investigations of clay colloid aggregates by scanning transmission X-ray microspectroscopy. *Earth Planet. Sci. Lett.* 24, 2015-2018

¹ KTH, Stockholm, Sweden

GARCIA GARCIA S.¹, DEGUELDRE C., FRICK S., WOLD S.¹ (2009)

Determining pseudo-equilibrium of montmorillonite colloids in generation and sedimentation experiments. *Sci. Tot. Environ.* 335, 54-61

¹ KTH, Stockholm, Sweden

GONZÁLEZ SÁNCHEZ F., GIMMI T., JURANYI F., VAN LOON L.R., DIAMOND L.¹ (2009)

Linking the diffusion of water in compacted clays at two different time scales: tracer through-diffusion and quasielastic neutron scattering. *Environ. Sci. Technol.* 43, 3487-3493

¹ Universität Bern, Switzerland

HUBER F.¹, KIENZLER B.¹, LÜTZENKIRCHEN J.¹, PFINGSTEN W., TIFFREAU C.² (2009)

Karlsruher Geochemical Workshop TRePro II 2009: Workshop on Modelling of Coupled Transport Reaction Processes. *atw - Internationale Zeitschrift für Kernenergie* 54, 478-479

¹ FZK, Karlsruhe, Germany

² Centre d'Etudes de Cadarache, St Paul lez Durance, France:

JAKOB A., PFINGSTEN W., VAN LOON L.R., (2009)

Effects of sorption competition on caesium diffusion through compacted argillaceous rock. *Geochim. Cosmochim. Acta* 73, 2441-2456

JURANYI F., GONZÁLEZ SÁNCHEZ F., GIMMI T., VAN LOON L.R., DIAMOND L.¹ (2009)

Linking the diffusion of water in clays at different time and length scales: insights from quasielastic neutron scattering and tracer through-diffusion. *Swiss Neutron News* 35, 4-9

¹ Universität Bern, Switzerland

KOSAKOWSKI G., BLUM P.¹, KULIK D., PFINGSTEN W., SHAO H.², SINGH A. (2009)

Evolution of a generic clay/cement interface. First reactive transport calculations utilizing a Gibbs energy minimization based approach for geochemical calculations. *J. Environ. Sci. Sustainable Soc.* 3, 41-49

¹ Universität Tübingen, Germany

² Helmholtz Centre for Environmental Research, Leipzig, Germany

MANDALIEV P., DÄHN R., WEHRLI B.¹, WIELAND E. (2009)

Macro- and microspectroscopic study of Nd(III) uptake mechanisms in hardened cement paste. *Environ. Sci. Technol.* 43, 8462-8468

¹ ETH, Zürich, Switzerland

MARQUES FERNANDES M., STUMPF T.¹, BAEYENS B., WALTHER C.¹, BRADBURY M.H. (2009)

Spectroscopic identification of ternary Cm-carbonate surface complexes. *Environ. Sci. Technol.* online

¹ FZK, Karlsruhe, Deutschland

MCDERMOTT C.¹, WALSH R.², METTIER R.³, KOSAKOWSKI G., KOLDITZ O.⁴ (2009)

Hybrid analytical and finite element numerical modelling of mass and heat transport in fractured rocks with matrix diffusion. *Comput. Geosci.* 13, 349-361

¹ University of Edinburgh, Midlothian, UK

² INTERA, Ottawa, Canada

³ Universität Bern, Switzerland

⁴ Helmholtz Centre for Environmental Research, Leipzig, Germany

PEKALA M.¹, KRAMERS J.D.¹, WABER H.N.¹, GIMMI T., ALT-EPPING P.¹ (2009)

Transport of ²³⁴U in the Opalinus Clay at centimetre to decimetre scales. *Appl. Geochem.* 24, 138-152

¹ Universität Bern, Switzerland

POPOV D., BULÉON A.¹, BURGHAMMER M.², CHANZY H.³, MONTESANTI N.³, PUTAUX J-L.³, POTOCKI-VÉRONÈSE G.⁴, RIEKEL C.² (2009)

Crystal structure of A-amylose: a revisit from synchrotron microdiffraction analysis of single crystals. *Macromolecules* 42, 1167-1174

¹ INRA, France

² ESRF, Grenoble, France

³ CERMAV-CNRS, Grenoble, France

⁴ LISBP, Toulouse, France

PURANEN A.¹, JONSSON M.¹, DÄHN R., CUI D.² (2009)

Immobilization of selenate by iron in aqueous solution under anoxic conditions and the influence of uranyl. *J. Nucl. Mat.* 392, 519-524

¹ KTH, Stockholm, Sweden

² Studsvik Nucl AB, Nyköping, Sweden

RIEKEL C.¹, BURGHAMMER M.¹, DAVIES R.¹, GEBHARDT R.¹, POPOV D. (2009)

Fundamentals of soft condensed matter diffraction with microfocus techniques. *Lecture Notes in Physics.* Chapter 91-104

¹ ESRF, Grenoble, France

ROZOV K., BERNER U., TAVIOT-GUEHO C.¹, LEROUX F.¹, RENAUDIN G.¹, KULIK D.A., DIAMOND L.W.² (2009)

Synthesis and characterization of the LDH hydroxalcite-pyroaurite solid-solution series. *Cem. Concr. Res. CEMCON-04007*, online

¹ CNRS UMR 6002, Université Blaise Pascal, Aubière, France

² Universität Bern, Switzerland

SHAO H.¹, DMYTRIEVA S.V.², KOLDITZ O.¹, KULIK D.A., PFINGSTEN W., KOSAKOWSKI G. (2009)

Modelling reactive transport in a non-ideal aqueous - solid solution system. *Appl. Geochem.* 24, 1287-1300

¹ Helmholtz Centre for Environmental Research, Leipzig, Germany

² SSE Technocentre, Kyiv, Ukraine

SHAO H.¹, KULIK D.A., BERNER U., KOSAKOWSKI G., KOLDITZ O.¹ (2009)

Modeling the competition between solid solution formation and cation exchange on the retardation of aqueous radium in an idealized bentonite column. *Geochem. J.* 43, 37-42

¹ Helmholtz Centre for Environmental Research, Leipzig, Germany

VAN LOON L.R., BAEYENS B., BRADBURY M.H. (2009)

The sorption behaviour of caesium on Opalinus Clay: A comparison between intact and crushed material. *Appl. Geochem.* 24, 999-1004

VOLKRINGER C.¹, LOISEAU T.¹, GUILLOU N.¹, FERREY G.¹, HAOUAS M.¹, TAULELLE F.¹, AUDEBRAND N.², MARGIOLAKI I.³, POPOV D., BURGHAMMER M.³, RIEKEL C.³ (2009)

Structural transitions and flexibility during dehydration-rehydration process in the MOF-type aluminum pyromellitate Al₂(OH)₂[C₁₀O₈H₂] (MIL-118). *Cryst. Growth Des.* 9, 2927-2936

¹ Institut Lavoisier, Versailles, France

² Université de Rennes, France

³ ESRF, Grenoble, France

WANG W.¹, KOSAKOWSKI G., KOLDITZ O.¹ (2009)

A parallel finite element scheme for thermo-hydro-mechanical (THM) coupled problems in porous media. *Comput. Geosci.* 35, 1631-1641

¹ Helmholtz Centre for Environmental Research, Leipzig, Germany

WU T.¹, AMAYRI S.¹, DREBERT J.¹, VAN LOON L.R., REICH T.¹ (2009)

Neptunium(V) sorption and diffusion in Opalinus Clay. *Environ. Sci. Technol.* 43, 6567-6571

¹ Johannes Gutenberg Universität Mainz, Germany

YAROSHCHUK A.E.¹, GLAUS M.A., VAN LOON L.R. (2009)

Determination of diffusion and sorption parameters of thin confined layers by direct fitting of through-diffusion flux. *J. Colloid Interface Sci.* 337, 508-512

¹ University of Catalonia, Barcelona, Spain

8.2 Publications in books

KULIK D.A. (2009)

Thermodynamic concepts of modeling sorption at the mineral-water interface. In: *Thermodynamics and Kinetics of Water-Rock Interaction* (Eds. E. Oelkers, J. Schott), *Reviews in Mineral. Geochem.* 70, 125-180

8.3 Conference proceedings

LOTHENBACH B.¹, WIELAND E., FIGI R.¹, RENTSCH, D.¹, SCHWYN B.²

Hydration of blended cements. 17. Internationale Baustofftagung (ibausil), Weimar, Germany, 23-25 September 2009, *Tagungsbericht Band 1*, 213-218

¹ Empa, Dübendorf, Switzerland

² Nagra, Wettingen, Switzerland

POPOV D., DÄHN R., GROLIMUND D., PATTISON P.^{1,2}, WIELAND E.

Application of X-ray micro-diffraction techniques for characterizing cement materials. 17. Internationale Baustofftagung (ibausil), Weimar, Germany, 23-25 September 2009, Tagungsbericht Band 2, 135-140

¹ EPFL, Lausanne, Switzerland

² ESRF/SNBL, Grenoble, France

8.4 Conference/Workshop Presentations

AL T.¹, XIANG Y.¹, CAVÉ L.¹, LOOMER D.¹, VILKS P.², VAN LOON L.R.

Diffusion measurements in low-permeability Ordovician sedimentary rocks from southern Ontario. Joint Assembly American Geophysical Union (AGU2009), Toronto, Canada, 24-27 May 2009

¹ University of New Brunswick, Canada

² Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada

ALTMANN S.¹, TOURNASSAT C.², GOUTELARD F.³, PARNEIX J.C.¹, GIMMI T., MAES N.⁴

Radionuclide migration in clay rock host formations for deep geological disposal of radioactive waste: advances in process understanding and up-scaling methods resulting from the EC integrated project FUNMIG. General Assembly European Geosciences Union, Vienna, Austria, 19-24 April 2009

¹ Andra, Chatenay Malabry, France

² BRGM, Orleans, France

³ CEA Saclay, Gif Sur Yvette, France

⁴ SCK-CEN, Mol, Belgium

AMAYRI S.¹, FRÖHLICH D.¹, WU T.¹, DREBERT J.¹, VAN LOON L.R., REICH T.¹

Sorption and diffusion behaviors of neptunium(V) in Opalinus Clay. Migration 09 Conference, Kennewick WA, USA, 20-25 September 2009

¹ Johannes Gutenberg Universität Mainz, Germany

AMAYRI S.¹, FRÖHLICH D.¹, WU T.¹, DREBERT J.¹, VAN LOON L.R., REICH T.¹

Untersuchung der Sorption und Diffusion von Neptunium(V) in Opalinuston. Wissenschaftsforum Chemie GDCh2009, Frankfurt am Main, Germany, 30 August–2 September 2009

¹ Johannes Gutenberg Universität Mainz, Germany

APPELO C.A.J.¹, WERSIN P.^{2,3}, VAN LOON L.R., DEWONCK S.⁴

Modeling cesium diffusion in a claystone formation. Goldschmidt 09 Conference, Davos, Switzerland, 21-26 June 2009

¹ Hydrochemical Consultant, Amsterdam, The Netherlands

² Nagra, Wettingen, Switzerland

³ Gruner AG, Basel, Switzerland

⁴ Andra, Bure, France

DÄHN R., MACÉ N., POPOV D., SHUH D.K.¹, WIELAND E.

Determination of the speciation of radionuclides in cementitious materials by micro-XRF/XAS/XRD and STXM. XAFS XIV. 14th International Conference on X-ray absorption fine structure, Camerino, Italy, 26–31 July, 2009

¹ LBNL, Berkeley, USA

DIAZ N., JAKOB A., VAN LOON L.R., GROLIMUND D. Modeling contaminant diffusion in highly complex rock structures. COMSOL Conference, Milano, Italy 14-16 October, 2009

DILNESA B.Z.¹, WIELAND E., LOTHENBACH B.¹, DÄHN R., SCRIVENER K.L.²

X-ray absorption spectroscopy investigation of iron phases, Fred Glasser Cement Science Symposium, Aberdeen, Scotland, 17–18 June 2009

¹ Empa, Dübendorf, Switzerland

² EPFL, Lausanne, Switzerland

GAONA X., TITS J., WIELAND E.

Uptake of Np by cementitious materials: redox behavior of Np(IV/V) under hyperalkaline conditions, Actinides Conference 2009, San Francisco, USA, 12-17 July 2009

GAONA X., KULIK D.A., TITS J., MACÉ N., WIELAND E.

Aqueous-solid solution model of U(VI) uptake in C-S-H phases, Actinides Conference 2009, San Francisco, USA, 12-17 July 2009

GAONA X., POPOV D., DÄHN R., TITS J., GROLIMUND D., BORCA C., WIELAND E.

Micro-spectroscopic and micro-diffraction study on Np(IV) uptake by cementitious materials. JUM@P'09 Joint Users' Meeting at PSI, Villigen, Switzerland, 12-13 October 2009

GIMMI T.¹, LEUPIN O.X.², VAN LOON L.R., WERSIN P.³, BAEYENS B., EIKENBERG J., SOLER J.M.⁴, SAMPER J.⁵, RÜBEL A.⁶, DEWONCK S.⁷, SAVOYE S.⁸, YI S.⁵, NAVES A.⁵

A field-scale solute diffusion and retention experiment in Opalinus Clay: Processes, parameters, sensitivities. General Assembly European Geosciences Union, Vienna, Austria, 19-24 April 2009

¹ Universität Bern, Switzerland

² Nagra, Wettingen, Switzerland

³ Gruner AG, Basel, Switzerland

⁴ CSIC-IJA, Barcelona, Spain

⁵ University of La Coruña, Spain

⁶ GRS, Germany

⁷ Andra, Bure, France

⁸ IRSN, Fontenay-aux-Roses, France

GIMMI T., CHURAKOV S.

Hierarchical modelling of solute diffusion in clays: From the molecular to the continuum scale. General Assembly European Geosciences Union, Vienna, Austria, 19-24 April 2009

GONZALEZ SANCHEZ F., GIMMI T., JURANYI F., VAN LOON L.R., KOSAKOWSKI G., UNRUH T.¹

Diffusion of water in compacted clays at different time scales. 9th International Conference on Quasielastic Neutron Scattering, QENS 2009, Paul Scherrer Institut, Villigen, Switzerland, 10-13 February 2009

¹ Forschungsneutronenquelle Heinz Maier-Leibnitz, Garching, Germany

GONZÁLEZ SÁNCHEZ F., GIMMI T., JURANYI F., VAN LOON L.R., UNRUH T.¹, DIAMOND L.W.²

Comparison of water diffusion in clays at microscopic and macroscopic scales. 9th International Conference on Quasielastic Neutron Scattering, QENS 2009, Paul Scherrer Institut, Villigen, Switzerland, 10-13 February 2009

¹ Forschungsneutronenquelle Heinz Maier-Leibnitz, Garching, Germany

² Universität Bern, Switzerland

GROLIMUND D., GÜNTHER D.¹, BORCA C.N., WANG H., VAN LOON L.R., STAMPANONI M., MARONE F., MOKSO R., DIAZ N., JAKOB A., BARMETTLER K.¹, AESCHLIMANN B.¹, WERSIN P.², HEALD S.M.³

Evolution of reactive transport plumes – decipher physico-chemical micro-complexity using micro-spectroscopy, chemical micro-imaging, and micro-tomography. Optics and Microanalysis (IXCOM2009), Karlsruhe, Germany, 14-18 September 2009

¹ ETH, Zurich, Switzerland

² Gruner AG, Basel, Switzerland

³ Advanced Photon Source, Argonne, USA

GROLIMUND D., GÜNTHER D.¹, BORCA C.N., VAN LOON L.R., STAMPANONI M., MARONE F., BARMETTLER K.¹, AESCHLIMANN B.¹, WERSIN P.², HEALD S.M.³

Contaminant transport in complex heterogeneous geological media: new insights through micro-imaging and micro-spectroscopy. Goldschmidt 09 Conference, Davos, Switzerland, 21-26 June 2009

¹ ETH, Zürich, Switzerland

² Gruner AG, Basel, Switzerland

³ Advanced Photon Source, Argonne, USA

HINGERL F.F., KOSAKOWSKI G., KULIK D.A., DMYTRIEVA S.V.¹, DRIESNER T.², THOMSEN K.³

Modelling fluid-rock interaction and scale formation during geothermal heat extraction. Workshop TRePro 2, Karlsruhe, Germany, 17-19 March 2009

¹ SSE Technocentre, Kyiv, Ukraine

² ETH, Zurich, Switzerland

³ Technical University of Denmark, Lyngby, Denmark

KITAMURA A., CURTI E., AIMOZ L.

Reductive sorption of Se(IV,VI) onto pyrite: a μ -XRF/XAS study. Goldschmidt 09 Conference, Davos, Switzerland, 21-26 June 2009

KOSAKOWSKI G., KULIK D.A., SHAO H.¹, DMYTRIEVA S.V.², KOLDITZ O.¹

Numerical modeling of the evolution for a generic clay/cement interface. General Assembly European Geosciences Union, Vienna, Austria, 19-24 April 2009

¹ Helmholtz Centre for Environmental Research, Leipzig, Germany

² SSE Technocentre, Kyiv, Ukraine

KULIK D.A.

Joint DMG, DGK and Helmholtz Virtual Institute "Advanced Solid-Aqueous Radiogeochemistry" Workshop "From atomistic calculations to thermodynamic modelling", Institute of Geosciences at the Universität Frankfurt, Frankfurt-am-Main, Germany, 23-27 February 2009

KULIK D.A., VINOGRAD V.L.¹, PAULSEN N.¹, WINKLER B.¹

(Ca,Sr)CO₃ aqueous- solid solution systems: from atomistic calculations to geochemical modeling. Migration 09 Conference, Kennewick WA, USA, 20-25 September 2009

¹ Universität Frankfurt, Frankfurt-am-Main, Germany

KULIK D.A., WAGNER T.¹, CHUDNENKO K.V.², DMYTRIEVA S.V.³, HINGERL F.F., BERNER U., KOSAKOWSKI G. (2009)

GEMIPM2K: A standalone solver of complex chemical equilibria for application in radiogeochemical coupled modeling codes. Migration 09 Conference, Kennewick WA, USA, 20-25 September 2009.

¹ ETH Zurich, Switzerland

² A.P.Vinogradov Inst. of Geochem., Irkutsk, Russian

³ SSE Technocentre, Kyiv, Ukraine

MACÉ N., WIELAND E., DÄHN R., TITS J., SCHEINOST A.C.^{1,2}, STUMPF T.³, WALTHER C.³

Determination of the local coordination environment of U(VI) sorption species on cementitious materials under alkaline conditions, MRS'09. 33rd International Symposium "Scientific Basis for Nuclear Waste Management", Saint Petersburg, Russia, 24-29 May 2009

¹ FZD, Dresden, Germany

² ESRF, Grenoble, France

³ FZK, Karlsruhe, Germany

MÄDER U.¹, GIMMI T.

Reactive transport modelling of a long-term core infiltration experiment with claystone. Goldschmidt 09 Conference, Davos, Switzerland, 21-26 June 2009

¹ Universität Bern, Switzerland

MARQUES FERNANDES M., BAEYENS B., STUMPF TH.¹, DÄHN R., BRADBURY M.H.

The influence of carbonate complexation on actinides sorption on clay minerals. Migration 09 Conference, Kennewick WA, USA, 20-25 September 2009

¹ FZK, Karlsruhe, Germany

POPOV D., DÄHN R., GROLIMUND D., PATTISON P.^{1,2}, WIELAND E.

Identification of crystalline phases of cements using X-ray microdiffraction techniques, 25th European Crystallographic Meeting, Istanbul, Turkey, 16-21 August 2009

¹ EPFL, Lausanne, Switzerland

² ESRF/SNBL, Grenoble, France

POPOV D., DÄHN R., GROLIMUND D., PATTISON P.^{1,2}, WIELAND E.

Application of X-ray micro-diffraction techniques for characterizing cement materials, 20th International Congress on X-ray Optics and Microanalysis, Karlsruhe, Germany, 14-18 September 2009

¹ EPFL, Lausanne, Switzerland

² ESRF/SNBL, Grenoble, France

POPOV D., DÄHN R., GROLIMUND D., PATTISON P.^{1,2}, WIELAND E.

X-ray micro-diffraction studies on cementitious materials. JUM@P'09: Joint Users' Meeting at PSI, Villigen, Switzerland, 12-13 October 2009

¹ EPFL, Lausanne, Switzerland

² ESRF/SNBL, Grenoble, France

POPOV D., DÄHN R., GROLIMUND D., PATTISON P.^{1,2}, MAEDER U.³, GAONA J., WIELAND E.

Application of X-ray micro-diffraction at the SLS microXAS beamline for the characterization of complex matrices. JUM@P'09: Joint Users' Meeting at PSI, Villigen, Switzerland 12-13 October 2009

¹ EPFL, Lausanne, Switzerland

² ESRF/SNBL, Grenoble, France

³ Universität Bern, Switzerland

REICH T.¹, AMAYRI S.¹, WENDT S.¹, BAEYENS B., DÄHN R., BRADBURY M.H., SCHEINOST A.C.², Spectroscopic study and surface complexation modelling of Np(V) sorption on montmorillonite. Migration 09 Conference, Kennewick WA, USA, 20-25 September 2009

¹ Johannes Gutenberg Universität Mainz, Germany

² FZD, Dresden, Germany

REICH T.¹, AMAYRI S.¹, FRÖHLICH D.¹, DREBERT J.¹, VAN LOON L.R., WU T.¹

Sorption and diffusion of Np(V) in Opalinus Clay. Goldschmidt 09 Conference, Davos, Switzerland, 21-26 June 2009

¹ Johannes Gutenberg Universität Mainz, Germany

ROBINET J.-C.¹, SARDINI P.², ALTMANN S.¹, VAN LOON L.R.

A multi-scale evaluation of the effects of mineral-porosity spatial variability on solute diffusion in clayrock geological formations considered for hosting repositories for radioactive waste. Migration 09 Conference, Kennewick WA, USA, 20-25 September 2009. Abstract No. PB2-15, 103-104

¹ Andra, Chatenay-Malabry, France

² Hydrasa, Poitiers, France

ROZOV K., BERNER U., KULIK D.A. (2009)

Solubility measurements of hydrotalcite-like solid solutions. Goldschmidt 2009 Conference, 21-26 June, 2009, Davos, Switzerland. Geoch. Cosmoch. Acta 73, A1128

SHAO H.¹, KOSAKOWSKI G., KULIK D.A., KOLDITZ O.¹

Modelling combined effects of solid solution formation and cation-exchange on the retardation of aqueous radium. 7th International Conference on Calibration and Reliability in Groundwater Modelling "Managing Groundwater and the Environment" Wuhan, China, 20-23 September 2009

¹ Helmholtz Centre for Environmental Research, Leipzig, Germany

SHAO H.¹, KOSAKOWSKI G., KULIK D.A., KOLDITZ O.¹

Modelling retardation effects by barium and strontium solid solutions on radium cations in the near field of radioactive waste repository. Workshop TRePro 2, Karlsruhe, Germany, 17-19 March 2009

¹ Helmholtz Centre for Environmental Research, Leipzig, Germany

SENTIS M.L.¹, ALTORFER F.¹, KOSAKOWSKI G.

Benchmark calculations with Tough2-EOS9nT of the transport of nuclides through clay and bentonite barriers in a geological repository. Tough symposium 2009, Berkeley, USA, 14-16 September 2009

¹ ENSI, Villigen, Switzerland

SENTIS M.L.¹, ALTORFER F.¹, HERFORT M.¹, JAKOB A., KOSAKOWSKI G., FRIEDEL S.²

Benchmark calculations with COMSOL of the Transport of Radionuclides through clay and bentonite barriers in a geological repository. COMSOL Conference, Milano, Italy, 14-16 October 2009

¹ ENSI, Villigen, Switzerland

² COMSOL, Zürich, Switzerland

TITS J., GAONA X., DÄHN R., POPOV D., WIELAND E.

Immobilization of neptunium in cementitious repository environments, NEA Workshop "Cementitious materials as safety case for geological repositories for radioactive waste: Role, evolution, interpretation", Brussels, Belgium, 17-19 November 2009

VAN LOON L.R., BAEYENS B., BRADBURY M.H.
The sorption behaviour of caesium on Opalinus Clay – a comparison between intact and crushed material. Migration 09 Conference, Kennewick WA, USA, 20-25 September 2009

VAN LOON L.R.
A semi-empirical approach for estimating effective diffusion coefficients in sedimentary rocks for safety assessment purposes. Migration 09 Conference, Kennewick WA, USA, 20-25 September 2009

VINOGRAD V.L.¹, KULIK D.A., PINA C.M.², FERNANDEZ GONZALEZ A.³, PRIETO M.³, WINKLER B.¹ (2009)
(Ba,Sr)SO₄ solid solution – aqueous solution system: Atomistic calculations and experimental constraints. Migration 09 Conference, Kennewick WA, USA, 20-25 September 2009

¹ Universität Frankfurt, Frankfurt-am-Main, Germany

² Complutense University of Madrid, Spain

³ University of Oviedo, Spain

8.5 Invited talks

CHURAKOV S., GIMMI T.
Up-scaling of molecular diffusion coefficients in clays: A two scale approach. TRePro II Workshop, Karlsruhe, Germany, 18-19 March 2009

CHURAKOV S.
Ab initio molecular dynamics simulations of clay minerals. 14th International Clay Conference Castellana Marina, Italy, 14-20 June 2009

LOTHENBACH B.¹, WIELAND E.
Chemical evolution of cementitious materials, NEA Workshop, Cementitious materials as safety case for geological repositories for radioactive waste: Role, evolution, interpretation, Brussels, 17–19 November 2009

¹Empa, Dübendorf, Switzerland

8.6 Other presentations

DEGUELDRE C.
Colloid analysis in a single particle mode: status of results at PSI and outlook for phase II. ISCO Meeting, Brienz, 23-24 June 2009

DEGUELDRE C.
Caracterización de coloides con análisis de partículas singulares: hoy y mañana. CIEMAT colloid Meeting, Madrid, 14 October 2009

DEGUELDRE C.
Generación y sedimentación de coloides de bentonita en agua. CIEMAT colloid Meeting, Madrid, 15 October 2009

GAONA X., MONTOYA V.¹, COLÀS E.¹, GRIVÉ M.¹, DURO L.¹

Thermodynamics of An(IV)-ISA and An(IV)-GLU complexes under hyper-alkaline conditions, Institut für Nukleare Entsorgung, Karlsruhe Institute of Technology, Germany, 10 September 2009

¹AMPHOS, Barcelona, Spain

GLAUS M.A.
Diffusion of charged species in swelling clays: Status at PSI. EBS Taskforce Meeting, Stockholm, 25-26 May 2009

GLAUS M.A.
Diffusion of cations and anions: Comparison of different clays. Swiss Bentonite Meeting, Bern, Switzerland, 8 June 2009

8.7 Other reports

MAZUREK M.¹, ALT-EPPING P.¹, BATH A.¹, GIMMI T., WABER H.N.¹ (2009)

Natural tracer profiles across argillaceous formations: The CLAYTRAC project. NEA Report #06253, OECD Publishing

¹ Universität Bern, Switzerland

WABER H.N.¹, GIMMI T., DE HALLER A., SMELLIE J.A.T. (2009)

Porewater in the rock matrix, site descriptive modelling, SDM-Site Laxemar. SKB Report R-08-112, Stockholm, Sweden, ISSN 1402-3091, 99p.

¹ Universität Bern, Switzerland

WABER H.N.¹, GIMMI T. (2009)
Out-Diffusion Experiments. In: Waber, H.N. (ed.), Borehole Oftringen: Mineralogy, porosimetry, geochemistry, porewater chemistry. NAB 08-18

¹ Universität Bern, Switzerland

8.8 Internal presentations

GLAUS M.A.
Diffusion of radionuclides in pure clay minerals status and prospects

MACÉ N.
Micro-scale investigations of the speciation and mobility of uranium in cementitious materials

POPOV D.
Application of micro-diffraction techniques for characterizing cement materials

VAN LOON L.R.
Diffusion of radionuclides in argillaceous materials: status and prospects

8.9 Others/Teachings

GIMMI T.

Geochemical Modelling II: Reactive Transport within the frame of the course for “Master of Environmental and Resource Geochemistry”. Universität Bern, Switzerland, Spring Semester 2009

JOHNSON A., HUMMEL W., PLÖTZE L.M.

Landfilling, nuclear repositories and contaminated sites. Course for Major in Biogeochemistry and Pollutant Dynamics “Master of Environmental Sciences” and for Major in Ecological Systems Design and Waste Management “Master of Environmental Engineering”, ETH Zurich, Autumn Semester 2009

KOSAKOWSKI G.

Geostatistics I. & II. Course for “Master in Applied Environmental Geoscience”, Universität Tübingen, Germany, Semester 2009/2010

KULIK D.A.

Short Course in Thermodynamics and Kinetics of Fluid-Rock Interaction. Thermodynamics of adsorption, Davos, Switzerland, 19-21 June 2009

MAZUREK M., CURTI E.

Geological Disposal of Radioactive Waste within the frame of the course for “Master of Environmental and Resource Geochemistry”, Universität Bern, Switzerland, Spring Semester 09

PRASSER H.-M., GÜNTHER-LEOPOLD I., HIRSCHBERG S., HUMMEL W., WILLIAMS T., ZUIDEMA P.K.

Nuclear Energy Systems. Lecture course with exercises, ETH Zurich, Spring Semester 2009

PAUL SCHERRER INSTITUT



Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
Tel. +41 (0)56 310 21 11, Fax +41 (0)56 310 21 99
www.psi.ch