PAUL SCHERRER INSTITUT

Progress Report September 2004 to August 2005

Laboratory for Waste Management

Nuclear Energy and Safety Research Department

Preface

The Laboratory for Waste Management has two tasks: (i) to carry out an R&D programme strengthening the scientific basis for nuclear waste management, and (ii) to build and then operate – together with the SLS team – a microXAS beamline.

In its first task, 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 and in the field, and theoretical modelling. The work is directed towards repository projects and the results find their application in comprehensive performance assessments carried out by Nagra.

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 sub-programmes and a section on the status of the microXAS beamline.

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1 OVERVIEW

Mike Bradbury

1.1 Introduction

The progress made in the Laboratory for Waste Management (LES) since September 2004 is summarised in this first section. The work within LES is organised in two projects.

The first is the **Waste Management Programme**. The progress made in each sub-programme is given in sections 2 to 7. There is a strong interaction between the sub-programmes as well as between modellers and experimentalists, as can be appreciated from the work descriptions in the different sections and from the list of co-workers on page 13. The results of the XAFS sub-programme are integrated into the other activities. It is also the aim in this first section to facilitate for the reader, an appreciation of these interactions.

The second is the **microXAS beamline project**. The status is presented in section 8. The main incentive for this project was to gain a better understanding and insights into reactions occurring at the molecular level at solid surfaces. X-ray absorption spectroscopy has become an integral tool in the waste management programme.

1.2 General

The current situation of nuclear waste management in Switzerland can best be characterised as an intermediate period: Decisions are pending on the **Demonstration of Disposal Feasibility for Spent Fuel (SF), Vitrified High-Level Waste (HLW) and Long-lived Intermediate-Level Waste (ILW)**, the so-called Entsorgungsnachweis. Different gremia are in the process of evaluating this work, and a decision at governmental level is expected towards the end of 2006.

Last year, we mentioned the very positive review performed by a peer group convened by OECD/NEA. This February, the **Commission of Nuclear Waste Management (KNE)** published their report on the Entsorgungsnachweis. They came to the conclusion "that the demonstration of a suitable geological site for final disposal of SF, HLW and ILW in the Opalinus Clay in the Zürcher Weinland has been achieved". They judged the reports submitted by Nagra as a good synthesis of field, laboratory and literature data.

With respect to the fields of competence of LES, they noted the careful evaluation of geochemical processes in the near field. They also identified **open questions** to be clarified in further investigations. These are notably: closing gaps in thermodynamic data, continuing the work on understanding of sorption processes and developing a better foundation for arguments based on chemical analogies. Furthermore, they advocated more detailed investigations on near field property changes induced by physical and chemical processes during construction, operation and disposal, and steps towards more realistic models for radionuclide transport in the near field.

On February 1st 2005 the new **Nuclear Energy Law**, and the corresponding ordinance, came into force. As has been mentioned in a previous progress report, the new law fixes the concept of monitored geological disposal for all kinds of wastes. It requires a phased approach, postulating an extended first period of retrievability and a streamlining at the actions for licensing. It also foresees the submission of a waste management programme to the authorities for approval. This will include a **plan for R&D**. It is the intention on the side of Nagra, as well as on the side of LES, that the Laboratory will be involved in its formulation. A new aspect is that the procedures for site selection will be carried through within the law of "land use planning" (Raumplanungsgesetz). This means that a so-called "Sachplan" for geological repositories will be formulated. The detailed criteria are under evaluation by the authorities at present. It is evident that long-term safety will be a main criterion, but also socio-economic and urban and regional planning will be important aspects. Nagra is working on a document describing the **options for host rocks and regions** from a safety point of view. It remains to be seen to what extent the proceeding within two different laws will help to reach the goals.

The main emphases within the **microXAS project** were (i) beamline commissioning and (ii) experimental feasibility studies.

Commissioning was considerably impeded by two main factors. First, ambiguities concerning the x-ray beam path meant that the x-ray beam could not be guided through all the front-end components as designed. The cause was traced to post-construction settling of the storage ring facility. Joint efforts by the groups within the SLS Division enabled this complex problem to be resolved.

Secondly, a major failure in the monochromator unit caused the whole unit to collapse with resulting damage to major components including the main rotation axis, the vacuum feed through system, the linear translation stages of the second crystal holder, as well as the entire double cam system. The reason was most likely the failure of a ball bearing unit which resulted in the cam mechanics becoming stuck. Investigations led by the manufacturer are still ongoing.

Soon after the delivery of the microfocusing unit – a system consisting of two reflective mirrors combined in a classic Kirkpatrick-Baez arrangement - the first x-ray beam focused by the KB-mirror unit was produced. Without optimization of the preceding beam line optics and either one of the elliptical figures of the two KB mirrors, a spot size of less than 13x13 μm^2 was achieved. One-dimensional focusing in the vertical direction yielded a spot size of ~6 micrometers. These exceptional results for this first try without mirror figure optimization means that the spot size is only a factor of 2.5 (horizontal) and about a factor of 5 (vertical) off the specified design goal.

Despite the difficulties, operational conditions were reached which allowed basic feasibility studies to be performed. A number of fruitful collaborations with internal and external research groups have resulted, and more are scheduled in the immediate future.

A special feature of the microXAS beamline is that **radioactive samples** can be measured. Since the SLS is a low-hazard, non-nuclear facility, and the dose rate will be limited to 20 microSv/week at a distance of 2 meters from the sample (the hutch wall), a modular and local shielding concept has been devised, and a *specimen containment system* for radioactive samples has been built. Dedicated loading glove boxes in the Hot Laboratory are foreseen and a safety concept was submitted to the 'Bundesamt für Gesundheit' (BAG, the regulatory agency for the SLS) in the summer of 2005. The Hot Laboratory will be available for the storage and loading of radioactive XAS samples. First XAS test experiments in transmission and fluorescence mode have been conducted using the specimen holder for radioactive samples.

It is anticipated that the beamline will be open to external users in general in the summer of 2006 and for active measurements in autumn, 2006.

Within the **6th EU Framework Programme**, LES is primarily involved in two Integrated Projects; "Understanding the Physical and Numerical Modelling of the key Processes in the Near-Field and their Coupling for Different Host Rocks and Repository Stratergies (**NF-PRO**)" and "Fundamental Processes of Radionuclide Migration'" (**FUNMIG**) and a Network of Excellence "Chemistry and Physics of Actinides in Solution and Solid State", **ACTINET-6**. The work to be carried out within the Integrated Projects consists mainly of two parts. The first concerns experimental and modelling studies on the influence of inorganic carbon on the sorption of Ni, Eu and U(VI) on montmorillonite/bentonite (NF-PRO) and illite/Opalinus Clay (FUNMIG). The second main activity involves measuring the diffusive transport characteristics of selected anions (e.g. I^-, Cl^-) and cations (e.g. Na, Cs, Ni) in compacted bentonite (NF-PRO) and Opalinus Clay (FUNMIG). Further activities include XAS measurements in a study on the immobilisation of Se(VI) and Tc(VII) in contact with canister components (reduced iron and Fe(II) corrosion products; "green rust") within NF-PRO and predictive and interpretive modelling in connection with the "Diffusion Retardation" (DR) experiments at Mont Terri, FUNMIG.

Within the ACTINET Network of Excellence a short course with tutorial on "Aqueous–Solid Solution Systems Involving Actinides, Thermodynamic and Experimental Aspects" will be held at PSI on the 16-18 November 2005. The micoXAS beam line will join the ACTINET pooled facilities in 2006 and will be included in the 5th call due in the spring of 2006.

Bilateral co-operations with external institutions and scientists have continued. The long-time co-operation with Nagra was intensive and fruitful, with frequent meetings concerning progress in the various research programmes and the future orientation of the work. The yearly meetings with the Institut für Nukleare Entsorgung (INE/FZK), Karlsruhe, Germany, the Chemical Physics Department (DPC/CEA), Saclay, France, and the Institut für Radiochemie (IRC/FZR), Dresden, Germany took place. Co-operation within a formal umbrella agreement also continued with CIEMAT, Spain. A new general agreement on scientific co-operation has been signed between PSI and EMPA Dübendorf covering predominantly cementitious materials. Again, XAS measurements were performed at the ESRF, Grenoble, at ALS, Berkeley, at APS, Chicago and at NSLS, Brookhaven and neutron back scattering experiments on the IN10 and IN16 backscattering spectrometers at ILL, Grenoble. TRLFS measurements were performed at INE/FZK and IRC/FZR as part of ongoing co-operations. The experimental work with CRIEPI, Japan, in the field of cementitious systems is finished and the LES contribution to the project has been written up. Co-operations continue on a person to person basis with the University of Bern, the Federal Institute of Technology ETHZ, EAWAG Dübendorf, the University of Tübingen, IRSN Paris, Technocentre Kiev, SBRAS Irkutsk, the University College of London, the Nuclear Research Centre Mol, Belgium, the University of Mainz, the Japan Nuclear Cycle Development Institute (JNC) and the University of Strasbourg. LES is participating in various gremia of the OECD/NEA; TDBSOL on the "scientific guidelines for the evaluation of thermodynamic data for solid solutions"; TDB Project Phase III on the thermodynamics of iron.

Two further **Ph.D. students** joined the three already studying in LES and proposals are in preparation for two more submissions during 2006. As in previous years we would like to express our appreciation to the faculty members at the ETH and the Universities of Bern and Tübingen who agreed to supervise the projects.

One **post doctoral student** working at the microXAS beam line is currently being supported from LES funds and a decision regarding an application made to the **Euratom Research and Trainings Programme on Nuclear Energy (2002-2006)** for a 2-year post doctoral position is expected in October 2005.

On September 20 and 21, 2004, the Waste Management Program Committee met for their annual meeting. The work performed within LES and the future plans were discussed (AN-44-04-11). As always the Laboratory received valuable help and input from the members, not only during the meeting but also throughout the year.

1.3 Performance assessment

In the past year there were no activities involving direct participation in performance assessment. However, the **comments and recommendations** made in the reviews of the Demonstration of Disposal Feasibility for Spent Fuel, Vitrified High-Level Waste and Long-lived Intermediate-Level Waste by the **OECD/NEA, HSK and the KNE** are being incorporated and addressed in the research activities of LES. A few examples are given below. For protactinium there is hardly any useful experimental data, and justifying a chemical analogue is difficult. Work has begun to directly measure and model the sorption of this metal in clay systems. The appropriateness of using Th as a chemical analogue for the tetravalent actinides (in all cases) has been questioned, and work to measure the sorption of actinides in near and far field systems under controlled redox conditions is intended to begin in 2006 and address this problem. The validity of the high sorption values selected in the SDBs is being checked within existing mechanistic sorption studies in which progress towards a self-consistent thermodynamic sorption database is being made. The indications that the Ra solubility in a bentonite system may be determined by solid solution formation with $BaSO_4$ will be pursued in an experimental programme of work currently being planned in co-operation with JNC, Japan. The formation of solid solutions in a number of systems is being investigated and assessed with respect to their potential importance for performance assessment. In this context the GEMS code has been incorporated into the coupled code MCOTAC. The surface complexation and cation exchange sorption model (2SPNE SC/CE) is also being incorporated into MCOTAC in order to model near field radionuclide transport and the temporal evolution of the bentonite water chemistry, for example. In addition, the question of the transferability of sorption values derived from dispersed batch tests and/or calculated from sorption models to intact rock/compacted bentonite systems is a very active area of research. The knowledge gained from such investigations will provide added confidence in, and justification for, the data used in future performance assessment studies carried out by Nagra.

1.4 Foundations of repository chemistry

Still in the year up to August 2005 work related to participation in **international reviews of themodynamic data** remained an important component in the activities of the group. The work carried out within the OECD/NEA Thermodynamic Data Base, Phase II review concerning the complexation of U, Np, Pu, Am, Tc, Zr, Ni and Se with selected organic ligands (oxalate, citrate, EDTA and α-iso-saccharinate), initiated in 1998, was completed. The manuscript was sent to the publishers in June 05. A pragmatic ionic strength correction procedure, the Specific Ion Interaction Theory, was applied successfully to organic ligands. Also, in the case of ligand protonation data, a multi-dimensional least squares regression method was used to extrapolate data to zero ionic strength for the first time in an NEA TDB review. In addition, a chapter on Zr aqueous complexes and solid phases was delivered for the NEA TDB Zr book which is now in press. Further, LES is participating in the TDBSOL expert group where the aim is to produce scientific guidelines for the evaluation of thermodynamic data for solid solutions. Finally, LES is providing the main contribution to the aqueous complexation of Fe(II) within the newly started NEA TDB project phase III.

Work to improve the user-friendliness and versatility of the **GEMS code** has continued. Three new modules are under development: “UnSpace” which implements the “uncertainty space” approach for quantifying the impact of uncertainty in the input data for calculating solid-aqueous chemical speciation; Dual Thermodynamic methods (DualTh) which facilitate the retrieval of mixing parameters or thermodynamic properties of solid solutions from experimental partitioning data and “GEMIPM2K” which facilitates communication with other programmes via the Data Bridge or Data Chemistry structures.

A Ph.D. project has begun which aims at providing, for the first time, comprehensive thermodynamic data for **Layered Double Hydroxide solid solutions**. The Hydrotalcite / Pyroaurite system has been chosen for this investigation which will be carried out in close co-operation with the Université Blaise Pascal, Clemont-Ferrand, France.

1.5 Repository near field

1.5.1 Clay systems

Because water is the medium through which radionuclides are transported in compacted clay mineral systems e.g. montmorillonite, illite, kaolinite and pyrophyllite, a key question concerns the properties of the **confined water**. Through-diffusion experiments with HTO are being performed at different ionic strengths and at different temperatures. Neutron scattering measurements on Na and Ca clay minerals using the time-of-flight spectrometer **FOCUS at PSI**, is providing information on the local diffusion of water in the pores. Classical **molecular dynamics** calculations are being performed to aid in the interpretation of the results. It has emerged that the standard tools for evaluating experimental **Quasi elastic Neutron Scattering** (QENS) measurements cannot always be applied, and “in-house” fitting routines for different diffusion models are being developed.

Monte Carlo simulations of NaCl in the interlayer of Na-montmorillonite are being carried out to investigate the possibility that anionic radionuclides could diffuse through the interlayer in compacted bentonite as neutral or positively charged ion pairs. Till now this aspect has been largely ignored and it has been assumed that Cl transport through the interlayers does not occur due to ion exclusion effects. The calculations indicate that decreasing interlayer spacings favour the formation of neutral and charged ion pairs such as Na_2Cl^+ and Na_3Cl^{2+}. Monte Carlo simulations are being combined with molecular dynamic simulations in order to estimate the diffusion rate of chloride ion pair species in the interlayer. Parallel molecular dynamic simulations on the diffusion of Na and Cs in the interlayer space of Na-montmorillonite are being carried out.

Ab initio molecular dynamics approaches are being developed to calculate the reactions at edge sites of clays: proton sorption/desorption, metal surface binding. The techniques brings factors such as relaxation of crystal geometries, the structure of edge sites and the reactive interaction of interlayer fluid with mineral surfaces within reach of theoretical investigation.

In a more conventional but indispensable area of work involving wet chemistry and sorption modelling studies on **montmorillonite**, the aim of producing **a thermodynamic sorption data base** comprising of clay mineral specific sorption parameters is progressing. The establishment of a linear free energy relationship, **LFER**, for 11 elements with valencies between II and VI between strong surface binding constants and corresponding aqueous hydrolysis constants has been complemented with a study on **sorption competition** effects between metals. Competition is an important performance assessment issue. The main conclusion was that metals with similar chemistries (valence state, hydrolysis behaviour) compete, ones with dissimilar chemistries do not. A XAS study broadly confirmed this result. The results from this work required some relatively simple modifications to be made to the 2SPNE SC/CE sorption model. The scope of the wet chemistry/ modelling/spectroscopy investigations into metal uptake on montmorillonite has widened to include the influence of inorganic carbon complexation. The latter work is part of the 6th EU Framework IP NF-PRO.

The planned series of **through-diffusion** experiments of Sr in compacted Na-montmorillonite as a function of sample thickness and the ionic strength of the saturating fluid were completed but proved difficult to interpret. The work on the influence of ionic strength on the effective diffusion coefficient is being extended to other clay minerals with different swelling properties in an attempt to gain more insight into the problem. An answer to the question “How thin can a through-diffusion sample be, and still remain representitive?” is being pursued in diffusion tests with weakly sorbing Na as tracer. The work on ultra thin clay membranes for studying diffusion of strongly sorbing tracers has been abandoned since a theoretical evaluation showed that the filters confining the samples would dominate the diffusive flux under steady state conditions. Electrochemical techniques, which are very rapid, are being investigated as a means of studying diffusion parameters and their dependency on for example ionic strength and pH.

1.5.2 Cement

In order to gain information on the mineralogical composition of hardened cement paste and the composition of the cement porewater, the **hydration behaviour** of a fresh and 15 years old sulphate resisiting Portland cement samples was investigated and modelled. (Mineral and porewater compositions were determined.) The agreements between the cement hydration model and the measurements were very good, and the model calculations could be extended to include cement alteration.

New results on the **transformation of ISA**, a major cellulose degradation product at high pH and metal complexant, performed in an oven within a glove box indicated that the initial rapid reactions slowed dramatically. The reasons are unclear.

Further investigations into the interaction of ^{63}Ni isotope with hardened cement paste suggest strongly that the mechanism is an isotope exchange process with stable **Ni existing in a solid solution** phase already present in the HCP. The sorption of ^{63}Ni is linear but only a small fraction of the stable Ni present is involved in the isotopic exchange; 3-4 % of the Ni inventory.

New measurements for Ra uptake on CSH phases (in co-operation with JNC, Japan) showed that at trace concentrations the sorption was linear and about 3-5 times greater than Sr. The sorption data for Ra can be interpreted in an analogous manner to that given previously for Sr. i.e. as a cation exchange process with Ca.

Certain experimental problems were encountered in the programme on the uptake of lanthanides and actinides by CSH phases and HCP. In the case of Eu(III) and Th(IV), sorption on colloids not removed from solution by centrifugation is thought to be influencing the measurements. The solubility of Np(V) at high pH appears to be much lower than predicted by the thermodynamic data.

In connection with the **High pH Plume experiment** (HPF) at the **Grimsel Test Site** (GTS), a final modelling and experimental report is in preparation which will summarise the activities of all participating partners. It will provide the experimental and theoretical basis for launching the **Long-term Cement Studies** (LCS) project to investigate the interaction of a high pH fluid with the backfill / host rock materials and tracer transport. The Colloid Chemistry sub-programme will be taking part in a further field investigation at the GTS, the **Colloid Formation and Migration** (CFM) experiment. The aim of this project is to understand the generation of colloids at a bentonite block/groundwater flow interface with a quasi-stagnant water.

1.6 Repository far field

The focus of the far field investigations has remained firmly fixed on the **Opalinus Clay**.

In the laboratory studies the approach to developing a mechanistic understanding to the sorption of radionuclides onto Opalinus Clay has remained the same i.e. a bottom up approach aimed at understanding and developing quantitative models for the uptake on **illite**. (Illite is one of the main clay mineral components of Opalinus Clay.) The longer-term aim is to develop LFERs similar to those already in place for montmorillonite and to use these as a basis for the construction of thermodynamic sorption data bases for argillaceous rocks.

In a first attempt to scope the problem of the influence of inorganic carbon on sorption by illite, a modelling exercise was carried out in which the uptake of Ni, Eu and UO_2 was calculated at trace concentrations using reference Opalinus Clay porewater compositions The calculations were carried out under the assumption that only metal cations and positively charged and neutral hydroxy complexes sorb, all other aqueous species were considered to be non sorbing. The indications are that the reductions in sorption in the cases of Eu and UO_2 are important, whereas those for Ni are negligeable. This work is part of the 6th EU Framework IP FUNMIG.

The through-diffusion experiments started last year with 10^{-3} M Cs concentrations labeled with ^{134}Cs are continuing. The samples from **Mont Terri** have reached steady state and out-diffusion tests were started, but the samples from **Benken** have still not reached steady state after 400 days. In order to analyse these data, the diffusion model had to be modified to take into account the temporal decrease in the source Cs concentration, the non-linear sorption behaviour of Cs, and the effect of the filters used in the experiment. Cs in-diffusion data measured at trace concentration were re-analysed with the modified diffusion model and better fits to the data were obtained. First in-diffusion experiments for ^{60}Co and ^{152}Eu were performed and the profiles measured by the **abrasive peeling technique**. Much of the activity used in these experiments was trapped on iron oxides in the porous filters which are believed to have come from the oxidation of the pyrite in the Opalinus Clay. Future experiments will have to be performed in N_2 controlled atmosphere glove boxes. In addition, modelling calculations on the possible effects of heterogeneous tracer release in laboratory diffusion experiments due to the “snake-shaped” groove in the filter plates were performed using **MCOTAC**. The indications were that there were no significant effects to be expected from this source for the current experimental conditions used in the diffusion tests.

Much of the laboratory diffusion work performed has a direct connection with current and planned diffusion experiments in the **Mont Terri Rock Laboratory**. Good sets of laboratory data for HTO, Na, Sr, Cs, Cl, Br and I are available. In those cases where field data are available and can be compared (HTO, Na, Sr, I), the agreement with laboratory data is very satisfactory. Scoping calculations for the diffusion of HTO, Cs, Ni, and Eu for planning and designing the next field diffusion tests at Mont Terri (**DR experiments**) have been performed.

NES, the Nuclear Energy and Safety Research Division, has decided to use its own funds in a “once-in-a-lifetime” way to finance time-limited research in novel domains, “**Seed Actions**”. At the end of a 3 year time limit, the seed actions should have evolved into self-sustaining R&D activities. In this context LES has submitted a proposal; **MAMOT**. The proposed field program at Mont Terri focuses on radionuclide transport through Opalinus Clay, predominantly in well designed **long-term diffusion experiments** under near in-situ conditions. A second topic addresses the excavation disturbed zone (EDZ) which represents a domain in the Opalinus Clay with fractures and joints where complex geochemical and transport properties prevail. In particular, the interaction of a high pH-plume, released by cementitious material in the near-field of a repository, with the host rock, and the consequences for radionuclide transport would be investigated.

In a Ph.D. project a (more) realistic model of the complex migration site fracture network at the Grimsel Test Site has been constructed on the basis of data from the excavation project (EP). Calculations indicate that the strong tailing towards late arrival times, which is usually interpreted by matrix diffusion, could be explained by geometric aspects of the fracture network only. The most important geometric feature in this context is the variation of the aperture widths of the fractures.

Laboratory for Waste Management: Sub-Programme Structure

Waste Management Programme

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Geochemical Modelling 4441xx

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Cement Systems 4445xx

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Mike Bradbury, OFLA/207 (2290)
Jean-Pierre Dobler, OHLD/003 (2289/2274)
Andreas Jakob, OFLA/202 (2420)
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Colloid Chemistry 4446xx

Claude Degueldre, OHLD/008 (4176/2276)
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Diffusion Processes 4447xx

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Studies 4449xx

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MicroXAS Beamline Project

Management 445xxx

Design and Construction 4451xx

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September 2005

2 GEOCHEMICAL MODELLING

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2.1 Overview

In the period September 2004 to August 2005, covered by this progress report, work related to thermodynamic databases was a substantial part of the activities of the geochemical modelling group.

The review work for the OECD/NEA TDB Phase II on selected organic ligands and zirconium has been concluded; the NEA TDB books are now with the publisher and will be available at the end of this year.

The review work for the OECD/NEA TDB Phase III concentrated on the solid solutions "Guidelines" project, whereas the iron review work has just begun.

On the modelling side, the Specific ion Interaction Theory (SIT) formalism has been implemented into the GEMS-code, Dual Thermodynamic methods (DualTh) for retrieval of thermodynamic data for solid solutions have been developed, the GEM surface complexation modelling concepts have been extended, and further development and improvement of GEMS-PSI software has been achieved, including the GEMIPM2 kernel for coupled reactive mass transport codes.

Activities in the field of solid solutions comprised EXAFS and microXRF studies of Nd-doped calcites and preparations for a Ph.D. project on layered double hydroxide solid solutions. The Ph.D. student, Haitao Gao, started his work in June 2005.

The Monte Carlo simulations of NaCl in the interlayer of Na-montmorillonite started during the last reporting period, have been continued. The purpose of these calculations is to see if it is possible that anionic radionuclides can diffuse through the montmorillonite interlayers in compacted bentonite in the form of neutral or positively charged ion pairs.

2.2 Thermodynamic databases and software

2.2.1 NEA TDB organics review

Within the scope of the OECD Nuclear Energy Agency (NEA) Thermochemical Data Base (TDB) Project a comprehensive review of selected organic ligands has been carried out.

The selected ligands are oxalate, citrate, ethylenediaminetetraacetate (EDTA) and α-iso-saccharinate (ISA), and the elements considered in the review are U, Np, Pu, Am, Tc, Ni, Se and Zr, and the necessary basic data concerning protonation of the ligands and their interactions with the major competing cations Na, K, Mg, Ca.

This organics review was initiated in 1998 by W. Hummel on behalf of the Management Board of the NEA Thermochemical Database Project Phase II (NEA TDB II), who also became chairman of the review project. Originally Giorgio Anderegg (ETH Zürich, Switzerland), Ignasi Puigdomènech (SKB, Sweden), Osamu Tochiyama (Tohoku University, Sendai, Japan), Josef Havel and Přemek Lubal (Masaryk University, Brno, Czech Republic) participated in the organics review. In August 2003 time constraints and the pressure of other commitments forced Josef Havel and Přemek Lubal to resign from the review team. In December 2003 Linfeng Rao (LBNL, Berkeley, USA) joined the review team.

All the members of the review team contributed fully to the main text and the discussions, and the excellent internal communication of the team has to be noted here. However, the workload was distributed according to the expertise of each member. Wolfgang Hummel was the principal author of the sections on oxalic acid, protonation and Na and K interactions of oxalate, while Josef Havel and Přemek Lubal were initially involved in reviewing the compounds and complexes of oxalate. Ignasi Puigdomènech reviewed citric acid and ethylenediaminetetraacetic acid, as well as protonation and Na and K interactions of citrate and EDTA. Osamu Tochiyama was the principal author of all sections concerning metal citrate complexes, whereas Giorgio Anderegg carried out the review of EDTA complexes with the editorial help of Wolfgang Hummel. After the resignation of Josef Havel and Přemek Lubal their remaining tasks were reassigned: Linfeng Rao reviewed uranium oxalate compounds and complexes, Wolfgang Hummel Ca and Mg oxalates, Osamu Tochiyama Zr and Am oxalates and Ignasi Puigdomènech Ni, Tc, Se, Np and Pu oxalates. The chapter on iso-saccharinic acid and compounds and complexes of ISA is a joint review by Linfeng Rao and Wolfgang Hummel.

A noteworthy result of this review was that it showed that the pragmatic ionic strength correction procedure, the SIT, chosen as the default method for all NEA TDB reviews, can also be applied successfully to organic ligands. In the case of ligand protonation data, a multi-dimensional least squares regression method was used for the first time in an NEA TDB review to extrapolate data to zero ionic strength (Fig. 2.1).

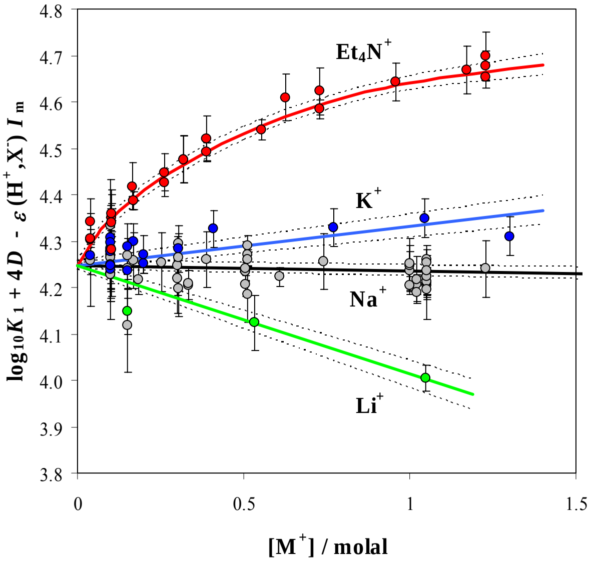

Fig. 2.1: *Weighted multi-dimensional least squares SIT regression plot for the first protonation of oxalate,* $ox^{2-} + H^{+} \Leftrightarrow Hox^{-}$*, in* Li^{+}*,* Na^{+}*,* K^{+} *and* Et_4N^{+} *(tetra-ethylammonium) media. All data can be fitted with a common parameter* $log_{10}K_1° = (4.25 \pm 0.01)$*.*

The SIT interaction parameters derived in this manner from ligand protonation data for different media, e.g. NaCl and KCl, pass the consistency test when applied to other systems evaluated in the organics review, e.g. solubility data. Hence, the thermodynamic constants selected in this NEA TDB organics review can be used in real world applications, provided that SIT is used in the speciation calculations.

After a substantial effort by the chairman and the team of proof reading 1130 pages, and checking 1300 references, the manuscript was sent to the publisher in June (HUMMEL et al. 2005a).

2.2.2 NEA TDB zirconium review

E. Curti was invited to contribute to the NEA TDB zirconium project with a chapter on aqueous Zr carbonate complexes and solid phases. The request came in at a late stage in the project and therefore required an intense effort during the past year. The first phase was devoted to a thorough literature study and a test of the hydrolysis model. This test revealed inconsistencies in the selected hydrolysis data which were resolved together with the other group reviewers. Thereafter, the available (scarce) published data on Zr carbonate complexes were re-interpreted in terms of the selected hydrolysis model. The data revealed – as expected – the formation of different Zr-CO_3 complexes depending on pH and the Zr/carbonate ratio in the system, and particularly the formation of ternary and polymeric complexes in dilute solutions. Nevertheless, in pH-neutral to mildly alkaline solutions with large carbonate excess, the monomer $Zr(CO_3)_4^{4-}$ forms as a limiting complex. For this complex, a formation constant could be selected from solubility data ($log_{10}\beta_4° = 42.9 \pm 1.0$). After amendments and additional calculations required by the peer reviewer, the chapter was delivered. The Zr book is now in press (BROWN et al. 2005) and the project has been officially concluded.

2.2.3 NEA TDB solid solution guidelines

D. Kulik is participating in the "TDBSOL" expert group aimed at producing "scientific guidelines for the evaluation of thermodynamic data for solid solutions". Other group members are J. Bruno (chairman, Spain), D. Bosbach (FZK/INE, Germany) and A. Navrotsky (UC Davis, USA).

It is recognised that the mobility of many radionuclides is reduced due to their incorporation into host minerals such as calcite, CSH phases or montmorillonite to form solid solutions. However, in many cases, the thermodynamics of such solid solutions are not known, and more experimental and theoretical work is needed.

Hence, the goal of the "Guidelines" is to provide researchers in nuclear waste geochemistry with the relevant theoretical and experimental background on aqueous – solid solution (AqSS) systems, and also to help decision makers in supporting AqSS related projects in the framework of repository performance assessments. The emphasis will be on the methods needed to retrieve solubility products of end members, or interaction parameters in the non-ideal mixing model, from the partitioning and phase characterisation data obtained from co-precipitation, recrystallisation or dissolution experiments.

After a meeting on 5 September 2004 in Karlsruhe, a prospective table of contents was agreed upon. D. Kulik prepared the first draft of Chapter 2.2 "Methods and tools for calculation and analysis of aqueous solid solution equilibria" and a first draft of Chapter 2.3 "Methods of retrieval of stoichiometry, stability of solid solutions end-members, and mixing parameters (inverse modelling)". Both were discussed at the meeting of TDBSOL Expert Group (3-4. 2. 2005) in Paris. Subsequently, a second draft of both chapters was prepared. The first draft of the whole "Guidelines" was distributed for peer review in August 2005.

2.2.4 NEA TDB iron review

Work for the OECD NEA TDB project phase III on the thermodynamics of iron has begun. U. Berner will provide the main contributions to the aqueous complexation of Fe(II).

2.2.5 Status of Portlandite/$CaOH^+$ problem

In last year's report it was demonstrated that, in general, the solubility of $Ca(OH)_2$ can be modelled equally well by the Davies equation, the extended Debye-Hückel equation, and the SIT ionic strength correction model. On a more detailed level, open questions were discussed, particularly the fact that there is no independent information confirming the predominance of the $CaOH^+$ complex.

In the interim a first implementation of the SIT formalism into GEMS has been completed. The core of this implementation is a 67 by 123 matrix (up to now) comprising of known SIT interaction coefficients (ε) between ions of opposite charge. Unfortunately, the major property of this matrix is its emptiness. Only about 256 values out of 8241 possible cation/anion combinations are presently known and the challenge here is to provide sensible values for the unknown interaction coefficients. This is essential because model applications using "incomplete" ε-data sets would produce inconsistent results. Hence, the present implementation relies on empirical relationships based on the charge of the complex as proposed by PETTIT et al. (2003). These authors propose to use

ε = 0 for neutral complexes,

ε = 0.15 + 0.15 × (complex-charge – 1) for positively charged complexes, and,

ε = 0.15 × (complex-charge + 1) for negatively charged complexes,

thus producing a sequence of multiples of 0.15.

This model was applied to literature data on the solubility of portlandite in (Na/K)OH. It was found that the "selection" of interaction coefficients including the hydroxide ion is a very critical issue because they are strongly correlated with formation constants. Particularly, the SIT formalism in the above mentioned system requires a simultaneous determination of $K_s(Ca(OH)_2)$, $K(CaOH^+)$, $\varepsilon(Ca^{2+}, OH^-)$ and $\varepsilon(CaOH^+, OH^-)$. In addition, the complex $Ca(OH)_2{}^0(aq)$ might become relevant at very high hydroxide concentrations, e.g. in cement pore waters. Although parameters fitting the data can be found (as was shown in the last report), a really consistent set of parameters is not yet available. Here, consistent means that interaction coefficients should fall into a sensible range, comparable with known chemically similar coefficients. A point still open to debate in this context is the problem of weak complexes such as $K(CaOH^+)$. It is not clear under which conditions (i.e. above which threshold stability) these species should be considered as real physical complexes and when they should rather be regarded as some sort of a "mathematical" construct improving the fit.

2.2.6 GEMS-PSI v.2 Program Package

The code, based on an advanced GEM-IPM algorithm (CHUDNENKO et al. 2002) has been under development at LES since June 2000. In combination with the Nagra/PSI TDB 01/01 adapted to GEMS (THOENEN & KULIK, 2003), the GEMS-PSI code is emminently suitable for advanced modelling of aqueous speciation, surface complexation, co-precipitation and solid solution formation, necessary in modelling applications related to the LES research program. The GEMS-PSI code package v. 2.1 (for Win32, Linux and Mac OS X) can be downloaded from our home page (KULIK, 2004). To date, more than 330 downloads from all over the world have been registered. At the same time, improvements to the existing code were continued along with the development of its new functionality (collaborator: S. Dmytriyeva). Three new modules for GEMS are currently being developed: UnSpace, DualTh and GEM2MT. The GEM IPM numerical kernel (CHUDNENKO et al. 2002) has been isolated into a separate small program GEMIPM2K for subsequent incorporation into coupled reactive mass transport codes, e.g. MCOTAC (PFINGSTEN et al. 2005), an important task in the LES research program.

The GEMS UnSpace module prototype implementation was completed in June 2005 (in collaboration with K. Chudnenko and the late I. Karpov). The module implements the innovative "Uncertainty Space" approach for sensitivity analysis of the impact of input data uncertainty on calculated solid-aqueous equilibrium chemical speciation (CHUDNENKO et al. 2004). The GEMS GUI graphics has been enhanced with the "isopixel" mode for better viewing of the UnSpace projections. The module is ready for research work on selected chemical thermodynamic systems, which should provide feedback for the further improvement of the module documentation and functionality.

The GEMS DualTh module is an implementation of Dual-Thermodynamic calculations which facilitate the retrieval of mixing parameters or thermodynamic properties of solid solution end-members from experimental or geochemical partitioning data (CURTI et al. 2005a). It was not completed as foreseen by the end of 2004 because of the emerging new ideas on including least-square statistical calculations (KULIK, 2005a). The module is expected to be ready by the end of 2005.

The GEMIPM2K program, prepared as a first prototype in November 2004, can communicate with other programs via the Data Bridge (DataBR) and Data Chemistry (DataCH) structures for data exchange (PFINGSTEN et al. 2005), either in the memory or through disk files. In February 2005, these data structures have been extended with data fields to exchange two-side kinetic constraints (in DataBR) and grid arrays with thermodynamic data for chemical species and water (in DataCH). Accordingly, a second prototype of GEMIPM2K module has been obtained, capable of incorporating mineral dissolution/ precipitation kinetics and automatically accounting for changes in temperature and pressure during the course of coupled reactive mass transport modelling. The T, P correction of thermodynamic data occurs via Lagrange polynomial interpolation over the T, P grid arrays. The data flow can now occur exclusively in the operative memory to speed up the calculation. The first benchmark tests of the GEMS-MCOTAC coupling have been performed (PFINGSTEN et al. 2005). Already these tests have shown that the GEM chemical system formulation must be checked and tested carefully before starting any sizable coupled modelling.

GEM2MT module development has just begun (March 2005) as a response to the above need. With the minimum functionality (available at the moment), the user can specify the chemical boundary conditions in the form of two or more chemical system compositions, calculate equilibria in all of them, and write on the disk a collection of DataCH, DataBR and other files that can be immediately read by for example the GEMIPM2K program or by a coupled code which incorporates it. Additionally, it is foreseen that the GEM2MT module will be able to perform simple coupled schemes directly (sequential reactors, box-flux models, numerical 1D advection/diffusion). In the future, this will allow the user to become well prepared for running 2D or 3D coupled models on parallel systems with a minimum risk of misbehaviour on the chemical side.

In the GEM surface complexation models, the site mole balance constraints are not needed; instead, special non-electrostatic surface activity terms are used (KULIK, 2002) in addition to the Coulombic electric double layer terms. Improvement of the GEM surface complexation models (Nov.-Dec. 2004) was based on a rigorous derivation of surface activity coefficients from Langmuir and Quasi Chemical Approximation (QCA) isotherms (KULIK, 2005b) that replace the earlier, less precise (now obsolete) surface activity terms (KULIK, 2002). In this way, the calculation of fully functional CD-MUSIC adsorption models on several surface types has been made possible. This approach becomes especially promising when combined with for example clay surface structure ab initio MD simulations which provide the site densities, the stoichiometries and, eventually, the relative stabilities of surface species (KULIK & CHURAKOV, 2005).

The latest development is an application of the new method (KULIK, 2005b) for obtaining the surface activity coefficients from the Frumkin adsorption isotherm equation which contains a correction term for the lateral interactions between adsorbed species.

More routine work on GEMS-PSI development consisted of increasing the user-friendliness by adding the configuration wizards for seven GEMS modules; bug fixing, improvement of the runtime help system; adding “cumulative diagram” and “isopixel diagram” plotting modes to GEMS GUI graphics module; improving documentation, etc. Still more work on the help system and tutorials is necessary.

2.3 Solid solution thermodynamics

2.3.1 Eu-calcite solid solutions

The results of the work on thermodynamic modelling of Eu-calcite solid solutions, carried out over the past few years and now documented in a publication (CURTI et al. 2005a), suggested that two distinct Eu coordination environments may coexist in calcite, depending on pH-pCO_2 conditions. At low pH and high pCO_2, the $EuH(CO_3)_2$ stoichiometry prevails, while at high pH and low pCO_2 the oxide end-member prevails.

In an effort to verify our model, EXAFS experiments on synthetic Nd-precipitated calcite samples produced at pH 8 and pH 11 (kindly supplied by M. Marquez, INE, FZK Karlsruhe) were attempted at the DUBBLE beamline (ESRF, Grenoble). The hope was to find distinct signatures in the coordination environments of the calcites synthesized at different pH-values, corresponding to the proposed end-member stoichiometries. Nd was selected to replace Eu since the latter element is apparently reduced in the X-ray beam during EXAFS measurements when it is incorporated in a mineral structure. Unfortunately, the Nd concentrations of the supplied calcites proved to be too low to obtain a good absorption signal, so that it was not possible to produce meaningful EXAFS spectra.

In addition, the Nd-calcites were investigated with microXRF at the ALS beamline 10.3.2, in the hope of finding regions with sufficiently high Nd-concentrations for EXAFS analyses. This test was also negative, since the Nd-distribution in the synthetic calcites proved to be fairly homogeneous at low concentration levels (see Fig. 2.2). This proves that the Nd-calcites are true solid solutions, since no separate Nd-rich phase was detected. This result indirectly justifies our thermodynamic treatment in terms of solid solution for Eu-calcites synthesized with the same experimental procedure (“constant addition” method).

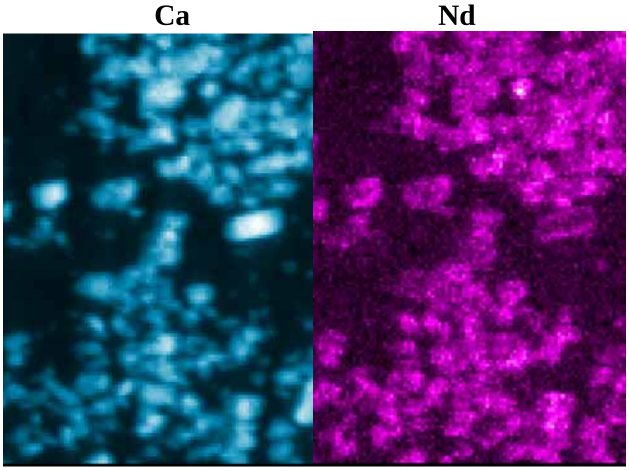

Fig. 2.2: *Ca and Nd distribution in synthetic calcite produced at pH 11. The brightness of the colours is proportional to the element content.*

2.3.2 Layered double hydroxide solid solutions

A Ph.D. work investigating the thermodynamics of Layered Double Hydroxide (LDH) solid solutions began recently. The Ph.D. student, Haitao Gao, started the work in June 2005.

Over the last decade these “anionic clays” have gained interest as “repository minerals” for hazardous anionic species. Other keywords in this context are the so called “green rusts”. Many of these solids are well characterised and have been investigated by modern spectroscopic techniques, but nearly nothing is known about their thermodynamic properties and reactions in aqueous solutions. The few available reports (Allada et al. 2002, Johnson & Glasser, 2003) provide results that are difficult to interpret.

The present Ph.D. work aims at providing, for the first time, comprehensive thermodynamic data for a full binary solid solution series. These data will provide an essential starting point for further quantitative modelling of such phases. Hydrotalcite was selected as a starting material. Fig. 2.3 demonstrates that several solid solution series can “easily” be accessed from hydrotalcite. However de Roy and Taviot-Guého (private communication, 2004) have put this "ease of access" in to perspective and led us to the conclusion that the hydrotalcite – pyroaurite solid solution series is perhaps an optimal series to begin with, because it seems to form crystalline products under readily achievable experimental conditions. The exchange of anions, e.g. NO_3^- against CO_3^{2-}, results in the formation of intimately mixed separate phases rather than solid solutions, and the exchange of divalent cations (i.e., the series with the takovite end-member) seems to be a slow process. Preparation and characterisation of the necessary solid solution phases will be performed in close collaboration with colleagues from the Université Blaise Pascal, Clermont-Ferrand, France.

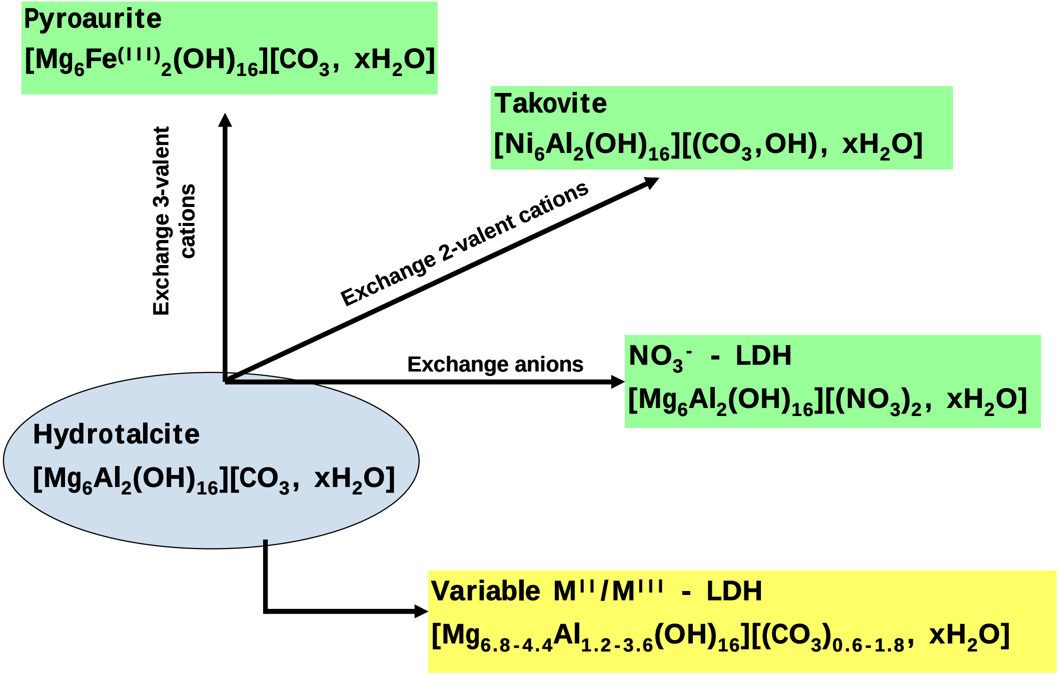

Fig. 2.3: *Sketch of potential Layered Double Hydroxide (LDH) solid solution series which could be investigated using hydrotalcite as starting phase. Exchange of divalent cations is considered to be a rather slow process. Recent investigations reveal that anion exchange leads to intimately mixed separate phases (with variable interlayer distance) rather than to solid solutions. The hydrotalcite – pyroaurite series is considered to be the optimum series to start with.*

2.4 Long-term glass corrosion experiments

Activities related to the long-term glass corrosion experiments, which have been running at PSI for the past 14 years, continued at a low level during the past year. Essentially, documentation work related to the (now completed) EU-project GLASTAB was carried out. A publication related to the alteration mineralogy and electron microscopy work performed during the above mentioned project in co-operation with the Université Louis Pasteur in Strasbourg has been prepared and submitted to Applied Geochemistry (CURTI et al. 2005b).

2.5 Molecular modelling of chloride-species in the interlayer of montmorillonite

The Monte Carlo simulations of NaCl in the interlayer of Na-montmorillonite, started during the last reporting period, have been continued. The purpose of these calculations is to investigate the possibility whether anionic radionuclides can diffuse through the montmorillonite interlayers in compacted bentonite in the form of neutral or positively charged ion pairs.

A series of simulations was made with the amount of water in the interlayers varying from 1000 molecules per simulation cell (corresponding to a layer spacing of about 35.7 Å and five water layers) down to 144 molecules (corresponding to a layer spacing of about 14.5 Å and two water layers in the interlayer) at a constant concentration (2.3 molal) of interlayer NaCl. It is evident from Fig. 2.4, that there is a clear trend of increasing proportions of neutral NaCl ion pairs as the amount of interlayer water is reduced. Low amounts of water also favour the formation of Na_2Cl^+ and Na_3Cl^{2+} species. These findings are also reflected in the cumulative coordination numbers of Na coordinated around Cl as a function of radial distance. The plateaus between 3 and 4 Å indicate the average number of Na cations in the first coordination shell of Cl. This number is 0.23 for 576 waters, 0.61 for 360 waters, 1.08 for 288 waters, and 1.51 for 144 waters.

Theses simulations are based on the TIP4P water model and the Lennard-Jones potentials for Na and Cl proposed by CHANDRASEKHAR et al. (1984). In order to test the sensitivity of the simulations to the chosen water model and Lennard-Jones potentials, the simulations with 144 H_2O and 6 NaCl were repeated with SPC/E water and the potentials for Na and Cl from SMITH & DANG (1994). First results indicate a smaller tendency towards the formation of ion pairs.

Monte Carlo simulations of a given system should lead to the same equilibrium properties when starting from different initial configurations. CHANG et al. (1999) found the selection of the initial configuration to be critical for system stability, especially for multilayer hydrates. In our simulations the starting configuration in the interlayer was obtained by placing the charge compensating cations at a fixed distance from the TOT-layer directly opposite to the charge deficient sites, while all other particles were placed randomly in the interlayer. For comparison, calculations have been started with a randomized initial configuration for all particles. The results obtained so far show smaller fluctuations in total potential energy and layer spacing, while, in most cases, the extent of ion pair formation is comparable.

Whereas Monte Carlo simulations provide only configurational information, dynamic properties can be calculated from molecular dynamics simulations. Based on equilibrium configurations obtained from the Monte Carlo simulations, molecular dynamics calculations have been started recently in order to estimate diffusion coefficients of the observed Cl species in the interlayer. This work is ongoing.

Complementary to our efforts to study the formation of NaCl ion pairs in montmorillonite, FERRAGE et al. (2005) have presented experimental evidence (based on X-ray diffraction data) for the presence of $CaCl^+$ ion pairs in the interlayer of SWy-2 montmorillonite equilibrated with aqueous solutions of $CaCl_2$. This prompted us to take up Monte Carlo simulations of this system. Preliminary results confirm the existence of $CaCl^+$ ion pairs in the interlayer, however, the formation of $CaCl_2(aq)$ and Ca_2Cl^{3+} was also observed.

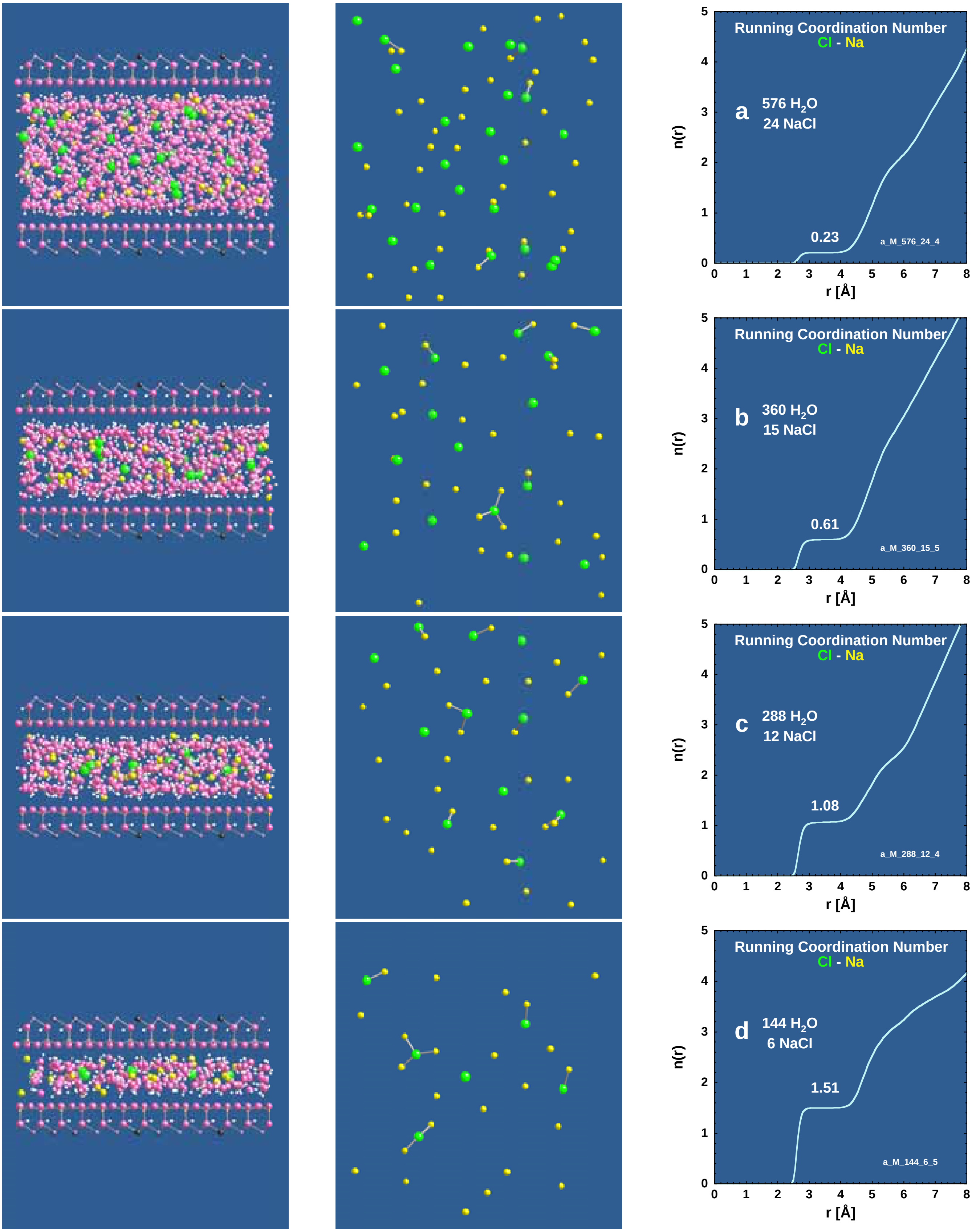

Fig. 2.4: *Interlayer configurations and running coordination numbers obtained from Monte Carlo simulations of Na-montmorillonite containing decreasing amounts of interlayer water at a constant concentration of interlayer NaCl (2.3 molal). Left: Projections of the simulation cell onto the xz-plane (dimension in the horizontal x-direction: 31.7 Å). Centre: Projections along the z-axis (perpendicular to the TOT-layers, TOT-layers and interlayer water omitted). Right: Running coordination numbers of Na coordinated to Cl as a function of radial distance. O: pink, H: white, Na: yellow, Cl: green. Simulation cell:* $Na_{18}(Si_{186}Al_6)_{tet}(Al_{84}Mg_{12})_{okt}O_{480}(OH)_{96} \cdot xH_2O \cdot yNaCl$.

2.6 Other activities

Since December 2004, we have been preparing within the ACTINET Network of Excellence a short course with tutorials on "Aqueous–Solid Solution Systems Involving Actinides, Thermodynamic and Experimental Aspects" to be held at PSI on the 16-18 Nov. 2005. The short course, held by D. Bosbach, E. Curti, D. Kulik and A. Navrotsky, will focus on thermodynamic and experimental aspects of solid solution formation in aquatic systems. This subject is gaining importance in radioactive waste repository management since many actinides and fission products can be incorporated in secondary phases formed in the near- and far field of nuclear waste repositories. Therefore, a sound understanding of solid solution concepts needs to be established in the nuclear waste geochemistry community. The short course is intended for students and young scientists in (geo)chemistry, physical chemistry and environmental sciences who have an interest in nuclear waste disposal research.

Further activities in the reporting period are the participation of E. Curti in EXAFS-measurements at ALS (Berkeley) in November 2004 and at ESRF (Grenoble) in April 2005, as well as his participation in the commissioning work of the X05 microXAS beamline at the SLS, PSI (see Chapter 8).

2.7 References

ALLADA R.K., NAVROTSKY A.,
THOMPSON BERBECO H., CASEY W.H. (2002)
Thermochemistry and aqueous solubilities of hydrotalcite-like solids. Science 296, 721-723.

CHANDRASEKHAR J., SPELLMAYER D.C.,
JORGENSEN W.L. (1984)
Energy component analysis for dilute aqueous solutions of Li^+, Na^+, F^-, and Cl^- ions. Journal of the American Chemical Society 106, 903-910.

CHANG F.-R.C., SKIPPER N.T., REFSON K.,
GREATHOUSE J.A., SPOSITO G. (1999)
Interlayer molecular structure and dynamics in Li-, Na-, and K-montmorillonite. In: SPARKS D.L., GRUNDL D.J. (eds.): Mineral-Water Interfacial Reactions: Kinetics and Mechanism. American Chemical Society, Washington, D.C., 88-106.

CHUDNENKO K.V., KARPOV I.K., KULIK D.A. (2002)
A high-precision IPM non-linear minimization module of GEM-Selektor v.2.x PSI program code for geochemical thermodynamic modelling. PSI Technical Report TM-44-02-06, Paul Scherrer Institut, Villigen, Switzerland.

CHUDNENKO K.V., KARPOV I.K., KULIK D.A., BERNER U., HUMMEL W., ARTIMENKO M.V. (2004)
GEM Uncertainty Space approach for sensitivity analysis of solid-aqueous chemical equilibrium models: A pilot study. PSI Technical Report TM-44-04-01, Paul Scherrer Institut, Villigen, Switzerland.

DE ROY A., TAVIOT-GUÉHO C. (2004)
Private communication during a visit at Laboratoire des Materiaux Inorganics, Université Blaise Pascal, Clermont-Ferrand, France.

FERRAGE E., TOURNASSAT C., RINNERT E., CHARLET L., LANSON B. (2005)
Experimental evidence for calcium-chloride ion pairs in the interlayer of montmorillonite. A XRD profile modelling approach. Clays and Clay Minerals (in press).

JOHNSON C.A., GLASSER F.P. (2003)
Hydrotalcite-like minerals $M_2Al(OH)_6(CO_3)_{0.5}$ xH_2O, where M = Mg, Zn, Co, Ni, in the environment: Synthesis, characterisation and thermodynamic stability. Clays and Clay Minerals 51, 1-8.

KULIK D.A. (2002)
Gibbs energy minimization approach to modelling sorption equilibria at the mineral-water interface: Thermodynamic relations for multi-site-surface complexation. American Journal of Science 302, 227-279.

PETTIT L.D., PUIGDOMÈNECH I., WANNER H. (2003)
Ionic Strength Corrections using Specific Interaction Theory. Version 1.5. ©IUPAC 2003.

SMITH D.E., DANG L.X. (1994)
Computer simulations of NaCl association in polarizable water. Journal of Chemical Physics 100, 3757-3766.

THOENEN T., KULIK D. (2003)
Nagra/PSI Chemical Thermodynamic Data Base 01/01 for the GEM-Selektor (V.2-PSI) Geochemical Modelling Code: Release 28-02-03. PSI Technical Report TM-44-03-04, Paul Scherrer Institut, Villigen, Switzerland.

2.8 Publications

2.8.1 Peer reviewed journals and reports

BROWN P.L.[1], CURTI E., GRAMBOW B.[2] (2005)
Chemical thermodynamics of zirconium. Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., Vol. 8, Chemical Thermodynamics, North Holland Elsevier Science Publishers B.V., Amsterdam, The Netherlands (in press).

[1] ASIRC, Monash University, Churchill, Australia

[2] Ecole des Mines de Nantes, Nantes, France

CURTI E., KULIK D., TITS J. (2005a)
Solid solutions of trace Eu(III) in calcite: Thermodynamic evaluation of experimental data over a wide range of pH and pCO_2. Geochimica et Cosmochimica Acta 69, 1721-1737.

CURTI E., CROVISIER J.L.[1], KARPOFF A.M.[1], MORVAN G.[1] (2005b)
Long-term corrosion of two nuclear waste reference glasses (MW and SON68): a kinetic and mineral alteration study. Applied Geochemistry (in review).

[1] Centre de Géochimie de la Surface CNRS, Université Louis Pasteur, Strasbourg, France

HUMMEL W. (2005)
Solubility equilibria and geochemical modelling in the field of radioactive waste disposal. Pure & Applied Chemistry 77, 631-641.

HUMMEL W., ANDEREGG G.[1], PUIGDOMÈNECH I.[2], RAO L.[3], TOCHIYAMA O.[4] (2005a)
Chemical thermodynamics of compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands. Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., Vol. 9, Chemical Thermodynamics, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands (in press).

[1] ETH, Zürich, Switzerland
[2] SKB, Stockholm, Sweden
[3] Lawrence Berkeley National Laboratory, Berkeley, USA
[4] IMRAM, Tohoku University, Sendai, Japan

HUMMEL W., ANDEREGG G.[1], PUIGDOMÈNECH I.[2], RAO L.[3], TOCHIYAMA O.[4] (2005b)
The OECD/NEA TDB review of selected organic ligands. Radiochimica Acta (in review).

[1] ETH, Zürich, Switzerland
[2] SKB, Stockholm, Sweden
[3] Lawrence Berkeley National Laboratory, Berkeley, USA
[4] IMRAM, Tohoku University, Sendai, Japan

KERSTEN M.[1], KULIK D.A. (2005a)
Competitive scavenging of trace metals by HFO and HMO during redox-driven early diagenesis of ferromanganese nodules. Journal of Soils and Sediments 5(1), 37-47.

[1] Gutenberg University, Mainz, Germany

KERSTEN M.[1], KULIK D.A. (2005b)
Thermodynamic modelling of trace element partitioning in the environment: New concepts and outlook. Chapter 3.1 in: Handbook of Elemental Speciation II: Species in the Environment, Food, Medicine & Occupational Health, Eds. R. Cornelis, H. Crews, J. Caruso and K. G. Heumann. London, John Wiley & Sons, 651 – 689.

[1] Gutenberg University, Mainz, Germany

KULIK D.A. (2005a)
Dual-Thermodynamic estimation of stoichiometry and stability of solid solution end members in aqueous - solid solution systems. Chemical Geology (submitted).

KULIK D.A. (2005b)
Incorporating classic adsorption isotherms into modern surface complexation models: Implications for sorption of radionuclides. Radiochimica Acta (submitted).

WERSIN P.[1], CURTI E., APPELO C.A.J.[2] (2004)
Modelling bentonite-water interactions at high solid/liquid ratios: swelling and diffuse double layer effects. Applied Clay Science 26, 249-257.

[1] Nagra, Wettingen, Switzerland
[2] Hydrochemical Consultant, Amsterdam, The Netherlands

2.8.2 Conferences/Workshops/Presentations

BERNER U.
Essential results and related research activities. Invited talk at the International Workshop on "Mechanisms and Modelling of Waste/Cement Interactions", Meiringen, Switzerland, May 8-12, 2005.

CURTI E.
Solid solutions of europium in calcite: integrating experimental data. Talk held on September 20, 2004 for the LES Programme Committee meeting.

CURTI E.
Solid solutions of Eu with calcite. Talk held on October 25, 2004, Institut für Radiochemie, Forschungszentrum Rossendorf, Germany.

CURTI E.
Solid solutions of Eu with calcite. Talk held on February 21, 2005, Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, Germany.

CURTI E.
Langzeitkorrosion schweizerischer HAA-Gläser: Wissensstand und Perspektiven. Invited talk, March 23, 2005, Eidgenössische Kommission für die Sicherheit der Kernanlagen (KSA), Olten, Switzerland.

CURTI E.
Long-term glass corrosion experiments at PSI. Invited talk at Université Marne-la-Vallée (ULMV), April 6, 2005, Paris, France.

HUMMEL W.
Advances in chemical thermodynamics database. Invited talk, CEA Séminaire Spéciation, Journées d'information CETAMA, November 15-16, 2004, Institut Curie, Paris, France.

HUMMEL W.
SIT coefficients for neutral species: Specific examples from the NEA TDB organics review. NEA workshop on the extension of the TDB-2 Guideline, February 21-22, 2005, Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, Germany.

HUMMEL W.
Treating weak complexes in the context of SIT: Specific examples from the NEA TDB organics review. NEA workshop on the extension of the TDB-2 Guideline. February 21-22, 2005, Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, Germany.

KULIK D.A.
Solid solutions in cement: Thermodynamic approach. (Oral presentation) International Workshop on "Mechanisms and Modelling of Waste/Cement Interactions", Meiringen, Switzerland, May 8-12, 2005. (Abstract: p. 44).

KULIK D.A., CHURAKOV S.V.
Matching a surface complexation model with ab initio molecular dynamics: Montmorillonite case. (Poster) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France (Abstract P/SRC/06, p.605).

THOENEN T.
Monte Carlo simulation of NaCl in Na-montmorillonite interlayers. New Developments in the Study of Clay Minerals and Fine-Grained Materials, One-Day Meeting, Clay Minerals Group of the Mineralogical Society, October 19, 2004, London, United Kingdom.

THOENEN T.
Monte Carlo simulation of NaCl species in Na-montmorillonite interlayers. 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

2.8.3 Internal reports

PFINGSTEN W., KULIK D.A., DMYTRIYEVA S.V.[1], ENZMANN F.[2] (2005)
First MCOTAC-GEMIPM coupling: Procedure, example calculations, and some performance considerations. PSI Internal Report AN-44-05-02, 18 p.

[1] Technocentre, Kiev, Ukraine

[2] Gutenberg University, Mainz, Germany

2.8.4 Others

KULIK D. (2004)
Web pages for distribution and documentation of GEMS-PSI modelling code, v.2.1
http://les.web.psi.ch/Software/GEMS-PSI/

2.8.5 Review work for scientific journals

Geochimica et Cosmochimica Acta,
Geologica Acta,
Journal of Noncrystalline Solids,
Pure & Applied Chemistry,
Radiochimica Acta.

3 TRANSPORT MECHANISMS

A. Jakob, S. Churakov, T. Gimmi, G. Kosakowski, R. Mettier, W. Pfingsten

This section gives an overview of the work carried out in the past year within the Geosphere Transport Subprogram.

Geosphere transport modelling is one of the key activities in the Laboratory for Waste Management LES and, hence, the working activities of the group cover a wide range of research areas and tackle many important scientific questions.

Our main goal is to achieve an increased understanding of the most important transport mechanisms and processes and to quantitatively estimate their effects on the mobility of migrating radionuclides. For this purpose, we develop state-of-the-art models whose quality is thoroughly investigated by modelling experiments on the laboratory and field scale. Furthermore, we require the predictive quality of such models to be tested in new experiments. Such a procedure leads to refined models, which are highly reliable and will be used periodically for safety assessment purposes.

Main areas of investigations in the last twelve months were:

- The analysis of diffusion experiments on the laboratory and field scale through Opalinus Clay from the Benken and Mont Terri area and through pure phases such as montmorillonite
- reactive transport modelling applying MCOTAC
- work in the frame of molecular modelling for investigating the mobility of radionuclides through clays and their interaction with the solid phase
- the derivation of more realistic fracture geometries from the analysis of Grimsel bore cores which can be used in transport modelling.

3.1 Modelling diffusion experiments

Laboratory experiments

Modelling small-scale diffusion experiments using radiotracers and Opalinus Clay samples from Benken (Northern Switzerland) and Mont Terri (underground laboratory in the western part of Switzerland), continued throughout this year. (For further details concerning the experiments see also Chapter 7, Diffusion Processes).

After the work with sodium and strontium, the more strongly sorbing caesium was used as a tracer in small-scale diffusion experiments. Diffusion was measured perpendicular to the bedding. Since the breakthrough for caesium at trace concentrations could not be expected on a reasonable time scale, diffusion was investigated by two different methods:

1) Caesium through-diffusion tests with a source reservoir concentration of 10^{-3} M Cs^{stable} labelled with 10^{-10} M $^{134}Cs^{+}$. Such conditions lead to relatively fast tracer breakthrough because sorption is relatively low at this high elemental concentration (see Fig. 3.1, top). However, from the mechanistic sorption model of BRADBURY & BAEYENS (2000) it is expected that caesium sorbs non-linearly under such circumstances. In addition, the effects of the filter end plates in the diffusion cells, and time-dependent boundary conditions, had to be taken into account in order to extract reliable values for diffusion and sorption. The modelling showed that the predicted sorption isotherm, for which competitive sorption effects of calcium and magnesium were taken into account, was a factor of 2–4 higher compared to the best-fit achieved for the breakthrough curve using a Langmuir type sorption isotherm. Since the uncertainties in measured log R_d values for Cs are ± 0.2 log units, this discrepancy is not too surprising. In addition it would be advantageous if the results from more than just one such diffusion experiment would be available.

2) An alternative method is the in-diffusion technique with a 10^{-7} M $^{134}Cs^{+}$ source solution. Due to the high sorption values anticipated at trace Cs concentrations, it is only practicable to measure the tracer profile in the rock sample. This was achieved using the high-resolution abrasive peeling method (ALBINSSON & ENGKVIST, 1989; VAN LOON & EIKENBERG, 2005). In this Cs concentration region, sorption is assumed to be well described by a linear isotherm formalism (BRADBURY & BAEYENS, 2000). Again, the effects of the filter, and the time-dependent up-stream boundary condition had to be included in the modelling. Since the transport properties of the filter were carefully determined in previous experiments, a unique best-fit could be achieved (Fig. 3.1, bottom).

Compared to other tracers such as tritated water (HTO) and sodium, the values for the effective diffusion coefficient for caesium are slightly larger. Our investigations in the framework of molecular modelling are anticipated to help to explain this observed trend in the cation mobility.

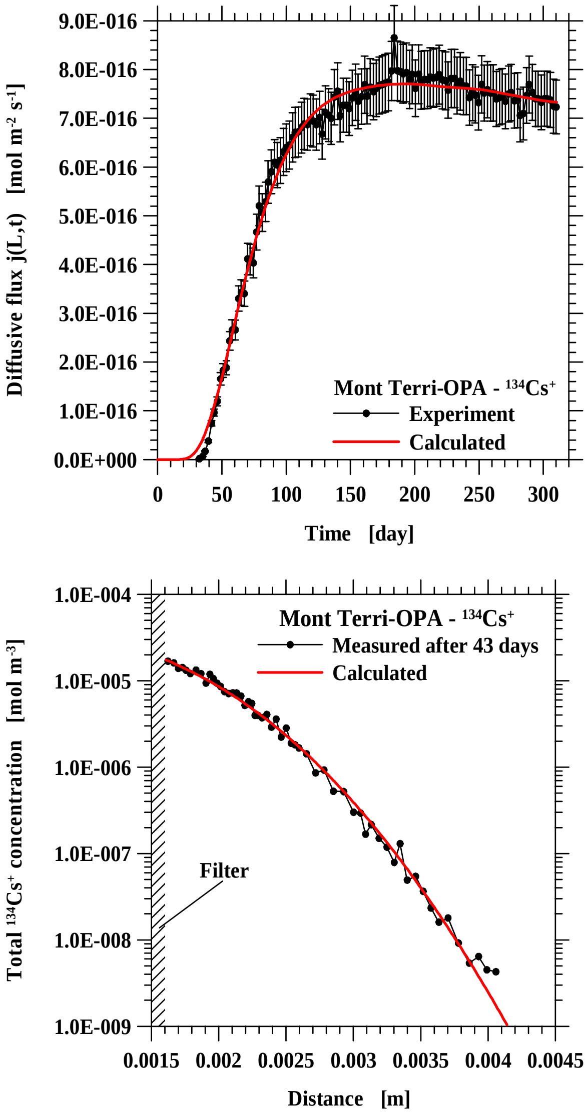

Fig. 3.1: *Measurements (dots) and best-fit (red lines) for* $^{134}Cs^{+}$ *tracer flux at the down-stream boundary as a function of time (upper figure) and for in-diffusion as a function of diffusion depth (lower figure) after 43 days. The influence of the filters, time-dependent boundary conditions as well as non-linear sorption had to be taken into account in the analysis in order to deduce reliable values for diffusion and sorption parameters.*

Accounting for heterogeneous tracer release

Data from small-scale diffusion experiments are commonly used to deduce values for the effective diffusion coefficients and for the sorption capacity for various radionuclides migrating through clays, cement and other relevant barrier materials. Together with other data from, for example, batch sorption experiments, they are essential for developing up-scaling procedures from the laboratory to the field or even to the performance assessment scale. In order to exclude sources of systematic errors caused by the experimental set-up e.g. the injection and sampling device, filters etc., careful modelling is needed which takes into account – if necessary – finer details of the diffusion experiment. A tracer injection which is not uniformly distributed across the upper boundary may result in multi-modal tracer breakthrough. (Note, a bi-modal tracer breakthrough was indeed observed in Opalinus Clay for some tracers such as HTO.) However, first calculations (Fig. 3.2) in which a non-uniform tracer release was taken into account indicate that for our small-scale diffusion experiments using conservative and weakly sorbing tracers, and using clay samples with thicknesses in the order of one centimetre, such an effect is negligible. Nevertheless, the result is strongly dependent on geometry and transport properties and further careful analysis is needed. A sensitivity study on the effects of heterogeneous tracer release at the upper boundary will be performed.

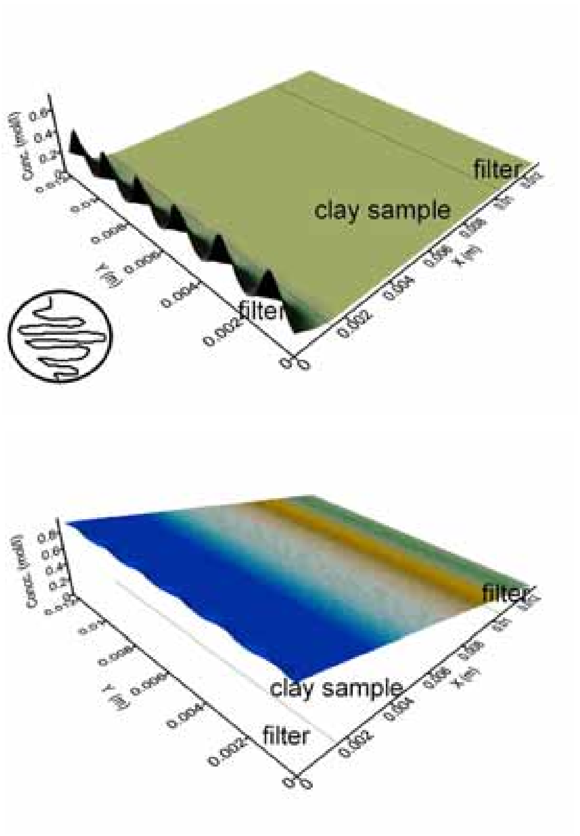

Fig. 3.2: *2D-tracer concentration distribution for early (upper plot) and late times (lower plot) calculated for a non-uniform upper boundary condition. As indicated in the left upper plot, the tracer fluid at the high-concentration side is introduced along the length of a "snake-shaped" groove in the filter plates. Calculations with MCOTAC can account for such a heterogeneous tracer release. The transport domain consists of the clay sample sandwiched between two stainless steel filters with well-known transport properties. (In the experiments, the filters are needed to maintain the integrity of the samples.) The analysis indicates that for all previous small-scale diffusion experiments, the heterogeneous tracer distribution in the sample becomes rapidly equilibrated, and hence has only a negligible effect on the measured tracer downstream breakthrough concentration.*

Field tracer tests at Mont Terri (DI-A and DR)

Similar to the DI-A1 tracer test (VAN LOON et al. 2004, WERSIN et al. 2004), a second diffusion experiment (DI-A2) was started at the Mont Terri Rock Laboratory at the end of April 2004. The main goal was to verify the results from the first experiments for HTO, I^-, Br^-, $^{85}Sr^{2+}$ and Cs^+, and to investigate some new tracers such $^{60}Co^{2+}$ and Eu^{3+}. One year later, the injection borehole was over-cored, sub-cored, sectioned and analysed to obtain tracer concentration distributions in the rock. The measured decrease of the HTO, I^-, Br^-, Cs^+, and $^{85}Sr^{2+}$ concentrations in the injection borehole could be modelled by applying diffusion parameters obtained from laboratory measurements. The temporal concentration of $^{60}Co^{2+}$ in the borehole decreased somewhat slower than expected. The decrease of the Eu^{3+} concentration in the borehole was, however, very fast, as expected from the available sorption data. In order to examine the reliability and consistency of the current results, the spatial distributions in the rock have to be analysed for all of the tracers, in particular for $^{60}Co^{2+}$ and Eu^{3+}.

A series of scoping calculations was performed in order to estimate the optimal thickness of the rock slices. Technically it is feasible to cut slices down to 0.35 mm, but the thinner the sample the smaller the total activity in it and the greater the sample loss. Thicknesses increasing from 1 to 3 mm for the first centimetres were finally considered as a reasonable compromise between resolution, activities and loss of material.

A careful sensitivity study showed that the diffusion parameters deduced from the field experiments are very dependent on the effective borehole radius i.e. on the dip angle, and on the volume of solution in the injection and recirculation system. These two quantities should be known as precisely as possible in order to be able to reliably estimate diffusion coefficients and porosities.

Regarding DI-A1, a refined analysis of the dip-angle revealed a new value of 34° instead of the 40° - 45° initially estimated. Due to this fact, the values for the newly determined effective diffusion coefficient were slightly larger (factor ~ 1.2) compared to the previous best-fit values.

The planning and designing of the DR (diffusion and retention) experiment at Mont Terri also continued this year. Additional scoping calculations for different geometrical scenarios for HTO, Cs^+, Ni^{2+}, and Eu^{3+} as tracers were performed. Presently, a two tracer compartment of about 20 cm in length and an external tank having a volume of about 20 litres is envisaged. This work was part of the European Union FUNMIG project.

3.2 Coupling of chemistry and transport

MCOTAC-GEMS coupling

After careful definition of the data bridge structure between the reactive transport code MCOTAC and GEMIPM, which is the kernel of the geochemical code GEMS, both parts could be coupled to each other. Originally, the data exchange was via data files, however, the performance was unacceptably low.

For the MCOTAC/GEMIPM code verification purposes, a hypothetical 1D-geochemical system of moving dolomite and calcite dissolution and precipitation fronts was considered, and modelled with MCOTAC using both the old and new geochemical modules. (PFINGSTEN et al. 2005) Major ion concentrations and mineral front locations could be reproduced with the GEMIPM-module (see Fig. 3.3).

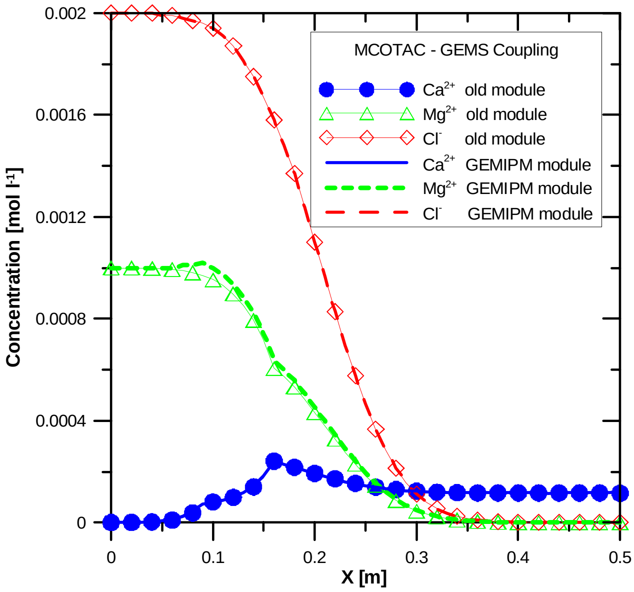

Fig. 3.3: *Spatial concentration distribution of the solute after 21'000 seconds as indicated in the legend. Transport is taking place in a hypothetical column filled with porous calcite. Transport of the solute is treated in terms of an advection-dispersion model. At the inlet, a solution rich in Mg^{2+} ions and poor in Ca^{2+} is released, resulting in the dissolution of calcite accompanied by the precipitation of dolomite along the column with subsequent re-dissolution. This geochemical system was used for verification purposes of MCOTAC-GEMIPM and to test the performance of this novel coupled code. Edges in the profiles reflect mineral fronts.*

However, calculation times are still a factor of 10 to 30 times longer using the new GEMIPM-module. The major reason for the longer calculation times lies in the internal structure of the GEMIPM-module. The modelled geochemical system has to be defined in much more detail than the original thermodynamic module, i.e. additional species are needed to characterise the geochemical system (e.g. redox sensitive species) in order to guarantee relatively fast convergence of the GEMIPM algorithm. However, further improvements of the performance should be feasible by an optimisation of the GEMIPM kernel and by porting the MCOTAC/GEMIPM to the new massively parallel computer HORIZON hosted by the Swiss Centre for Scientific Computing (CSCS) in Manno.

Redox-sensitive transport of U(IV) and U(VI) influenced by humic acids (HA)

Redox-sensitive transport of U(IV) and U(VI) in the presence of humic acids has been investigated in quartz-filled column experiments (MIBUS et al. 2004). These experiments indicated an increased mobility of both species compared to results from experiments in which humic acids were absent. HTO was used as a reference tracer to obtain the parameter values characterising transport in the column. U(VI) transport was modelled considering global kinetic effects (sorption and/or precipitation) and the interaction with humic acids, taking into account irreversible filtration effects of these substances.

Breakthrough data showed a clear indication of humic-acid facilitated uranium transport for both U(VI) and U(IV) species. In order to study in depth the redox-sensitive transport processes, our model/ code MCOTAC was applied. Our analyses which is still on-going, will help to better understand the migration behaviour of redox-sensitive uranium.

3.3 Molecular modelling

Proton transfer reactions

The hydration mechanism and cation sorption by highly compacted clays were the subject of a number of force field-based Monte Carlo and molecular dynamics (MD) studies. These investigations showed that pair-wise additive atomistic models are capable of reproducing the swelling behaviour of real clay samples. However, a very careful tuning of the pair potentials is required to achieve this. The question of which interaction potential to choose for hydrated smectites with different counter ions is still a matter of intensive debate. Particular difficulties are related to the modelling of uncommon geometries such as the edge sites of clays and the reactions at these sites, for which the empirical force fields are not available.

One way of tackling such problems is through the use of ab initio molecular dynamics. The interatomic forces in this scheme are obtained from a continuously updated electronic structure calculation. This electronic structure calculation is based on the density functional theory for periodic extended systems as originally developed for application to solids. Because of the coupling to MD, the ionic dynamics at finite-temperature is also described by this technique, opening up the modelling of liquids and interfaces to electronic structure methods. This enables us to account for the presence of the aqueous fluid in a manner similar to that used in classical simulations. A definite advantage of the ab initio MD approach over previous modelling studies is that the constraint of rigid clay platelets, needed to stabilize the solid framework, can be eliminated. This brings the relaxation of the crystal geometry, structure of the edges, the vibrational dynamics of the mineral layers and the reactive interaction of the interlayer fluid with mineral surface within reach of detailed theoretical investigation.

Different macroscopic surface complexation models have been proposed to describe the sorption of cations on clays. Most of them consider two major contributions to the electrostatic potential, namely, the electric field produced by a permanent structural charge in the TOT layer, and a pH-dependent potential due to proton sorption/de-sorption at edge sites. To a first approximation, both contributions can be considered independently. The calculation of the electrostatic potential due to a permanent structural charge is straightforward since it is determined by the extent of the isomorphic substitution in the TOT layer only. An accurate estimation of the pH-dependent potential requires the values of several fundamental parameters, which are poorly, if at all, constrained:

1) the effective surface area and the structure of the edge sites;
2) the density of sites involved in the protonation/de-protonation reactions; and
3) the equilibrium absorption constants for the reactive sites.

The available experimental data alone are not sufficient for rigorous estimation of these parameters by direct fitting. Extensive studies have shown that different models produce satisfactory fits to the experimental data with non-unique values for the fit parameters. Thus, a mechanistic understanding of the sorption processes on a molecular level is not possible without additional information for the sorption models.

In compacted systems, the proton sorption may buffer the pH in the interlayer water. It is therefore important to know the proton affinity of the mineral surface and the mechanism of proton sorption in order to model the thermodynamic equilibrium correctly. Little attention has been paid so far to the interaction of protons with the basal surfaces of clays. Our calculations suggest that the proton can dock to the siloxane cavity and form an inner-sphere complex as the hydronium atom. The density of such sorption sites is in the order of 4.0 per nm^2.

Using ab initio calculations (CHURAKOV, 2005) we can predict the structure and the surface energy of the different facets of pyrophyllite as a function of water coverage. The calculations suggest that at the pH of zero charge the edges of the pyrophyllite particles should be preferentially formed by the (110) and (-110) facets. This conclusion is in agreement with high resolution images of pyrophyllite nano-particles where the crystals of the pseudorhombic form were observed. It should be remembered, however, that other edge types such as the (010) facet can be stabilised in other pH ranges due to the protonation/deprotonation reactions and dissolution/ precipitation processes.

Knowing the structure of the most common edge facets, it is straightforward to calculate the density of the functional groups. The (110) edge contains 1.6 sites per nm^2 ≡Si1-OH, ≡ Si2-OH, ≡Al-OH, ≡Al-(OH)-Al≡, and ≡Al-O-Si≡ groups. The proton affinity of the surface groups was analysed using the Fukui indexes. The calculation allowed a linear relationship to be established between the electronic properties of the surface groups and their pK values. Using this relation, the relative acidities of the edge sites could be constrained. The absolute values of pK should be obtained, however, using the experimental data.

Bringing together the site densities and the relative proton affinities of the surface sites obtained in ab initio calculations and the conventional thermodynamic modelling with the GEMS package, the titration data of montmorillonite were modelled using the Basic Stern Multi-Site Triple Layer model (Fig. 3.4). The results show that the mechanism of the proton sorption depends on pH. At high pH the proton equilibrium is controlled by concurrent deprotonation of the edge sites while at low pH the capacity of the edge sites is used up and the protonation is dominated by inner sphere complexation on the basal plane. The density of the edge sites alone is not sufficient to explain the details of the titration curve at low pH.

At finite temperatures the system reaches pH equilibrium through a dynamic exchange of the protons between the aqueous solution and the different surface complexes.

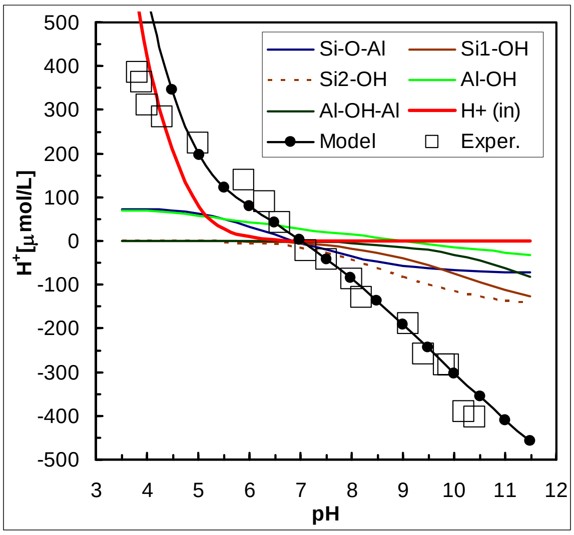

Fig. 3.4: *Basic Stern Multi-Site Triple Layer Model fitted to the H^+ sorption data of* BAEYENS & BRADBURY *(1997). The filled symbols (Model) show the total concentration of H^+ adsorbed by montmorillonite on the different surface sorption sites (colored lines). The site densities and the relative acidities of the surface sites including the inner-sphere hydronium on the basal plane were independently determined by ab initio calculations. At high pH, the titration data can be explained by the concurrent deprotonation of the edge sites. However, at low pH protons are mainly absorbed as inner-sphere complexes on the basal plane. The plot clearly illustrates that the density of the edge sites alone is not sufficient to explain the details of the titration curve at low pH.*

Using the ab initio MD simulation of the water-pyrophyllite interface, at a (010) facet spontaneous proton exchange between ≡SiOH and ≡AlOH surface sites occurs (Fig. 3.5).

The reaction takes place in two steps. In the first step, a water molecule near the surface dissociates, donating a proton to the surface ≡Al-OH group:

$$\equiv\text{Al-OH} + \text{H}_2\text{O}_{\text{solv}} \rightarrow \equiv\text{Al-OH}_2^+ + \text{OH}_{\text{sol}}$$

Subsequently, the hydroxyl dissolved in the fluid interacts with ≡Si-OH, and the surface donates a proton back to the fluid:

$$\equiv\text{Si-OH} + \text{OH}_{\text{sol}} \rightarrow \equiv\text{Si-O}^- + \text{H}_2\text{O}_{\text{solv}}$$

The sum of the two reaction steps results in surface proton diffusion:

$$\equiv\text{Al-OH} + \equiv\text{Si-OH} \rightarrow \equiv\text{Al-OH}_2^+ + \equiv\text{Si-O}^-$$

Although the surface remains electrically neutral after the proton transfer, the formation of locally charged sites occurs. Such a redistribution of protons might be a necessary precursor to the sorption of the ions from the solution.

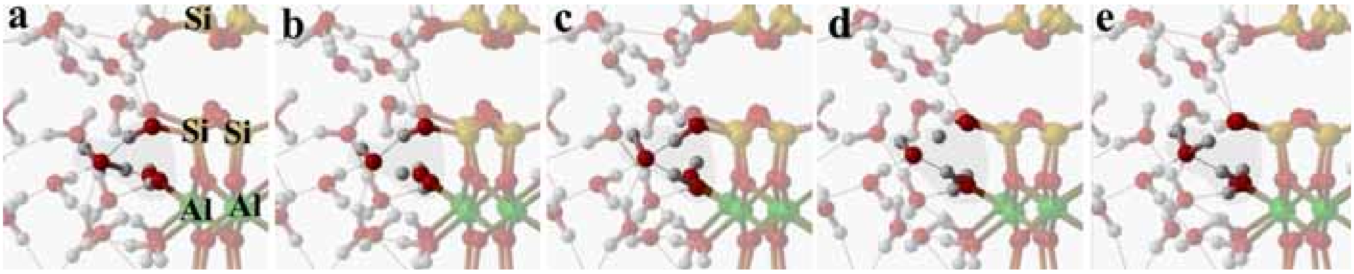

Fig 3.5: *Illustration of the proton transfer reaction on the (010) edge of pyrophyllite computed by ab initio molecular dynamics simulations at 300K.*
Oxygen atoms are red, aluminum green, silicon light-brown, and hydrogen grey. The thin lines show hydrogen bonds between water molecules.
From left to the right:

(a) A pyrophyllite surface with ≡Al-OH and ≡Si-OH groups.
(b) Dissociation of a water molecule in solution and proton sorption on the ≡Al-OH site.
(c) Formation of a solvated OH^- group and of a $\equiv Al\text{-}OH_2^+$ surface complex.
(d) The ≡Si-OH surface complex donates the proton to the solvated OH^- group.
(e) Finally, the surface consists of the $\equiv Si\text{-}O^-$ and $\equiv Al\text{-}OH_2^+$ complexes.

The mechanism of the proton transfer observed in the direct molecular MD confirms the predictions made based on the analysis of the Fukui functions; these suggest that on the (010) facet of pyrophyllite, both the $\equiv Al\text{-}OH_2^+$ and ≡Si-OH groups can be deprotonated and that the ≡Al-OH sites are available for the protonation.

Calculations and analysis of quasi-elastic neutron spectroscopy (QENS) spectra with classical molecular dynamics techniques

The main quantity of interest in Quasi Elastic Neutron Scattering (QENS) measurements is the incoherent dynamic structure factor (ISF-SPECT). From such measurements, the type of diffusion (3D-diffusion or 2D-surface-diffusion) and the values for the diffusion coefficient can be evaluated with the help of different models. Hence, a sophisticated analysis of experimental QENS data from saturated clay samples (see also section 7) requires that several alternative techniques and hypotheses for the state of the water in the clay samples are thoroughly investigated.

In analogy to the QENS measurements, classical molecular dynamics calculations were carried out at different temperatures for water, montmorillonite and pyrophyllite. From the trajectories of the hydrogen atoms in these simulations, the ISF-SPECT can be calculated via the intermediate scattering function.

Fitting the ISF-SPECT with different programs and approaches showed that the standard tools for evaluating experimental QENS measurements cannot always be applied. Therefore, "in-house" fitting routines for different diffusion models were developed using the statistical package R (see references).

First results show a qualitative agreement only between model and QENS measurements for the temperature dependence of diffusion. The Arrhenius-type increase of the diffusion coefficients with temperature and the corresponding activation energies could be reproduced. Currently, the work concentrates on the evaluation of the rotational component of the diffusion and the fitting with 2D-rotational-translational-diffusion models. Further, it is planned to extend this study to other clay minerals such as illite and kaolinite.

Cs^+ and Na^+ diffusion in the interlayer of montmorillonite

Complementary to the small-scale laboratory diffusion experiments of Na^+ and Cs^+ in clays we are presently investigating the mobility of these ions in the interlayer of Na-montomorillionite with the help of molecular dynamic simulations. We found that charged sites in the tetrahedral layer strongly influence the diffusion behaviour, since ions are strongly bound to those sites. However, these investigations are presently only in their initial phase and will continue.

3.4 Other activities

Tracer profiles at Benken (Entsorgungsnachweis)

The interpretation of tracer profiles in the borehole Benken was presented in a Nagra Technical Report (GIMMI & WABER, 2004). The report also contains extensive information about the palaeo-hydrogeology of the site. Such information is essential for deriving boundary and initial conditions for modelling purposes.

Structure and dynamics of confined water in compacted clays – support for the Ph.D. study

Support was provided for our Ph.D. student, Fatima Gonzàlez, mainly with respect to the characterisation of the clay materials she is using for the macroscopic and microscopic QENS (quasi-elastic neutron scattering) experiments, and to the subsequent analysis of the QENS data. For that purpose, an extensive literature study was made for evaluating different models that can be used for the analysis of the QENS data (GIMMI, 2004).

Modelling Grimsel HPF (LCS)

Our activities concerning the Grimsel high-pH plume project are coming to an end. A final modelling and experimental report, to be published as a Nagra-NTB, will summarise the activities of all participating partners. This report will provide the experimental and theoretical basis for launching the Long-term Cement Studies (LCS) project to investigate the interaction of a high pH fluid with the backfill / host rock materials and tracer transport. After excavation, a possible starting point could be an analysis of the radionuclide tracer distribution for Cs, Co, Eu within the transport domain. However, it is currently still an open question as to whether these data will be sufficient for a sophisticated benchmarking of competing coupled transport models.

Flow and transport in fractured crystalline rock[1]

In contrast to the flow and transport behaviour in porous media, such as sedimentary rocks, the study of similar processes in fractured crystalline rock, such as granites, or in this particular case, granodiorite from the Grimsel test site, depends almost entirely on the predominance of flow in fractures and joints. The dataset from the excavation project (EP) allows us to construct a more realistic model of a complex fractured network in a limited volume of rock. Data from tracer experiments performed in situ on the same rock volume typically show tracer breakthrough curves with strong tailing towards late arrival times. This pronounced tailing is often explained by means of matrix diffusion. However, our models which incorporate various degrees of complexity seem to hint that this type of tailing may also be explained by geometric aspects of the fracture network only (KOSAKOWSKI & SMITH, 2005). A model geometry consisting of three main fracture planes, interconnected by 19 minor fractures, all of constant aperture, already shows substantial late arrival tailing when solute transport is modelled using a particle tracker. The tailing becomes more pronounced if varying apertures of the fractures are taken into account. A simpler model geometry, consisting of a single fracture, albeit with similarly variable apertures, also reproduces the observed tailing effect nicely.

Realistic aperture distributions for the mentioned models can be obtained by a geostatistical analysis of the larger fractures in the EP dataset images. Such an analysis confirmed the suspicion that the values for the fracture apertures are roughly log-normally distributed, at least for those fractures with apertures above 5 mm. It was assumed that this distribution continues to hold for smaller fractures. Also, an averaged aperture value for a model with three parallel fractures can be extracted from the average permeability data obtained through the in situ experiments (FRICK et al. 1990). This allowed an aperture distribution to be generated for application in our model (Fig. 3.6).

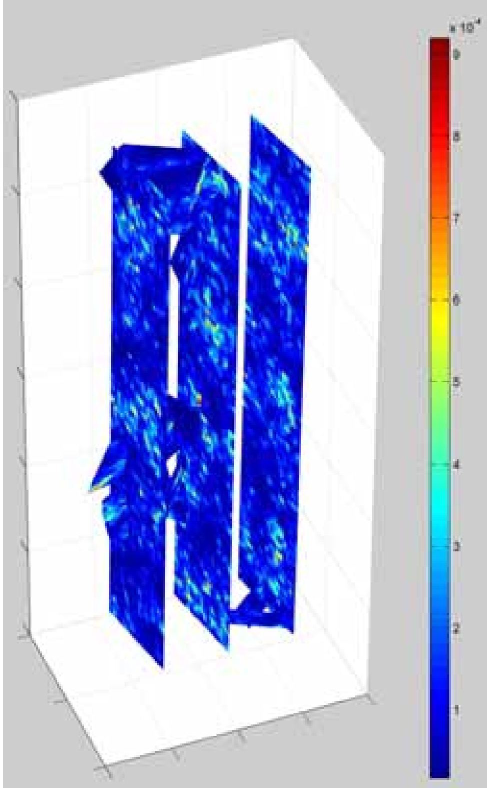

Fig. 3.6: *The figure shows a simplified geometry of a complex fracture network system based on the information from the EP dataset images. This is the model variant with three major fractures, interconnected by 19 minor fractures, all with variable apertures. The colour coding displays the aperture for each mesh element in multiples of 10^{-4} metres. For illustration purposes, the x-axis has been stretched by a factor of three to allow a better view of the details between the major fractures.*

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[1] This work is part of the ongoing Ph.D. thesis of Ralph Mettier and is based on a collaboration between the LES (Georg Kosakowski) and the Center for Applied Geoscience at the University of Tübingen (Prof. Olaf Kolditz).

Breakthrough curves obtained by running several realisations with a particle tracking program show strong tailing in the region of the late arrival times, along with a linear decline in concentration when plotted on a log-log scale.

According to the continuous-time-random-walk (CTRW) theory, the slope of the log-log plot of the velocity distribution in such a model should be correlated to the slope visible in the breakthrough curve, by means of the ß-value, one of the main parameters used in fitting CTRW solutions to experimental breakthrough curves. This correlation can be confirmed in our three model variants, a fact that corresponds well with the observation that CTRW can model the breakthrough curves much more precisely than a simple advection-dispersion model.

Further developments in this project will see the introduction of additional mechanisms such as sorption or matrix diffusion, as well as possibly increases in geometric complexity.

Complementary to the above Ph.D. study, tracer transport in complex 3D fracture networks was investigated in co-operation with Gennady Margolin (University of Notre Dame, USA) and Brian Berkowitz (Weizmann Insitute, Israel). The basic approach is very similar to the one used in the Ph.D. study outlined above. The advective transport in fracture networks with different network properties was calculated in many realisations. The first arrival time distributions at different distances and spatial profiles of particle densities at different times are described with the help of the continuous time random walks (CTRW) theory. The parameter values of the CTRW model are compared to the underlying velocity distribution of the flow model. It can be shown that a special form of the velocity distribution is responsible for the non-Fickian transport behaviour in the investigated fracture network and that a knowledge of this velocity distribution allows the basic transport behaviour to be predicted. A publication with further details is currently being finalised.

MAMOT: Migration of radionuclides at Mont Terri – A proposal for a new long-term research program

In the autumn of 2004 the management of NES decided – with the approval of the director of PSI – to use its own funds in a “once-in-a-lifetime” way to finance time-limited research in novel domains, an activity denoted as “seed actions”. At the end of the time limit, which is set at three years, the seed actions should have evolved into self-sustaining R&D activities. The main objectives of the seed actions are:

- to identify and initiate new research fields that could be focal points for NES research in the mid-term as replacement for current R&D activities and to strengthen NES position in the forefront of innovative research; and
- to encourage and foster researchers to address new questions in innovative research fields.

LES submited a proposal related to the future research program at Mont Terri including the novel use of actinides. The proposed scientific program of work focuses on radionuclide transport through Opalinus Clay, predominantly in well designed long-term diffusion experiments under near in-situ conditions. A second topic addresses the excavation disturbed zone (EDZ) which represents a domain in the Opalinus Clay with fractures and joints where complex geochemical and transport properties prevail. In particular, the interaction of a high pH-plume released by cementitious material in the near-field of a repository with the host rock and the consequences for radionuclide transport will be investigated.

There were nine pre-proposals submitted in response to the first seed action call in 2005. After a thorough examination and evaluation by a NES internal committee three proposals – one of which was MAMOT – were selected for further development. A final decision as to which of the three proposals will be financed this year will be made in mid September, 2005.

3.5 References

ALBINSSON Y., ENGKVIST I. (1989)
Diffusion of Am, Pu, Np, Cs, I and Tc in compacted sand-bentonite mixtures, SKB Report TR 89-22, SKB, Stockholm, Sweden.

BAEYENS B., BRADBURY M.H. (1997)
A mechanistic description of Ni and Zn sorption on Na-montmorillonite – Part I: Titration and sorption measurements. Journal of Contaminant Hydrology 27, 199 - 222.

BRADBURY M.H., BAEYENS B. (2000)
A generalised sorption model for the concentration dependent uptake of caesium by argillaceous rocks. Journal of Contaminant Hydrology 42, 141 - 163.

CHURAKOV S.V. (2005)
Ab initio modelling of surface site reactivity and fluid transport in clay minerals case study: Pyrophyllite. PSI Scientific Report 2004/Volume IV. ISSN 1423 - 7334. 109 - 120.

Frick U., Alexander W.R., Baeyens B., Bossart P., Bradbury M.H., Bühler C., Eikenberg J., Fierz T., Heer W., Hoehn E., McKinley I.G., Smith P.A. (1990)
The radionuclide Migration Experiment – Overview of Investigations 1985 - 1990, PSI-Bericht Nr. 120, Paul Scherrer Institut, Würenlingen and Villigen, Switzerland.

Gimmi T., Waber H.N. (2004)
Modelling of tracer profiles in pore water of argillaceous rocks in the Benken borehole: Stable water isotopes, chloride, and chlorine isotopes. Nagra Technical Report NTB 04-05, Nagra, Wettingen, Switzerland.

Gimmi T. (2004)
Short literature overview on models used to analyze QENS spectra of water. PSI-Internal Report AN-44-04-12, Paul Scherrer Insitut, Villigen, Switzerland.

Kosakowski G., Smith P. (2005)
Modelling the transport of solutes and colloids in the Grimsel Migration shear zone. PSI-Bericht Nr. 05-03, Paul Scherrer Institut, Villigen PSI, Switzerland and Nagra NTB 02-04, Nagra, Wettingen, Switzerland.

Mibus J., Sachs S., Nebelung C., Bernhard G. (2004)
Migration of uranium (IV/VI) in the presence of humic acids in quartz sand. Annual Report 2003, Institut for Radiochemistry, Forschungszentrum Rossendorf, Rossendorf, Germany, p. 58.

Pfingsten W., Kulik D.A., Dmytriyeva S.V., Enzmann F. (2005)
First MCOTAC - GEMIPM coupling: Procedure, example calculations, and some performance considerations. AN-44-05-02, Paul Scherrer Institut, Villigen, Switzerland.

Van Loon L.R., Eikenberg J. (2005)
A high-resolution abrasive method for determining diffusion profiles of sorbing radionuclides in dense argillaceous rocks. Applied Radiation and Isotopes 63, 11 - 21.

Van Loon L.R., Wersin P., Soler J.M., Eikenberg J., Gimmi T., Hernan P., Dewonck S., Savoye S. (2004)
In-situ diffusion of HTO, $^{22}Na^+$, Cs^+ and I^- in Opalinus Clay at the Mont Terri Rock Laboratory. Radiochimica Acta 92, 757 - 763.

Wersin P., Van Loon L.R., Soler J.M., Yllera A., Eikenberg J., Gimmi T., Hernan P., Boisson J.Y. (2004)
Long-term diffusion experiment at Mont Terri: first results from field and laboratory data. Applied Clay Science 26(1 - 4), 123 - 135.

R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, (http://www.R-project.org)

3.6 Publications

3.6.1 Peer reviewed journals and reports

Churakov S.V. (2005)
Thermo-elastic properties of solid phases: C++ object oriented library. Computers & Geoscience 31, 786 - 791.

Churakov S.V., Iannuzzi M.[1], Parrinello M.[1] (2004)
Ab-initio study of dehydroxylation carbonation reaction on brucite surface. J. Phys. Chem. B 108(31) 11567 - 11574.

[1] Laboratory of Physical Chemistry, ETH Zurich, USI Campus, Via Giuseppe Buffi 13, CH-6904 Lugano, Switzerland

Churakov S.V., Wunder B.[1] (2004)
Ab-initio calculations of the proton location in topaz-OH, $Al_2SiO_4(OH)_2$. Phys. Chem. Min. 31(3) 131 - 141.

[1] GeoForschungsZentrum Potsdam, Division 4, Telegrafen-berg,14473 Potsdam, Germany

Gimmi T. (2004)
Verlagerung gelöster Stoffe durch den Boden ins Grundwasser. Schriftenreihe Umwelt Nr. 349. Bundesamt für Umwelt, Wald und Landschaft, Bern. 46 S. BUWAL, Bern, 2004, SRU-349-D.

Gimmi T., Ursino N.[1] (2004)
Mapping material distribution in a heterogeneous sand tank by image analysis. Soil Sci. Soc. Am. J. 68, 1508 - 1514.

[1] University of Padova, Italy

Gimmi T., Waber H.N.[1] (2004)
Modelling of tracer profiles in pore water of argillaceous rocks in the Benken borehole: Stable water isotopes, chloride, and chlorine isotopes. Nagra Technical Report NTB 04-05, Nagra, Wettingen, Switzerland.

[1] RWI, Institute of Geological Science, University of Bern, Switzerland

Heinrich W.[1], Churakov S.V., Gottschalk M.[1] (2004)
Mineral-fluid equilibria in the system CaO-MgO-SiO_2-H_2O-CO_2-NaCl and the record of reactive fluid flow in contact metamorphic oreols. Contrib. Miner. Petrol. 148(2), 131 - 149.

[1] GeoForschungsZentrum Potsdam,Division 4, Telegrafenberg, 14473 Potsdam, Germany

Kosakowski G., Smith P.[1] (2005)
Modelling the transport of solutes and colloids in the Grimsel Migration shear zone. PSI-Bericht Nr. 05-03, Paul Scherrer Institut, Villigen PSI, Switzerland and Nagra NTB 02-04, Nagra, Wettingen, Switzerland.

[1] Safety Assessment Management Ltd., UK

Marschall P.[1], Horseman S.[2], Gimmi T. (2005)
Characterisation of gas transport properties of the Opalinus Clay, a potential host rock formation for radioactive waste disposal. Oil & Gas Science and Technology – Rev. IFP 60(1), 121-139.

[1] Nagra, Wettingen, Switzerland
[2] British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham NG12 5 GG - United Kingdom

Pfingsten W., Paris B.[1], Soler J.M.[2], Mäder U.K.[3] (2005)
Tracer and reactive transport modelling of interactions between high-pH fluids and fractured rock: Field and laboratory experiments. Journal of Geochemical Exploration (in press).

[1] ITASCA Consulting, Lyon, France
[2] CSIC, Barcelona, Spain
[3] RWI, Institute of Geological Science, University of Bern, Switzerland

Soler J.M.[1], Pfingsten W., Paris B.[2], Maeder U.K.[3], Frieg B.[4], Neall F.[5], Kaellvenius G.[6], Yui M.[7], Shi P.[8], Rochelle C.A.[9], Noy D.J.[9] (2005)
Grimsel Test Site – Phase V HPF Experiment: Modelling Report. Nagra NTB (in prep.), Nagra, Wettingen, Switzerland.

[1] CSIC, Barcelona, Spain
[2] ITASCA Consulting, Lyon, France
[3] RWI, Institute of Geological Science, University of Bern, Switzerland
[4] Nagra, Wettingen, Switzerland
[5] Neall Consulting, United Kingdom
[6] Chalmers University, Gothenburg, Sweden
[7] JNC, Japan
[8] SKB, Stockholm, Sweden
[9] BGS, United Kingdom

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 of through- and out-diffusion techniques. Transport in Porous Media 61, 193 - 214.

Van Loon L.R., Wersin P.[1], Soler J.M.[2], Eikenberg J., Gimmi T., Hernan P.[3], Dewonck S.[4], Savoye S.[5] (2004)
In-situ diffusion of HTO, $^{22}Na^+$, Cs^+ and I^- in Opalinus Clay at the Mont Terri Rock Laboratory. Radiochimica Acta 92, 757 - 763.

[1] Nagra, Wettingen, Switzerland
[2] CSIC, Barcelona, Spain
[3] ENRESA, E-28043 Madrid, Spain
[4] ANDRA, F-55290 Bure, France
[5] IRSN, 92265 F-Fontenay-aux-Roses, France

Wersin P.[1], Van Loon L.R., Soler J.M.[2], Yllera A.[3], Eikenberg J., Gimmi T., Hernan P.[4], Boisson J.Y.[5] (2004)
Long-term diffusion experiment at Mont Terri: first results from field and laboratory data. Applied Clay Science 26(1 - 4), 123 - 135.

[1] Nagra, Wettingen, Switzerland
[2] CSIC, Barcelona, Spain
[3] CIEMAT, E-28040 Madrid, Spain
[4] ENRESA, E-28043 Madrid, Spain
[5] IRSN, 92265 F-Fontenay-aux-Roses, France

3.6.2 Conferences/Workshops/Presentations

Arcos D.[1], Gimmi T., Duro L.[1], Waber H.N.[2]
Modelling of tracer behaviour and dominant reactions during the pore water chemistry (PC) experiment in the Opalinus Clay, Switzerland. (Poster) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

[1] ENVIROS SPAIN, Passeig de Rubí, 29-31, 08197 Valldoreix, Spain
[2] RWI, Institute of Geological Science, University of Bern, Switzerland

Churakov S.V.
Ab initio study of edge sites reactivity on pyrophyllite. (Oral presentation) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

Churakov S.V.
Molecular modelling of protonation deprotonation reactions on clay particles: Application to the surface complexation modelling. 10th Coordination Meeting INE/LES, March 10, 2005 Karlsruhe, Germany.

CHURAKOV S.V.
Ab initio modelling with CPMD package: Chemical reactions in complex environment. (invited talk). ACTINET Meeting, January 26, 2005 Karlsruhe, Germany.

GIMMI T., MAZUREK M.[1]
Porosity, pore structure, and binding state of water in Opalinus Clay, Switzerland. (Poster) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

[1] RWI, Institute of Geological Science, University of Bern, Switzerland

GONZÁLEZ F., JURÁNYI F., GIMMI T., VAN LOON L.R., SEYDEL T.[1]
Dynamics of confined water in compacted clay systems. (Poster) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

[1] Institut Laue-Langevin, 38042 Grenoble, France

KOSAKOWSKI G.
Research Activities of the Laboratory for Waste Management. (Oral presentation) Special Seminar. Faculty of Environmental Science and Technology, Okayama University, Japan, 24 November 2004.

KOSAKOWSKI G.
Modelling the transport of colloids and radionuclides in a shear zone. (Oral presentation) Proceedings of the International Symposium on Numerical Simulation of Environmental Problems, Okayama University, Japan, 22-23 November 2004, 133-142.

KOSAKOWSKI G.
Numerical Investigations about the Influence of Glacial Loading on the Transport of Radionuclides in the Opalinus Clay Formation. "Clay club" workshop Proceedings on "Stability and buffering Capacity of the Geosphere for Long-term Isolation of Radioactive Waste: Application to Argillaceous Media", 9 - 11 December 2003, Braunschweig, Germany, 177 - 182, Source OECD Nuclear Energy, Vol. 2005, no. 5, Paris, France.

KOSAKOWSKI G., METTIER R., KOLDITZ O[1].
Hyperbolic-parabolic problems in discontinous porous media (fracture networks), Part I: Small scale approaches. (Oral presentation) 2005 SIAM Conference on Mathematical and Computational Issues in the Geosciences, June 7 – 10, 2005, Avignon, France.

[1] University of Tübingen, Germany

KULIK D. A., CHURAKOV S.V.
Matching a surface complexation model with ab initio molecular dynamics: montmorillonite case. (Poster) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

MÄDER U.[1], WABER H.N.[1], GIMMI T., VINSOT A.[2], WERSIN P.[3]
Determination of porewater composition and species-specific transport parameters by a new method using laboratory core infiltration: Examples from Opalinus Clay (Mont Terri) and Callovo-Oxfordian clay (Bure). (Oral presentation) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

[1] RWI, Institute of Geological Science, University of Bern, Switzerland
[2] ANDRA, F-55290 Bure, France
[3] Nagra, Wettingen, Switzerland

METTIER R., KOSAKOWSKI G.
Using reconstructed shear zone fracture network geometry as a base for flow and transport modelling. (Oral presentation) 5th Workshop "Porous Media", Blaubeuren, Germany, 2-3 December 2004.

PFINGSTEN W., MIBUS J.[1], KUECHLER R.[2]
Reactive transport codes applied to gypsum dissolution in a laboratory column experiment with focus on sensitivity of model concepts and data uncertainty. (Oral presentation) ModelCARE2005, The Hague, Netherlands, IAHS, 6-9 June 2005, 335-341.

[1] Institut für Radiochemie, Forschungszentrum Rossendorf (FZR), Deutschland
[2] Institut für Sicherheitsforschung, Forschungszentrum Rossendorf (FZR), Deutschland

SOLER J.M.[1], GIMMI T., CARTALADE A.[2], WERSIN P.[3], VAN LOON L.R.
In-situ diffusion at Mont Terri URL. (Oral presentation) 15th Annual Goldschmidt Conference, Moscow, Idaho, USA, 25 May 2005.

[1] CSIC, Barcelona, Spain
[2] CEA, 91191 Gif-sur-Yvette, France
[3] Nagra, Wettingen, Switzerland

WABER H.N.[1], GIMMI T., VINSOT A.[2], GAUTSCHI A.[3]
Chloride and stable water isotopes in pore water of the Callovo-Oxfordian and surrounding formations at the Bure site, France. (Oral presentation) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

[1] RWI, Institute of Geological Science, University of Bern, Switzerland
[2] ANDRA, F-55290 Bure, France
[3] Nagra, Wettingen, Switzerland

WERSIN P.[1], DEWONCK S.[2], SAVOYE S.[3], HERNÁN P.[4], VAN LOON L.R., SOLER J.M.[5], GIMMI T., CARTALADE A.[6], YLLERA A.[6], EIKENBERG J., GROLIMUND D., BAEYENS B., VAN DORP F.[1]
Diffusion of HTO, iodide, sodium-22 and caesium in Opalinus Clay: A combined field, laboratory and modelling study. (Oral presentation) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France..

[1] Nagra, Wettingen, Switzerland
[2] ANDRA, F-55290 Bure, France
[3] IRSN, 92265 F-Fontenay-aux-Roses, France
[4] ENRESA, E-28043 Madrid, Spain
[5] CSIC-IJA, E-08028 Barcelona, Spain
[6] CEA, 91191 Gif-sur-Yvette, France

3.6.3 Internal reports

CHURAKOV S.V. (2005)
Ab initio modelling of surface site reactivity and fluid transport in clay minerals case study: Pyrophyllite. PSI Scientific Report 2004/Volume IV. ISSN 1423 - 7334. 109 - 120.

GIMMI T. (2004)
Short literature overview on models used to analyze QENS spectra of water. PSI-Internal Report AN-44-04-12, Paul Scherrer Insitut, Villigen, Switzerland.

NUSSBAUM C.[1], BOSSART P.[1], GRAF A.[1], METILLE J.[1], OYAMA T.[2], MOREL J.[3], ANDRE G.[3], PFINGSTEN W., TRABER D.[4] (2005)
Studies on weathered Opalinus Clay in 130 year old railway tunnel (Col de la Croix). Mont Terri Project, Technical Note, TN 2005-31.

[1] Geotechnical Institut Ltd, Bern, Switzerland
[2] CRIEPI, Japan
[3] ANDRA, France
[4] RWI, Institute of Geological Science, University of Bern, Switzerland

PFINGSTEN W., KULIK D.A., DMYTRIYEVA S.V.[1], ENZMANN F.[2] (2005)
First MCOTAC - GEMIPM coupling: Procedure, example calculations, and some performance considerations. AN-44-05-02, Paul Scherrer Institut, Villigen, Switzerland.

[1] SSC Technocentre, Pr. Nauky 46, 03650 Kiew, Ukraine
[2] Institut für Geowissenschaften, Johannes Gutenberg Universitaet, Mainz, Germany

3.7 Teaching

KOSAKOWSKI G. (2004)
Geostatistics II. Lecture series for the course “Masters in Applied Environmental Geoscience”, University of Tübingen, Germany, WS 2004/2005.

KOSAKOWSKI G. (2005)
Geostatistics I. Lecture series for the course “Masters in Applied Environmental Geoscience”, University of Tübingen, Germany, SS 2005.

4 CLAY SYSTEMS

B. Baeyens, M. Bradbury, R. Dähn, A. Schaible, N. Verde

4.1 Introduction

Mechanistic sorption studies on montmorillonite and illite were the dominant activities in the Clay Systems sub-programme. Four key papers have been published in Geochimica et Cosmochimica Acta. The first concerns linear free energy relationships for metal binding on montmorillonite (BRADBURY & BAEYENS, 2005a) and the second focuses on competitive sorption on montmorillonite (BRADBURY & BAEYENS, 2005b). Two further papers have been written on the uptake of Eu(III)/Cm(III) on montmorillonite and illite. Time resolved laser fluorescence spectroscopy (TRLFS) and batch sorption experiments were combined with cation exchange and surface complexation modelling studies. (RABUNG et al. 2005, BRADBURY et al. 2005).

The experimental and modelling studies on illite du Puy have been published (BRADBURY & BAEYENS, 2005c). This extensive study investigated the acid-base behaviour and the sorption of strontium, nickel, europium and uranyl on Na-illite.

Activities within the 6th EU framework projects NF-PRO and FUNMIG are ongoing. The main subject in both programmes is the investigation of the influence of the presence of inorganic carbon on the uptake of Ni(II), Eu(III) and U(VI) on montmorillonite and illite. The near-field studies (montmorillonite/ bentonite) are within NF-PRO whereas the far-field studies (illite/Opalinus Clay) are part of the FUNMIG project.

The EXAFS activities within the Clay Systems sub-programme have continued at a reduced level due to the high manpower requirements for the commissioning of the microXAS beam line at the SLS. One measurement campaign took place at the Dutch Belgian Beam Line (DUBBLE) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, in which the competition between Ni(II) and Nd(III) on Na-montmorillonite was investigated.

The co-operation between LES and the Institut für Radiochemie (FZR) has been strengthened in the field of uranium sorption on clay minerals, including TRLFS investigations. A proposal for a 2-year Euratom fellowship at LES has been submitted. Further, a 2 months stay of a guest scientist (Dr. T. Arnold) in the Clay Systems sub-programme has taken place.

4.2 Performance assessment

Fundamental research with direct relevance to safety analysis studies has continued in the current year. The linear free energy relationship work for metal binding on montmorillonite has been published (BRADBURY & BAEYENS, 2005a) and extended further by carrying out sorption measurements and modelling studies on actinides (see section 4.3.1).

The issue of competitive sorption on clay minerals is highly relevant to repository safety work. A paper has been published (BRADBURY & BAEYENS, 2005b) on the first experimental and modelling investigations into this topic. One of the main conclusions was that all metals are not mutually competitive, but rather competition is selective. Metals with similar chemical characteristics (valence state, hydrolysis behaviour) compete with one another, whereas metals with dissimilar chemistries do not compete (see section 4.3.2).

Within the framework of the 6th EU projects the influence of the presence of inorganic carbon on the sorption behaviour of radionuclides on clay minerals is being studied. In a first attempt to scope the problem, a modelling exercise was carried out in which the uptake of the Ni, Eu and UO_2 was calculated at trace concentrations for illite and montmorillonite in equilibrium with complex water chemistries. For montmorillonite the MX-80 reference porewater compositions were used and for illite the reference Opalinus Clay porewater compositions. These reference porewaters were the same as those used in the performance assessment studies (NAGRA, 2002).

The calculations were carried out under the assumption that only metal cations and positively charged and neutral hydroxy complexes sorb, all other aqueous species were considered to be non sorbing. This is a conservative approach which was intended to yield first estimates of the possible influences of complexation in “realistic” water chemistries on sorption. The results of the calculations are illustrated for illite in Fig. 4.1. Clearly, the calculations indicate that the reductions in sorption in the case of Eu and UO_2 are important whereas those for Ni are negligeable.

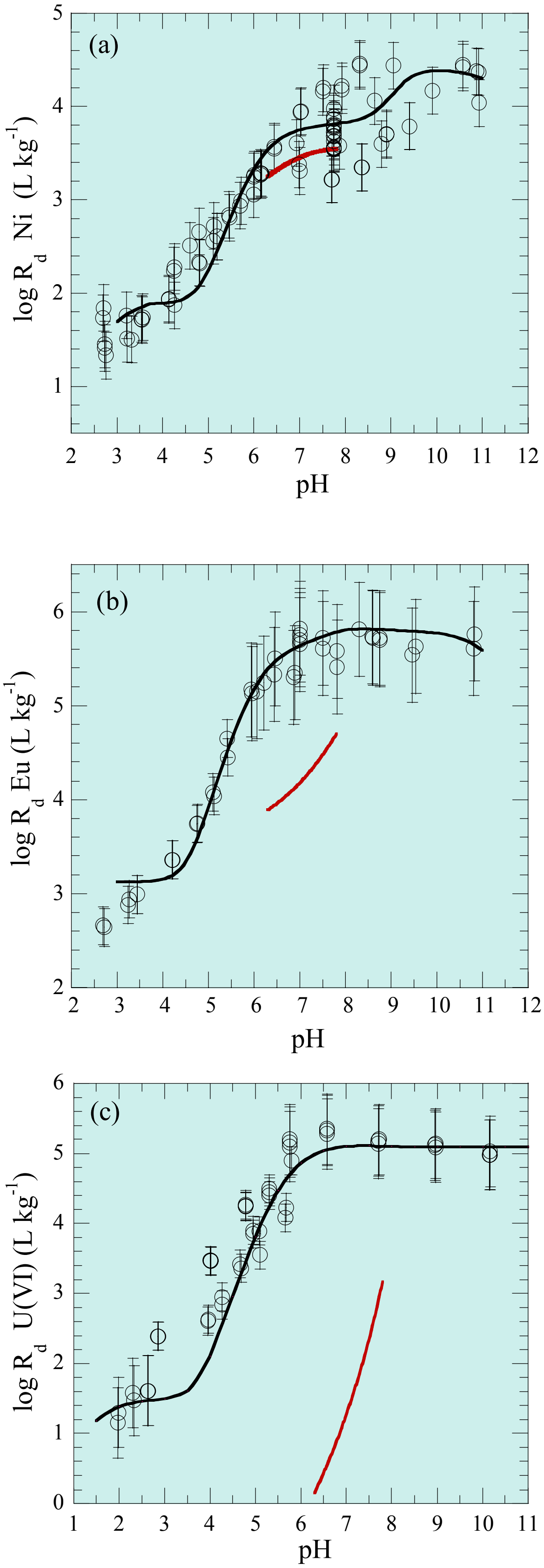


Fig. 4.1: *Results of model calculations on the sorption of (a) Ni(II), (b) Eu(III) and (c) U(VI) on Na-illite in 0.1 mol L^{-1} $NaClO_4$ (solid lines) and in the presence of the Opalinus Clay groundwater (red lines).*

4.3 Mechanistic sorption studies

4.3.1 Actinide sorption studies

The retention characteristics of the bentonite near-field engineered barrier proposed in most of the concepts for the deep geological disposal of high-level waste and spent fuel are an important component in repository performance assessment studies. Montmorillonite generally constitutes 65 to 90 wt. % of the bentonite. Sorption edge measurements have been performed for the actinides Am(III), Np(V) and Pa(V) on purified and conditioned SWy-1 montmorillonite under anoxic, carbonate free conditions in 1:1 and 2:1 background electrolytes. The experimental and modelling studies will be presented at the Migration 2005 Conference, 18-23 September, Avignon, France.

As an example, the sorption edges for neptunyl (^{239}Np) on Na-SWy-1 in 0.1 and 0.01 mol L^{-1} $NaClO_4$ are presented in Fig. 4.2. The pH dependent uptake behaviour is very similar to the neptunyl (^{237}Np) sorption data on montmorillonite presented in the open literature (Gorgeon 1994; Turner et al. 1998). The 2 site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) quasi mechanistic sorption model, used in a number of previous investigations (Bradbury & Baeyens, 1997, 1999, 2002), has been applied to model the neptunyl edges. Protolysis constants and site capacity values had the same fixed values as in the earlier studies. Table 4.1 summaries the selectivity and surface complexation constants used to model the NpO_2 sorption edges.

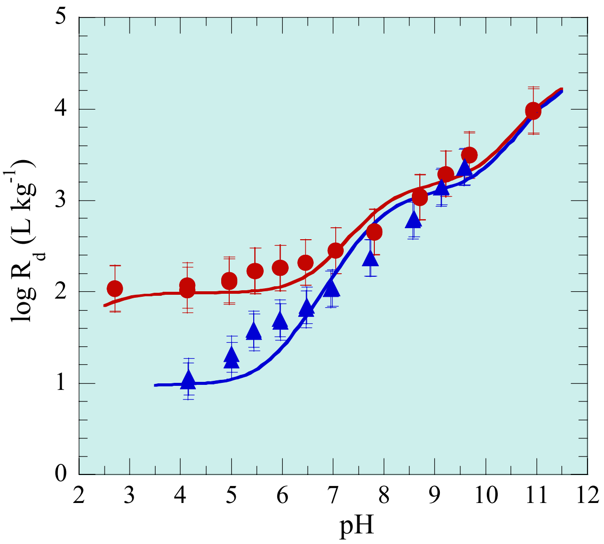


Fig. 4.2: *^{239}Np(V) sorption edges on Na-SWy-1 at (●) 0.01 and (▲) 0.1 mol L^{-1} $NaClO_4$. The continuous curves are calculated using the 2SPNE SC/CE model and the sorption reactions and surface binding constants given in Table 4.1.*

Table 4.1: *Mass action equations and associated surface binding constants used in the modelling of NpO_2 uptake on Na-montmorillonite.*

Cation exchange reaction	K_c
Na-mont. + NpO_2^+ ⇔ NpO_2-mont. + Na^+	1.1
Surface complexation reactions on strong sites	**log K_{int}**
$\equiv S^SOH + NpO_2^+ \Leftrightarrow \equiv S^SO\,NpO_2^0 + H^+$	-2.0
$\equiv S^SOH + NpO_2^+ + H_2O \Leftrightarrow \equiv S^SO\,NpO_2OH^- + H^+$	-12.0

A milestone in the mechanistic sorption investigations of metal uptake on montmorillonite was recently achieved with the establishment of a linear free energy relationship (LFER) for 11 elements between the strong site surface binding constants and the corresponding aqueous hydrolysis constants (BRADBURY & BAEYENS, 2005a). The results of the newly obtained NpO_2 sorption data are plotted on the LFER as red symbols in Fig. 4.3. This result illustrates not only the consistency of the NpO_2 data with the other measured/modelled metal sorption data but also confirms the usefulness of such a LFER for estimating unknown stability constants from given hydrolysis constants.

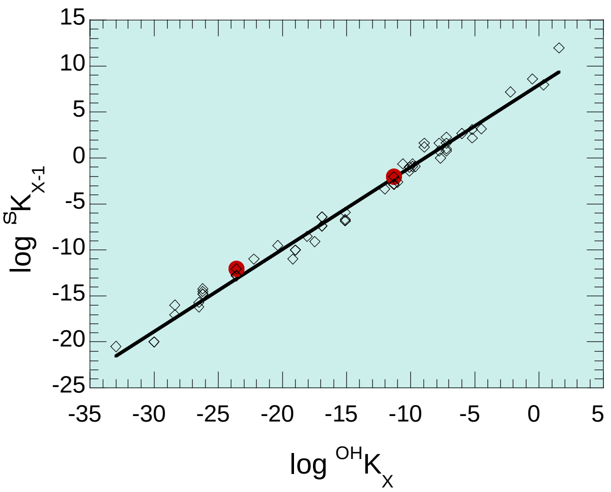


Fig. 4.3: *Relation between the NpO_2 aqueous hydrolysis constant and the strong site surface complexation constants used to model the sorption of NpO_2 on Na-SWy-1 montmorillonite.*

4.3.2 Competitive sorption

The source terms arising from radioactive/toxic metal waste repositories will contain a multitude of dissolved metal species, as do all natural systems. The influence of sorption competition on the uptake of safety relevant metals, and the effects this may have on transport rates to the biosphere, is an important repository performance assessment issue which has not, as yet, been quantitatively resolved. The main aim of this work was to quantify the influence of competition between metals in different valence states on their individual sorption characteristics under conditions dominated by pH dependent sorption. The sorption experiments were carried out on Na- and Ca-montmorillonites using various combinations and concentrations of Co(II), Ni(II), Zn(II), Eu(III), Nd(III), Am(III), Th(IV) and U(VI). For metals sorbing at trace concentrations in a background electrolyte containing a competing metal up to mmolar concentrations, and at pH values generally greater than 6, all of the experimental results were consistent with the observation that metals with similar chemistries (valence state, hydrolysis behaviour) compete with one another but metals with dissimilar chemistries do not compete i.e. competition is selective. This is illustrated in Fig. 4.4a for the sorption of Ni at trace concentrations in the presence of high concentrations of Co as the blocking metal. (The concentration of the blocking metals is more than sufficient to saturate the strong site capacity of 2 mmol kg^{-1}.) These elements are chemically similar and sorption competition is clearly evident. In Fig. 4.4b the influence of high background concentrations of Zn on the uptake of Eu at trace concentrations is negligible since these are chemically dissimilar elements.

Further, the studies clearly indicated that Eu(III), Nd(III), and Am(III) exhibit unambiguous sorption competition. On the other hand, competition between divalent transition metals and trivalent lanthanides, and between Th(IV) and U(VI) was not found experimentally. In order to explain the competitive effects observed it is proposed that multiple sets of strong sites exist as sub sets of the 40 mmol kg^{-1} of $\equiv S^{W1}OH$ weak sites in the conceptual sorption model for montmorillonite. It is shown in this work that if the 2SPNE SC/CE sorption model is extended to include multiple strong sites, and the average site capacity and protolysis constant values defined in previous publications are assigned to each of the sets of strong sites, then the model can be used to reproduce all of the experimental data, provided it can be specified which groups of metals are competitive and which are not. This work has now been published (BRADBURY & BAEYENS, 2005b).

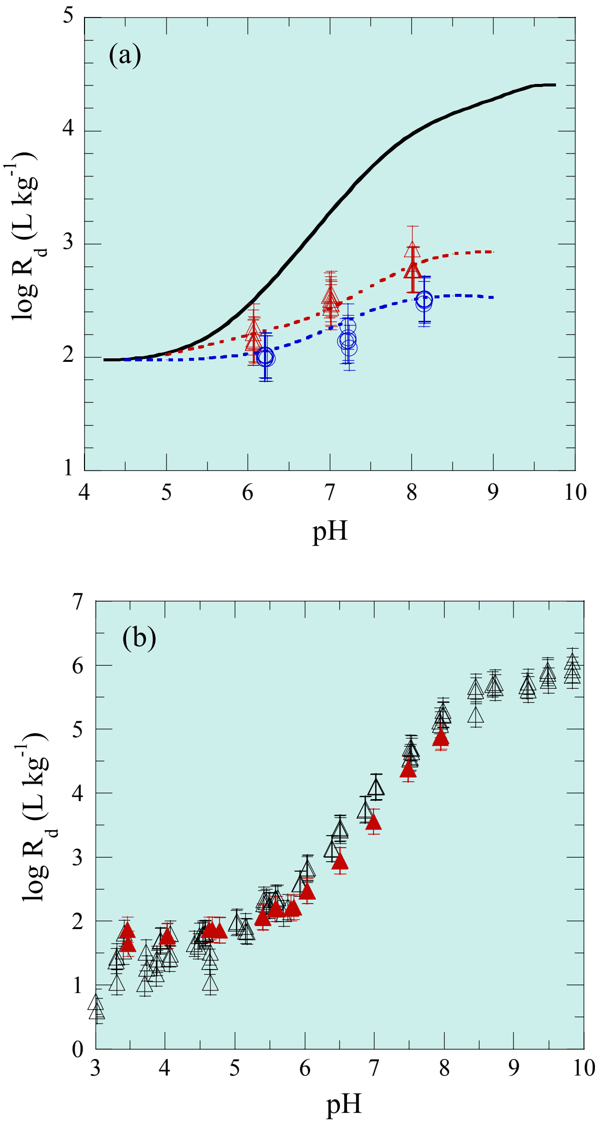


Fig. 4.4: *(a) Sorption values of ^{63}Ni(II) on Na-SWy-1 measured at pH values near 6, 7 and 8 in 0.1 mol L^{-1} NaClO$_4$ solution in the presence of two concentrations of Co(II) as blocking metal. (△) 8.5 x 10^{-6} mol L^{-1} Co(II) and (○) 10^{-4} mol L^{-1} Co(II). The continuous line is the modelled sorption edge for trace ^{63}Ni(II) in the absence of Co(II), and the red and blue dotted lines are the modelled curves in the presence of 8.5 x 10^{-6} and 10^{-4} mol L^{-1} Co(II) respectively, assuming competition. (b) Eu(III) sorption edge on Ca-SWy-1 in 0.066 mol L^{-1} Ca(NO$_3$)$_2$ in the absence and presence of Zn(II). (△) sorption in the absence of blocking metal, (▲) sorption in the presence of 7.2 x 10^{-6} mol L^{-1}* Zn(II). *The presence of Zn(II) has no influence on the uptake of Eu(III).*

4.4 Surface analysis studies, EXAFS

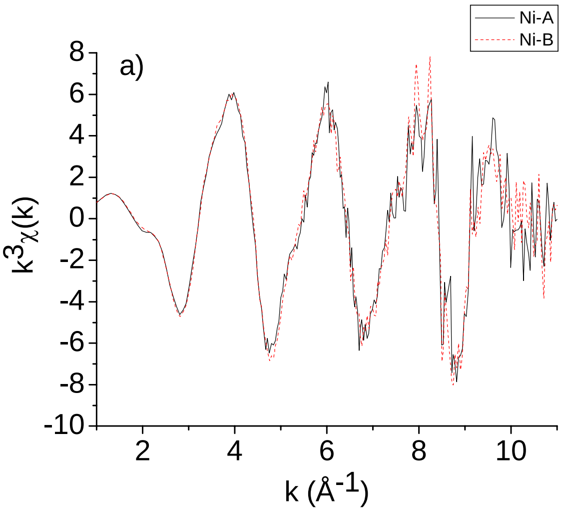
To further investigate the competition of metal uptake onto clays (see section 4.3.2) an EXAFS study was carried out. Two series of montmorillonite samples were prepared. In the first series, samples of Ni loaded montmorillonite in the absence of Nd (Ni-A) and the presence of Nd (Ni-B) were prepared. (Nd was added as the blocking metal.) In the second series, Nd loaded samples prepared in the absence of Ni (Nd-A) and the presence of Ni (Nd-B) as blocking metal was investigated. The experimental conditions are summarized in Table 4.2.

Table 4.2: *Summary of experimental conditions for the sorption of Ni and Nd on Na-STx-1 (0.3 mol L^{-1} NaClO$_4$) at trace concentrations in the absence and presence of Nd, respectively Ni, as blocking metal.*

Experiment	Trace metal loading (µmol g^{-1})	Blocking metal concentration (mol L^{-1})	S:L ratio (g L^{-1})	pH
Ni-A	3.9	-	2.06	7.1
Ni-B	2.5	5 x 10^{-5} (Nd)	2.06	6.7
Nd-A	7.5	-	2.06	6.7
Nd-B	7.8	5 x 10^{-4} (Ni)	2.06	6.7

The EXAFS measurements were performed at the Dutch-Belgium beamline (DUBBLE) at the ESRF. The k^{3-}weighted K-edge Ni-EXAFS spectra and k^{3-}weighted L$_{III}$-edge Nd-EXAFS spectra of treated montmorillonite are shown in Fig. 4.5a and 4.5b. The figures reveal that both of the Ni and both of the Nd EXAFS spectra are very similar. This indicates that the presence of Ni as a blocking metal for the sorption of trace Nd or the presence of Nd as a blocking metal for the sorption of trace Ni, does not have any influence on the surface structural environment of Nd, respectively Ni, taken up on the montmorillonite.

These surface analysis results confirm the wet chemistry measurements discussed above (see section 4.3.2) in that the Ni and Nd do not compete during uptake onto montmorillonite. It thus appears that the two metals are sorbed to different edge sites on the clay structure. A thorough multi-shell data analysis is currently underway.



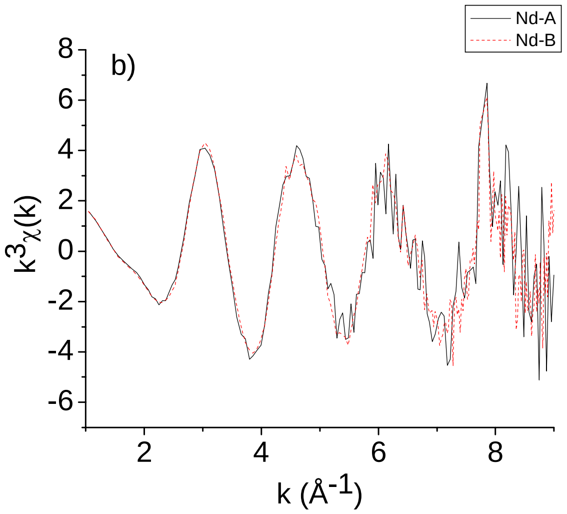


Fig. 4.5: *(a) k^3-weighted Ni K-edge EXAFS spectra of Ni loaded montmorillonite in the absence of Nd (Ni-A, solid line) and in the presence of Nd (Ni-B, red dotted line). (b) k^3-weighted Nd L_{III}-edge EXAFS spectra of Nd loaded montmorillonite in the absence of Ni (Nd-A, solid line) and in the presence of Ni (Nd-B, red dotted line).*

4.5 6th EU framework projects

The aim of the work carried out within the Clay System sub-programme in the NF-PRO and FUNMIG projects is to investigate and quantify the influence of carbonate complexation on the uptake characteristics of Ni(II), U(VI) and Eu(III) on Na-montmorillonite and Na-illite. Montmorillonite is the dominant clay mineral in bentonite whereas illite is an important clay mineral component in the Opalinus Clay formation. Where there is evidence that carbonate/ hydroxycarbonate complexes are sorbing, the intention is to derive surface binding constants.

Once these studies have been completed, a further aim will be to try to model sorption isotherms of the above three radionuclides on montmorillonite and illite in equilibrium with complex water chemistries corresponding to reference porewater chemistries used in the performance assessment (NAGRA 2002). Finally, similar work will be carried out using bentonite and Opalinus Clay themselves.

The above follows the "bottom up" approach in which the step-by-step procedure is intended to identify any unforeseen processes/factors, which could have an important influence on the sorption.

A key point in the investigations is to design experiments in which the chosen experimental conditions yield unambiguous results enabling clear conclusions to be drawn concerning the influence of carbonate complexation, and eventually to allow, where appropriate, complexation constants for carbonate species to be deduced. Factors which need to be taken into consideration are: (i) the range of CO_2 partial pressure readily achievable in our laboratory, (ii) any effect needs to be unambiguous and should be lie outside the range of sorption data measurement uncertainties which in practice means sorption reduction factors of at least 5 are needed, (iii) solubilities under the chosen experimental conditions, (iv) the desirability of being able to carry out experiments over a range of pH values at trace concentrations and as a function of concentration.

Three basic types of experiment are envisaged. The first type is sorption experiments at trace concentrations with constant concentrations of $NaHCO_3$ and varying the pH in the range ~6 to ~9. In the second type of experiment, sorption will be measured at trace concentrations in the pH range 6 to 9 but with variable $NaHCO_3$ concentrations; likely ranges are 10^{-3} to 10^{-1} mol L^{-1}. The third type of experiments are sorption isotherm measurements at constant pH (chosen within the range 6 – 9) and variable $NaHCO_3$ concentrations. In the latter type of experiments there are restrictions on the accessible concentration range due to solubility constraints.

A first result is shown in Fig. 4.6 where the sorption of Ni on Na-illite in the presence of 10^{-3} mol L^{-1} $NaHCO_3$ at pH 7.5 is given. These results are compared with data taken from BRADBURY & BAEYENS (2005c) in the absence of carbonate.

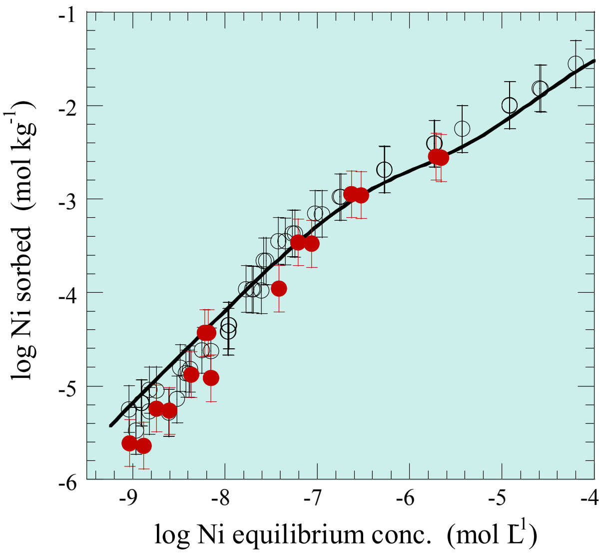


***Fig. 4.6:** Effect of inorganic carbon on Ni sorption isotherm on Na-Illite (0.1 mol L^{-1} $NaClO_4$, pH = 7.5(○) in the absence of $NaHCO_3$ and (●) in the presence of 10^{-3} mol L^{-1} $NaHCO_3$.*

4.6 Other activities

Bentonite porewater modelling: A paper on the pH buffering of the porewater in compacted MX-80 bentonite has been written and is at present under review (Bradbury & Baeyens, 2005d). This work was presented at the 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement", Tours, March 14-18, 2005. In co-operation with Posiva, Finland, model predictions have been carried out in a similar manner to those in the above work, and the calculated pH values will be compared with experimental measurements on compacted bentonite.

A porewater chemistry for MX-80 was calculated in connection with the NF-PRO programme and will be used in the experimental studies.

Retention in Opalinus Clay: A study on the diffusion and sorption properties of Na and Sr in Opalinus Clay has been written (Van Loon et al. 2005). In this work a comparison was made between the sorption data obtained from diffusion and batch type sorption experiments, and those from geochemical calculations. The sorption values for Na and Sr obtained from the three different methods were within a factor of 2. This result is a fairly strong indication that there is no significant difference between the exchange capacity available in the dispersed and in the intact rock systems.

The aim is to continue these types of investigations, and a continuous close collaboration with the diffusion mechanism group is foreseen.

TRLFS studies: Co-operations with other research institutes (FZK, FZR) in the field of sorption on clay systems coupled with surface analysis methods have been strengthened. Sorption of Eu/Cm on illite and montmorillonite coupled with TRLFS measurements has been synthesised in a two part paper and has been published (Rabung et al. 2005, Bradbury et al. 2005).

4.7 References

Bradbury M.H., Baeyens B. (1997)
A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part II: Modelling. J. Cont. 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. (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. (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 (in press).

Bradbury M.H., Baeyens B. (2005c)
Experimental and modelling investigations on Na-illite: Acid-base behaviour and the sorption of strontium, nickel, europium and uranyl. PSI Bericht Nr. 05-02 and Nagra NTB 04-02.

Bradbury M.H., Baeyens B. (2005d)
pH buffering of the porewater in compacted MX-80 bentonite. (in review)

Bradbury M.H., Baeyens B., Geckeis H., Rabung Th. (2005)
Sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite Part 2: Surface complexation modelling. Geochim. Cosmochim. Acta (in press).

Gorgeon L. (1994)
Contribution à la modélisation physico-chimique de la retention de radioéléments à vie longue par des matériaux argileux. Ph.D. thesis. Université Paris 6.

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 Technical Report NTB 02-05, Nagra, Wettingen, Switzerland.

Rabung Th., Pierret M.C., Bauer A., Geckeis H., Bradbury M.H., Baeyens B. (2005)
Sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite Part 1: Batch sorption and Time Resolved Laser Fluorescence Spectroscopy experiments. Geochim. Cosmochim. Acta (in press).

Turner D.R., Pablan R.T., Bertetti F.P. (1998)
Neptune(V) sorption on montmorillonite: An experimental and surface complexation modelling study. Clays Clay Minerals 46, 256-269.

Van loon L.R., Baeyens B., Bradbury M.H. (2005)
Diffusion and retention of sodium and strontium in Opalinus Clay: Comparison of sorption data from diffusion and batch sorption measurements, and geochemical calculations. Applied Geochemistry (accepted).

4.8 Publications

4.8.1 Peer reviewed journals and reports

Bradbury M.H., Baeyens B. (2004)
Sorption data bases for safety assessment of a waste repository for spent fuel, high-level and long-lived intermediate-level waste: Influence of the interaction between a high pH plume and the Opalinus Clay host rock on sorption. PSI Bericht Nr. 04-07 and Nagra NTB 03-12.

Bradbury M.H., Baeyens B. (2005c)
Experimental and modelling investigations on Na-illite: Acid-base behaviour and the sorption of strontium, nickel, europium and uranyl. PSI Bericht Nr. 05-02 and Nagra NTB 04-02.

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 (in press).

Bradbury M.H., Baeyens B., Geckeis H.[1], Rabung Th.[1] (2005) Sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite Part 2: Surface complexation modelling. Geochim. Cosmochim. Acta (in press).

[1] Forschungszentrum Karlsruhe, Karlsruhe, Germany

Nachtegaal M.[1], Scheidegger A.M., Dähn R., Chateigner D., Furrer G.[2] (2005)
Im-mobilization of Ni by Al-modified montmorillonite: A novel uptake mechanism. Geochim. Cosmochim. Acta (in press).

[1] ETH Zürich, Switzerland
[2] Ecole Nationale Supérieure d'Ingénieurs de Caen, Caen, France

Rabung Th.[1], Pierret M.C.[1,2], Bauer A.[1], Geckeis H.[1], Bradbury M.H., Baeyens B. (2005)
Sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite Part 1: Batch sorption and Time Resolved Laser Fluorescence Spectroscopy experiments. Geochim. Cosmochim. Acta (in press).

[1] Forschungszentrum Karlsruhe, Karlsruhe, Germany
[2] Centre de Géochimie de la Surface/Ecole et Observatoire des Sciences de la Terre, Strasbourg, France

Van loon L.R., Baeyens B., Bradbury M.H. (2005)
Diffusion and retention of sodium and strontium in Opalinus Clay: Comparison of sorption data from diffusion and batch sorption measurements, and geochemical calculations. Applied Geochemistry (accepted).

4.8.2 Conferences/Workshops/Presentations

Bradbury M.H., Baeyens B.
pH buffering of the porewater in compacted MX-80 bentonite. (Poster) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

Dähn R., Scheidegger A.M., Grolimund D., Harfouche M., Willimann M., Meyer B.
The Micro-XAS Beamline at The Swiss Light Source(SLS): A New Analytical Facility Dedicated to Micro-Beam Applications in the Environmental Sciences. 3rd Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources (Actinide-XAS-2004), Berkeley, USA, 14-16 September 2004.

5 CEMENT SYSTEMS

E. Wieland, J. Tits, J.P. Dobler, D. Kunz, P. Mandaliev, M. Vespa

5.1 Introduction

Cementitious materials are foreseen to be used in the planned deep underground repositories for long-lived intermediate-level (ILW) and low-level and short-lived intermediate-level (L/ILW) radioactive waste in Switzerland. Similar to the concepts developed worldwide, cement is employed to condition the waste and to construct the engineered barrier system (components of lining, backfill material). Thus, the near field will consist of about 90 weight percent (wt.%) cementitious materials, of which hardened cement paste (HCP) will be about 20 wt.%. In performance assessment studies it is considered that the source term for radionuclide migration into the host rock is determined by a combination of solubility and sorption constraints in the cementitious near field. Therefore, the uptake of radionuclides by HCP and cement minerals plays a decisive role in limiting and retarding the release from the near field.

The long-term aim of the sub-programme *Cement Systems* is to develop mechanistic models for the interaction of HCP with safety relevant radionuclides. The studies are directed towards improving the quantification of the source terms and strengthening the credibility of sorption values used in performance assessment studies. HCP is a complex matrix consisting of mainly calcium (aluminium) silicate hydrates (C(A)SH), portlandite and calcium aluminates (e.g., AFt- and AFm-type phases). Therefore, to gain the required understanding, it is necessary to conduct macroscopic and spectroscopic studies on the complex cement matrix and single cement minerals, namely calcium silicate hydrates (CSH).

The following sections give an overview of the main areas investigated in the past year:

New HCP samples were prepared using the sulphate-resisting Portland cement CEM I 52.5 N HTS (Lafarge, France), which is used for the conditioning of radioactive waste in Switzerland.

The investigations on the composition of HCP and the porewater during hydration have been completed, and the results are currently being published. The investigations were started using the new series of cement samples prepared for use in future sorption studies. The project was carried out within the framework of a bilateral co-operation with EMPA (Swiss Laboratories for Materials Testing and Research, Dübendorf).

Mechanistic sorption studies with Ni(II) on HCP, and Sr(II) and Ra(II) on HCP and CSH phases have been completed. The project on the interaction of Ra(II) with HCP and CSH phases was carried out within the framework of a joint research project with JNC, Japan.

Uptake studies with Eu(III), Th(IV), Am(III) and Np(V) on HCP and CSH are ongoing. Filtration techniques have been tested with a view to performing uptake studies with strongly sorbing Eu(III) and Th(IV) tracers on HCP and CSH at high solid to liquid (S/L) ratios. Stability test with Am(III) and Np(V) solutions have been carried out under alkaline conditions.

A Ph.D. project on the influence of the inherent micron-scale spatial heterogeneity of HCP on the immobilization mechanisms of Ni(II) and Co(II) is ongoing. An overview of the progress made in the past year is given in the summary report of the “XAS beamline” group (section 8).

A new Ph.D. project proposal entitled "A combined macroscopic and spectroscopic study of actinide and lanthanide binding mechanisms in cementitous waste repository materials" was approved by the NES Division Committee (BERK) and the PSI Research Commission. The Ph.D. student, (P. Mandaliev), joined the *Cement Systems* sub-programme in August 2005.

In May 2005 an international workshop on "Mechanisms and modelling of waste/cement interactions" was held in Meiringen, Switzerland. LES was involved in the organization of the workshop (E. Wieland) and had a member in the advisory panel (U. Berner). The workshop was organized jointly by EAWAG (Swiss Federal Institute of Environmental Science and Technology, Dübendorf), EMPA and PSI, and financially supported by Nagra, BUWAL (Bundesamt für Umwelt, Wald und Landschaft) and Cemsuisse (Swiss cement industry).

5.2 Hydration of Portland cement

Information on the mineralogical composition of HCP and the composition of the cement pore water in contact with the hydrated cement is needed for the correct design of the macroscopic and spectroscopic studies, for example, to ensure system equilibrium conditions at the start of the sorption experiments or to select appropriate reference systems for the spectroscopic experiments. Also, knowledge of the mineralogical composition of HCP is of major importance if sorption values of metal cations and anions that have been determined on different cement formulations are assessed for use in sorption data bases (e.g., WIELAND & VAN LOON, 2002).

The hydration of the sulphate-resisting Portland cement (CEM I 52.5 N HTS) was investigated in order to characterize a new series of cement samples, which had to be prepared for use in future sorption studies. In the hydration process the clinker minerals react with water to form the hydrate assemblage consisting of CSH, portlandite, calcium aluminates and some minor phases. The hydration studies were carried out at 20° C using two different cements (A, B). Cement B was obtained about 15 years ago and contained no calcite, whereas cement A is a "modern" cement, which contains roughly 4% calcite (Table 5.1). Over the past years cement B has been used for the macroscopic and spectroscopic investigations, whereas cement A will be employed in future studies.

A series of cement pastes were prepared at a water to cement ratio (w/c) = 0.4 and at 20° C to investigate the hydration of cement A over the time period of 150 days. For the short-term experiments up to six hours the pore solutions were collected by vacuum filtration using 0.45 µm Nylon filters. For longer hydration times pore fluids of the hardened samples were extracted using the steel die method and pressures up to 530 N/mm^2. Aliquots of the filtered pore solutions were used for pH measurements. The total concentrations of the elements in the pore fluids were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). The solid fractions of the samples were crushed, washed in acetone and dried at 40°C. The compositions of the materials were determined using X-ray diffraction (XRD) and thermogravimetric analysis-differential thermogravimetry (TGA/DTG). Experimental details are given in LOTHENBACH & WIELAND (2005).

Hydrated samples using cement B were prepared in 1989, and thus subjected to a long hydration period. The pore solution and the solid fraction were prepared and analysed as described above for cement A samples.

The hydration process was modelled using the thermodynamic model previously developed by LOTHENBACH & WINNEFELD (2005). The model is based on 1) the phase composition of the cement powders (Table 5.1), 2) the calculated dissolution rates of the clinker phases used as kinetic input (PARROT & KILLOH, 1984), and 3) thermodynamic equilibria for the solid phases and solid solutions involved. The thermodynamic calculations were carried out using the Gibbs free energy minimisation program GEMS (KULIK et al. 2004) together with the internally consistent data set reported by HUMMEL et al. (2002). Supplementary data for solids and solid solutions expected to form in cementitious systems were also included.

Table 5.1: *Composition of the cements A and B (CEM I 52.5 N HTS, Lafarge France). Blaine surface area: cement A = 354 m^2/kg; cement B = 334 m^2/kg.*

Chemical analysis [g/100g]			normalised phase composition [ii] [g/100g]		
	A	B		A	B
SiO_2	22.3	23.8	alite	61	60
Al_2O_3	2.7	2.7	belite	18	23
Fe_2O_3	1.9	2.8	aluminate	3.9	2.4
CaO	65.7	66.4	ferrite	5.8	8.5
MgO	0.85	0.88	CaO	0.45	0.61
K_2O	0.22	0.37	$CaCO_3$	3.7	0
Na_2O	0.13	0.09	$CaSO_4$ [iii]	3.6	2.9
CaO (free)	0.45	0.61	K_2SO_4 [i]	0.14	0.23
CO_2	1.6	0.0	Na_2SO_4 [i]	0.09	0.06
SO_3	2.2	1.8	K_2O [iv]	0.14	0.24
			Na_2O [iv]	0.09	0.06
			MgO [iv]	0.85	0.88
readily soluble alkalis [i]			SO_3 [iv]	0.01	0.01
K_2O	0.08	0.13 *(35% of total K)*			
Na_2O	0.04	0.03 *(30% of total Na)*			

[i] A: readily soluble alkalis were calculated from the concentrations of alkalis measured in the solution after 5 minutes agitation at a w/c of 10; present as alkali sulphates. B: Estimate based on the alkali content of B and on the alkali distribution of A.

[ii] calculated from the chemical analysis.

[iii] A: anhydrite (1.5 g/100g), hemihydrate (1.1 g/100g), gypsum (1.3 g/100g); B: anhydrite (1.8 g/100g), hemihydrate (1 g/100g), gypsum (0.1 g/100g)

[iv] present as solid solution in the major clinker phases.

The complete set of thermodynamic data is given in LOTHENBACH & WINNEFELD (2005). Further details of the modelling approach are given in LOTHENBACH & WIELAND (2005). Time-dependent changes in the compositions of the hydrate assemblage and the pore solution during hydration were calculated. These predictions are compared with the experimental data in Fig. 5.1.

Figs. 5.1a/b show that the agreement between experimental and modelling data is excellent in view of the somewhat simplistic modelling approach and the limited thermodynamic information available on the cement phases formed. In the case of Na, K and S, agreement is less satisfactory. The reasons are currently unclear. Fig. 5.1 shows that the main hydration process is completed within about 28 days. After that, the bulk and solution compositions change very slowly with time. The OH$^-$ concentration was determined to be about 180 mM after 28 days hydration, which corresponds to a pH of ~13.3.

Concerning the evolution of the hydrate assemblage, good agreement between predictions and the experimental data can be seen, Figs. 5.1 c/d. The model correctly predicts the reduction in the volume of the pore solution with time. The volume of free water decreases as it is becomes bound in the hydrates due to reaction with the clinker minerals. Interestingly, the formation of calcium monocarbonate is predicted in the calcite-containing cement, implying that the mono- or hemi-carboaluminates are more stable in the presence of carbonate than the monosulphate or other AFm phases (e.g., LOTHENBACH & WINNEFELD, 2005). The modelling approach was applied further to predict the compositions of the cement matrices and the pore solutions for pastes prepared with cement A and B at w/c = 1.3. Increasing the water volume was expected to enhance the degree of hydration of the pastes. Model predictions and the few experimental data that are available, agreed well (LOTHENBACH & WIELAND, 2005).

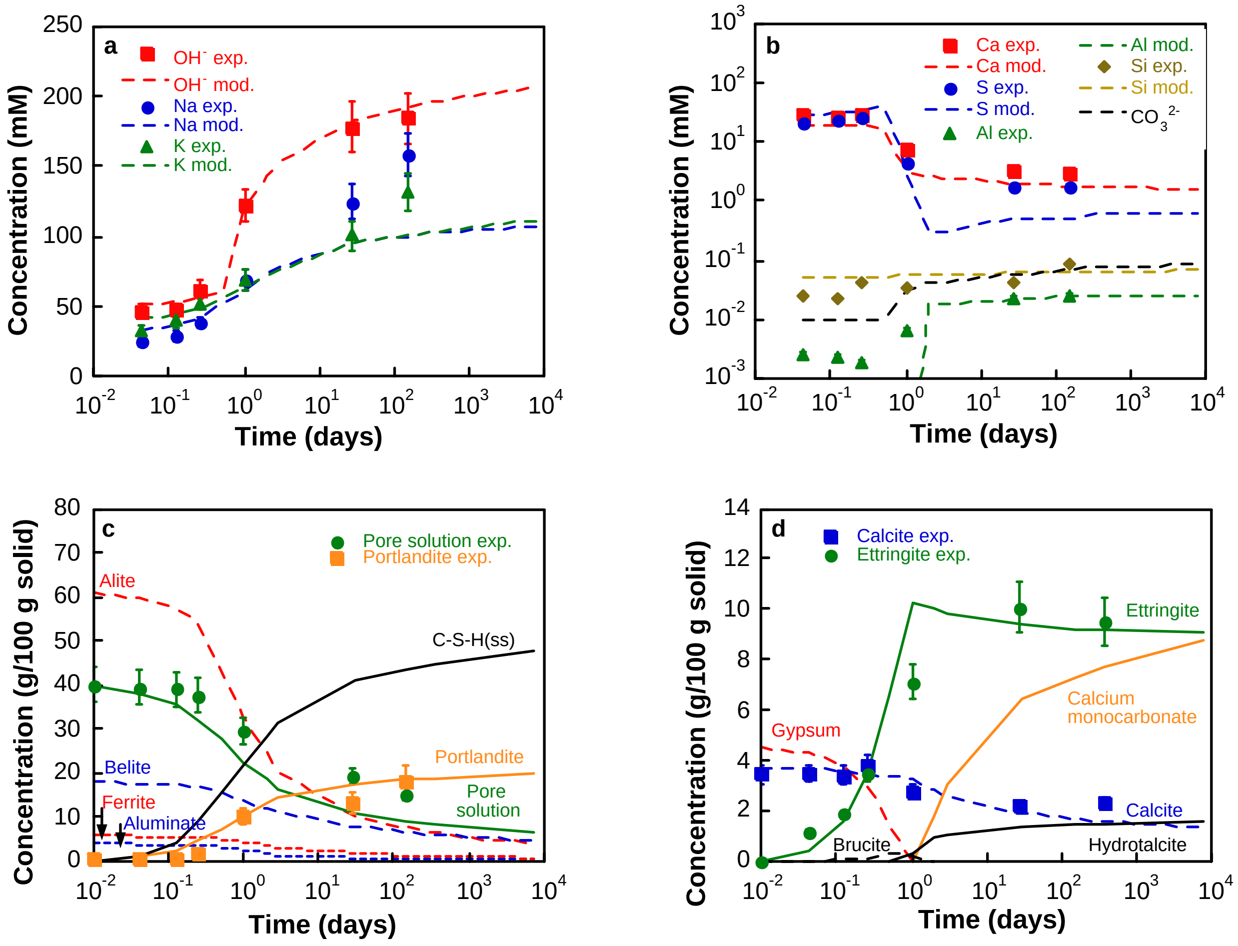


Fig. 5.1: Modelled evolution of the liquid and solid phases during the hydration of cement A (w/c = 0.4) compared to the experimentally determined concentrations in the pore solution and the measured amount of pore solution and portlandite, calcite and ettringite. a/b) The concentrations in the pore solutions refer to total concentrations with the exception of OH$^-$ which refers to free concentrations. c/d) Time-dependent evolution of the solid phase. In order to facilitate the comparison with XRD and TGA data, the values refer to 100 g of HCP. The mass of the solid phase increases with time as more and more hydration products precipitate and the amount of pore solution is reduced (ss = solid solution).

These findings show that the present thermodynamic model of cement hydration allows adequate predictions of the composition of hydrated cement and the corresponding equilibrium composition of the pore solution to be made for varying conditions. The study further revealed that the composition of the Portland cement CEM I 52.5 N HTS used in the Swiss waste management programme has changed slightly since 1990, when the first series of cement pastes for research purposes was prepared (SAROTT et al. 1992). The small portion of calcite present in the "modern" cement has an influence on the composition of the hydrate assemblage. However, it is unclear at the moment whether or not these changes in composition have any significant effect on the immobilization potential of the cement. The findings from this study will be considered in the design of future macroscopic and spectroscopic investigations.

5.3 Ni(II) uptake by HCP

In the past year a mechanistic model for Ni(II) uptake by HCP has been developed based on experimental investigations of the interaction of non-radioactive Ni and ^{63}Ni with HCP in contact with artificial cement pore water (ACW). ACW has the composition of a (Na/K) rich cement pore water in the first stage of cement degradation (pH = 13.3).

A Ni sorption isotherm was determined and the ^{63}Ni uptake by Ni loaded HCP was measured to quantify the exchange of ^{63}Ni with the non-radioactive Ni in the cement matrix. The results from this new series of experiments, reported in WIELAND et al. (2005), allowed a mechanistic interpretation of the sorption data reported earlier by WIELAND et al. (2000) and WIELAND & VAN LOON (2002).

The results presented in Fig. 5.2 show that the uptake of Ni by HCP cannot be interpreted in terms of a linear sorption process since the slope is greater than unity. Furthermore, the experimental data are not in accord with the idea that a pure phase, e.g. β-$Ni(OH)_2$(cr), controls the Ni concentration in the cementitious system. If this were to be the case, the Ni concentration in solution should be constant, i.e. fixed at ~$2 \cdot 10^{-6}$ M at pH = 13.3. However, the results presented in Fig. 5.2, show increasing concentrations of dissolved Ni at increasing concentrations of total Ni, indicating that the solubility limit is controlled by a solid phase with a variable composition (solid solution) rather than a phase with a fixed bulk composition.

The influence of the Ni concentration in HCP suspensions on the ^{63}Ni binding is shown in Fig. 5.3. Non-radioactive Ni was added to the HCP suspensions, which gave rise to an increase in the concentration of sorbed Ni from 19.9 ppm (pristine HCP), to 22.1 ppm (inital Ni concentration = 10^{-6} M) and 255.3 ppm (initial Ni concentration = 10^{-4} M). The distribution ratio (R_d) was found to increase with the increasing quantity of sorbed Ni (Fig. 5.3).

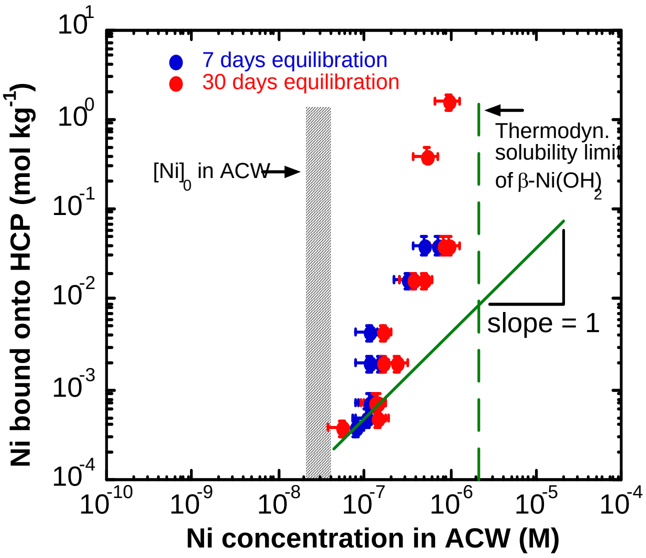


Fig. 5.2: *Ni sorption isotherm on HCP in ACW (pH = 13.3). Ni taken up by HCP is shown as a function of the concentration of dissolved Ni. The shaded area indicates the Ni background in ACW.*

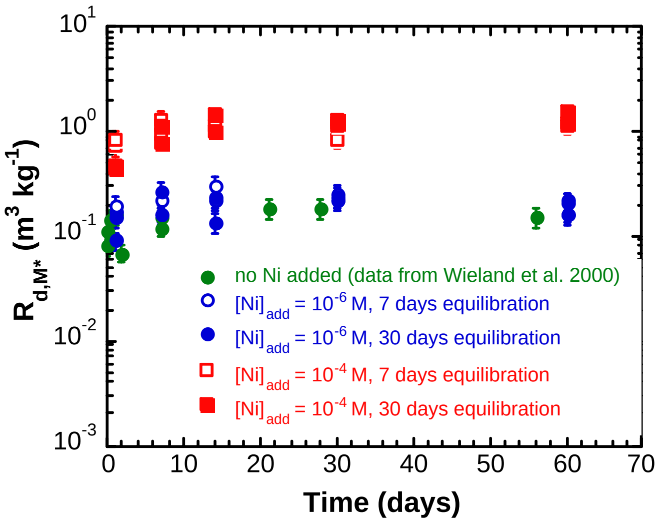


Fig. 5.3: *Time-dependent uptake of ^{63}Ni by pristine HCP (WIELAND et al. 2000) and HCP loaded with Ni in ACW. The Ni concentrations added to the HCP suspensions (S/L ratio = $2.5 \cdot 10^{-2}$ kg L^{-1}) were 10^{-6} M (Ni loading = 22.1 ppm) and 10^{-4} M (Ni loading = 255.3 ppm). The Ni containing HCP suspensions was pre-equilibrated with the HCP for 7 and 30 days before ^{63}Ni was added.*

Table 5.2: *Isotopic exchange of ^{63}Ni in HCP*

Conditions	$R_{d,M*}$ [m^3 kg^{-1}]	$R_{d,M}$ [m^3 kg^{-1}]	α
No Ni addition	0.15±0.02	4.6±2.3	$(3.3\pm1.7)\cdot10^{-2}$
$[Ni]_{add} = 10^{-6}$ M			
7 days equil.	0.22±0.02	4.9±1.0	$(4.5\pm1.0)\cdot10^{-2}$
30 days equil.	0.20±0.02	6.9±1.4	$(2.9\pm0.6)\cdot10^{-2}$
$[Ni]_{add} = 10^{-4}$ M			
7 days equil.	1.1±0.1	38.6±7.5	$(2.8\pm0.6)\cdot10^{-2}$
30 days equil.	1.2±0.1	26.8±5.4	$(4.5\pm1.0)\cdot10^{-2}$

Isotopic exchange of ^{63}Ni with a small fraction of non-radioactive Ni in the cement matrix was considered to account for the uptake of ^{63}Ni by HCP in these experiments. The partitioning of ^{63}Ni between HCP and ACW can be described in terms of a partition coefficient, α (LIESER, 2001):

$$\alpha = \frac{(n_{s,M*} / n_{s,M})}{(n_{l,M*} / n_{l,M})} = \frac{R_{d,M*}}{R_{d,M}}$$

$n_{s,M*}$ and $n_{s,M}$ denote the mole number of ^{63}Ni or non-radioactive Ni, respectively, in HCP; $n_{l,M*}$ and $n_{l,M}$ denote the respective mole numbers in ACW.

Note that the distribution coefficient, α, would equal 1 if the total inventory of Ni in HCP were accessible to isotopic exchange. The $R_{d,M*}$ value for ^{63}Ni was taken from Fig. 5.3. The R_d value of non-radioactive Ni, $R_{d,M}$, was determined based on the sorption isotherm measurements (Fig. 5.2). The partition coefficient, α, was found to vary in the range between $(2.8\pm0.6)\cdot10^{-2}$ and $(4.5\pm1.0)\cdot10^{-2}$ (Table 5.2). Note that the observed variation is small compared to the large variation of the Ni inventory in these experiments. Furthermore, α was found to be significantly less than unity, indicating that only a small portion of the Ni inventory in the cement matrix, i.e., between 2.8±0.6% and 4.5±1.0%, is accessible to isotopic exchange in HCP. Thus, the study shows that isotopic exchange is responsible for the observed immobilization of ^{63}Ni in HCP, but only a small portion of non-radioactive Ni in the HCP is accessible for exchange.

5.4 Sr(II) and Ra(II) uptake by CSH and HCP

5.4.1 Adsorption and co-precipitation processes of Sr in CSH systems

The objective of this project is to develop a mechanistic model which allows the binding of alkaline earth metals with CSH phases and HCP to be quantified. CSH phases are assumed to be the main minerals responsible for the uptake of alkaline earth metal cations in HCP. Sr(II) was chosen as being representative of this group of metals and is normally taken as an analogue for Ra(II). Furthermore, Sr radioisotopes are found in operational waste from reactors and reprocessing.

In the framework of the ECOCLAY-II project (5th EU framework programme) comprehensive sorption data sets for Sr on CSH phases were generated over a wide range of experimental conditions (solid compositions, solution compositions, S/L ratios). In the past year additional sorption experiments were performed to complete the data set.

The experimental data indicate that the sorption of Sr by CSH phases strongly depends on the $CaO:SiO_2$ (C:S) ratio of the CSH phases and on the pH. Plotting the Sr R_d values obtained on CSH phases having different C:S ratios as a function of the equilibrium Ca(II) concentration shows two lines each with a slope close to -1 (Fig. 5.4). The observed inverse correlation with the Ca concentration suggests that Sr binding to CSH phases is controlled by a cation exchange mechanism in which Sr replaces Ca at specific cation exchange sites.

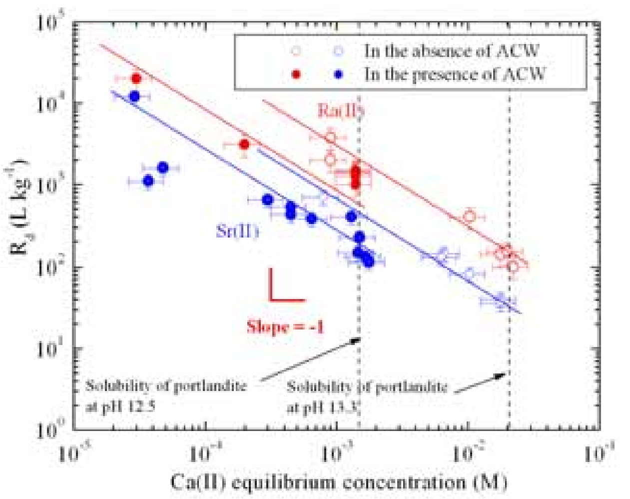


Fig. 5.4: *Sorption of Sr and Ra on CSH phases in (Na/K) rich ACW and in the absence of alkali metals. R_d values are plotted as a function of the Ca concentration in solution at equilibrium.*

In Fig. 5.4 the two distinct data sets are shown: R_d values determined in (Na/K) rich ACW and those determined in the absence of alkali metals. The lower values measured in ACW are interpreted as an effect due to the competition of Na and K on Sr uptake. The Sr sorption data determined under alkali metal free conditions has been interpreted in terms of a cation exchange reaction with a selectivity coefficient, ${}^{Sr}_{Ca}K_c$ = 1 (TITS et al. 2005b). A model of the Sr binding in the presence of Na and K is currently being developed.

5.4.2 Study of the Ra sorption on CSH and fresh and degraded HCP and co-precipitation of Ra with CSH phases

Due to the paucity of sorption data for Ra, it is common to estimate the Ra uptake by HCP and CSH phases based on the Sr sorption values (e.g., WIELAND & VAN LOON, 2002). To assess this approach it was decided to start a short-term experimental programme on the Ra uptake by cementitious materials. The project was conducted in the framework of a bilateral co-operation with the Japanese Nuclear Cycle Development Institute (JNC). The experimental programme was carried out between May 2004 and October 2004 at the JNC hot laboratory, QUALITY, in Tokai-Mura, Japan.

As a consequence of experimental constraints in connection with radiation protection and incorporation risks associated with the use Ra-226, it was not possible to collect a comprehensive set of experimental data that would allow the development of a mechanistic sorption model for Ra. Thus, the study focused on the acquisition of experimental data in cementitious systems needed to fill gaps existing in the Nagra/PSI sorption database. Further, an assessment of the sorption behaviour of Ra in comparison with Sr was made.

A series of sorption and co-precipitation tests was performed on CSH phases using a fixed total Ra concentration of $1.3 \cdot 10^{-8}$ M. The experiments were carried out in ACW at pH = 13.3 and, depending on the C:S ratio of the CSH phases, in solutions with pH ranging between 11.5 and 12.5. Sorption kinetics, effects of the S/L ratio and the C:S ratio, and reversibility of the uptake process were studied.

Ra uptake by CSH phases was found to be fast. Equilibrium was attained within 3 days, which is comparable to the time scale determined in the experiments with Sr (TITS et al. 2004). R_d values obtained from sorption and co-precipitation experiments were identical, indicating that internal and external sites are accessible to Ra binding. In general, the R_d values for Ra were factors of 3 to 5 times higher than those previously determined for Sr under similar experimental conditions (TITS et al. 2004; 2005b). As no measurable dependence of the R_d values on the S/L ratio was observed, it is concluded that the sorption of Ra at low Ra concentrations is linear. However, Ra uptake was found to depend on the C:S ratio of the CSH phases, comparable to the findings previously reported for Sr. The R_d value was found to decrease with increasing C:S ratio. Finally, the desorption experiments did not provide any evidence for irreversible sorption.

Although the data set is limited, and the uncertainties in the data are significant, the sorption data for Ra can be interpreted in an analogous manner to Sr. In Fig. 5.4 the R_d values for Ra are presented as a function of the equilibrium Ca concentration. By analogy to the previous work with Sr (TITS et al. 2005b), the Ra uptake by CSH phases can be interpreted in terms of a cation exchange process with Ca. The presence of alkali metals slightly reduces the Ra uptake at fixed Ca concentrations, suggesting that Na and K compete with Ra for the same cation exchange sites. Applying the cation exchange model previously developed for Sr to Ra yields a selectivity coefficient, ${}^{Ra}_{Ca}K_c$, of 6±4 (TITS et al. 2005c).

In addition to the Ra sorption studies on CSH phases, sorption kinetic tests on fresh HCP at pH 13.3 and on degraded HCP at pH 12.5 were performed. The Ra uptake in the degraded HCP was found to be fast and equilibrium was attained within one day. The R_d value at equilibrium was approximately 0.14 $m^3\ kg^{-1}$. The Ra uptake in fresh HCP might be interpreted as a two step process. A first fast step was finished within one day attaining an R_d value of 0.26 $m^3\ kg^{-1}$. In a second step the Ra slowly increased to an R_d value of 0.4 $m^3\ kg^{-1}$ over a period of 60 days. It is however not clear if the increase in R_d during the second step is significant due to the high uncertainties in the data.

The cation exchange model developed for the Ra sorption on CSH phases was applied to estimate the extent of Ra uptake by a degraded HCP (pH = 12.5). In the calculation it was assumed that the CEC of degraded HCP is about 60% of the CEC of CSH phases (HCP contains approximately 60 wt.% CSH). The equilibrium Ca concentration was assumed to be 0.02 M. The R_d value was estimated to be 0.09±0.04 $m^3\ kg^{-1}$, which is in good agreement with the experimentally determined value on degraded HCP at pH 12.5 ($R_d = 0.14 \pm 0.03\ m^3\ kg^{-1}$).

From the above study we conclude that in cementitious systems, the sorption behaviour of Ra is similar to that of Sr. Ra and Sr binding takes place via a cation exchange process on the CSH phases.

However, Ra binds more strongly to CSH/HCP than Sr.

5.5 Sorption studies with Eu(III), Th(IV) and Np(V)

The experimental programme on the uptake of actinides and lanthanides by CSH phases and HCP was continued in 2005. Lanthanides are considered to be appropriate analogues for the trivalent actinides.

Previous sorption studies indicated that the R_d values for Eu and Th on CSH and HCP could depend on the S/L ratio of the systems. Nevertheless, due to the extremely strong binding of these elements it was speculated that the interaction with colloids may be the main reason for the apparent decrease in the R_d values with increasing S/L ratio. Centrifugation of the suspensions for 1 h at 95,000 g (max) was the procedure used for the separation of the solid and liquid phases in these experiments. This allowed colloids with a diameter ≥ 15 nm to be removed from solution. In the past year an alternative separation method was tested to further assess the potential effect of colloids on the sorption measurements. The method is based on ultrafiltration using membranes with a MWCO of 10,000 Dalton. In order to avoid any loss of the strongly sorbing ^{152}Eu and ^{228}Th tracers on the filter holders and membranes, attempts were made to saturate the potential sorption sites either by filtering up to 20 aliquots of the suspension using the same filter prior to sampling, or by pre-saturating the filter using stable Eu or Th solutions having concentrations up to 10^{-5} M. The latter method is based on the assumption that the desorption process is significantly slower than sorption. The tests revealed that site saturation could not be achieved, and thus uptake of the ^{152}Eu and ^{228}Th tracers by the filtration unit could not be avoided. In a next step it is foreseen to test other separation methods which will allow an efficient removal of colloids from solution.

Np radioisotopes are associated with radioactive waste streams from medicine, industry and research (MIF wastes). Analytical procedures for measuring ^{237}Np and its daughter ^{233}Pa using alpha-beta discrimination in the liquid scintillation counting have been developed and optimised for activity measurements under alkaline conditions. Furthermore, a first series of solution stability tests and sorption kinetic tests on CSH phases and HCP were performed. The results indicate that, under ACW conditions, ^{237}Np solutions are not stable at concentrations above $8 \cdot 10^{-7}$ M. For Np(V) this concentration is well below the thermodynamically predicted solubility limit. Furthermore, sorption tests with ^{237}Np on CSH phases and HCP indicate a very strong uptake of Np(V) (R_d values up to 10 m^3 kg^{-1}). The above findings may be indicative of interfering additional reactions, such as the presence or formation of Np(IV) in these systems. More detailed solution stability and sorption tests are required.

5.6 Diffusion experiments

In the past year a new series of diffusion studies using non- and weakly sorbing tracers was planned. Analytical methods have been developed which allow simultaneous activity measurements of tritiated water (HTO), $^{134}Cs^+$ and $^{36}Cl^-$ tracers using β and γ counting. HTO will be used as the standard tracer for assessing the transport properties of the HCP discs. $^{134}Cs^+$ and $^{36}Cl^-$ represent weakly sorbing cationic and anionic species, respectively. Furthermore, the abrasive peeling method ALBINSSON & ENGKVIST, 1989; VAN LOON & EIKENBERG, 2005) was tested and optimised for our cementitious materials. The first series of through- and out-diffusion experiments using a combination of the above tracers is currently being started.

5.7 Workshop on waste/cement interactions

The workshop "Mechanisms and modelling of waste/cement interactions", held in Meiringen, Switzerland, between May 8-12, 2005, was attended by 85 scientists from 15 countries. The workshop focused on the chemical understanding and the thermodynamic modelling of those processes responsible for the solidification and stabilisation of hazardous and radioactive wastes in cementitious systems. The objectives of the workshop were to bring together scientists from various disciplines such as cement chemistry and radioactive and hazardous waste disposal, to stimulate discussions on current developments and to identify future potentials and needs in this field of research. The topics treated at the workshop were chosen to maximize the benefit for the different fields of research. Cement chemists reported on developments in the understanding of the cement mineralogy and thermodynamic modelling of cement systems. The hazardous and radioactive waste management communities presented their ideas on the mechanisms of contaminant binding to cement minerals as well as field, laboratory and modelling results from practical applications.

It is planned that the next workshop on waste/cement interactions will take place in 2008 in France.

5.8 References

ALBINSSON Y., ENGKVIST I. (1989)
Diffusion of Am, Pu, Np, Cs, I and Tc in compacted sand-bentonite mixtures. SKB Report TR 89-22, SKB, Stockholm, Sweden.

Hummel W., Berner U., Curti E., Pearson F.J., Thoenen T. (2002)
Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers/uPUBLISH.com, Parkland, Florida.

Kulik D., Berner U., Curti E. (2004)
Modelling chemical equilibrium partitioning with the GEMS-PSI code. PSI Scientific Report 2003, Vol. IV, 109-122. http://les.web.psi.ch/Software/GEMS-PSI/.

Lieser K.H. (2001)
Nuclear and Radiochemistry. 2nd ed. Wiley-VCH, Weinheim, Germany.

Lothenbach B., Winnefeld F. (2005)
Thermodynamic modelling of the hydration of Portland cement. Cem. Concr. Res. (in press).

Parrot L.J., Killoh D.C. (1984)
Prediction of cement hydration. British Ceramic Proceedings 35, 41-53.

Sarott F.-A., Bradbury M.H., Pandolfo P., Spieler P. (1992)
Diffusion and adsorption studies on hardened cement paste and the effect of carbonation on diffusion rates. Cem. Concr. Res. 22, 439-444.

Tits J., Wieland E., Dobler J.-P., Kunz D. (2004)
Uptake of strontium by calcium silicate hydrates under high pH conditions: An experimental approach to distinguish adsorption from co-precipitation processes. Mater. Res. Soc. Symp. Proc. 807, 689-694.

Van Loon L.R., Eikenberg J. (2005)
A high-resolution abrasive method for determining diffusion profiles of sorbing radionuclides in dense argillaceous rocks. App. Radiat. Isotopes (in press).

Wieland E., Tits J., Spieler P., Dobler J.P., Scheidegger A.M. (2000)
Uptake of nickel and strontium by a sulphate-resisting Portland cement. In: *Applied Mineralogy*, *Vol. 2*. (D. Rammlmair, J. Mederer, T. Oberthür, R.B. Heimann, H. Pentinghaus, eds.), Balkema, Rotterdam, 705-708.

Wieland E., Van Loon L.R. (2002)
Cementitious near-field sorption data base for performance assessment of an ILW repository in Opalinus Clay. PSI Bericht 03-06, Paul Scherrer Institute, Villigen, Switzerland (2003), and Nagra Technical Report NTB 02-20, Wettingen, Switzerland (2002).

5.9 Publications

5.9.1 Peer reviewed journals and reports

Bonhoure I.[1], Baur I.[2], Wieland E., Johnson C.A. [2], Scheidegger A.M. (2005)
Uptake of Se(IV/VI) oxyanions by hardened cement paste and cement minerals: An X-ray absorption spectroscopy study. Cem. Concr. Res. (in press).

[1] CTB-UPC, Manresa, Spain
[2] EAWAG, Dübendorf, Switzerland

Lothenbach B. [1], Wieland E. (2005)
A thermodynamic approach to the hydration of sulphate-resisting Portland cement. Waste Manage. (submitted).

[1] Empa, Dübendorf, Switzerland

Scheidegger A.M., Vespa M., Grolimund D., Wieland E., Harfouche M., Bonhoure I.[1], Dähn R. (2005)
The use of (micro)-x-ray absorption spectroscopy in cement research. Waste Manage. (submitted).

[1] CTB-UPC, Manresa, Spain

Tits J., Wieland E., Bradbury M.H. (2005a)
The effect of isosaccharinic acid and gluconic acid on the Eu(III), Am(III) and Th(IV) retention by calcite. Appl. Geochem. (in press).

Tits J., Wieland E., Müller C.J.[1], Landesmann C.[2], Bradbury M.H. (2005b)
A wet chemistry study of the strontium binding by calcium silicate hydrates. Appl. Geochem. (submitted).

[1] ETH Zürich, Switzerland
[2] SUBATECH, Nantes, France

Tits J., Iijima K. [1], Wieland E., Kamei G. [1] (2005c)
Radium binding by calcium silicate hydrates and hardened cement paste. Radiochim. Acta (submitted).

[1] JNC, Tokai, Japan

Vespa M., Dähn R., Grolimund D., Harfouche M., Wieland E., Scheidegger A.M. (2005)
Speciation of heavy metals in cement-stabilized waste forms: A micro-spectroscopic study. J. Geochem. Exploration (submitted).

Wieland E., Tits J., Ulrich A.[1], Bradbury M.H. (2005)
Experimental evidence for the solubility limitation of the aqueous Ni(II) concentration and isotopic exchange of ^{63}Ni in cementitious systems. Radiochim. Acta (in press).

[1] Empa, Dübendorf, Switzerland

5.9.2 Conferences/Workshops/Presentations

BONHOURE I.[1], WIELAND E., TITS J., SCHEIDEGGER A.M. (2004)
X-ray absorption spectroscopy (XAS) study of U(VI) immobilization by hardened cement paste. Oral presentation, 6th International Conference on Nuclear and Radiochemistry (NRC-6), Aachen, Germany, August 29 - September 3, 2004.

[1] CTB-UPC, Manresa, Spain

CUI D.[1], WERSIN P.[2], SPAHIU K.[3], SCHEIDEGGER A.M., WIELAND E. (2004)
X-ray absorption spectroscopy (XAS) study of U(VI) immobilization by hardened cement paste. (Poster) International Workshop on “Mechanisms and Modelling of Waste/Cement Interactions”, Meiringen, Switzerland, May 8-12, 2005.

[1] Studsvik Nuclear AB, Nyköping, Sweden
[2] NAGRA, Wettingen, Switzerland
[3] SKB, Stockholm, Sweden

LOTHENBACH B.[1], WIELAND E. (2004)
Thermodynamic modelling of the solid and pore water compositions during the hydration of a sulphate resisting Portland cement. (Oral presentation) International Workshop on “Mechanisms and Modelling of Waste/Cement Interactions”, Meiringen, Switzerland, May 8-12, 2005.

[1] EMPA, Dübendorf, Switzerland

TITS J., LANDESMANN C.[1], WIELAND E., MÜLLER, C.J.[2], BRADBURY M.H., RICHET C.[3] (2005)
A wet chemistry study of the strontium binding by calcium silicate hydrates. (Poster) International Workshop on “Mechanisms and Modelling of Waste/Cement Interactions”, Meiringen, Switzerland, May 8-12, 2005.

[1] SUBATECH, Nantes, France
[2] ETH Zürich, Switzerland
[3] CEA, Saclay, France

VESPA M., WIELAND E., DÄHN R., GROLIMUND D., SCHEIDEGGER A.M. (2004)
Immobilization of Ni and Co in cement-stabilized waste forms: A micro-spectroscopic study. Oral presentation, 3rd Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources (Actinides-XAS-2004), Berkeley, USA, September 14-17, 2004.

VESPA M., WIELAND E., DÄHN R., GROLIMUND D., HARFOUCHE M., SCHEIDEGGER A. M. (2004)
Immobilization of Ni and Co in cement-stabilized waste forms: A micro-spectroscopic study. NES Colloquium, PSI, Switzerland, November 11, 2004.

VESPA M., DÄHN, R., GROLIMUND D., SCHEIDEGGER A.M., WIELAND E. (2005)
Spectroscopic investigation of the Ni speciation in hardened cement paste. (Oral presentation) International Workshop on “Mechanisms and Modelling of Waste/Cement Interactions”, Meiringen, Switzerland, May 8-12, 2005.

VESPA M., DÄHN R., GROLIMUND D., HARFOUCHE H., WIELAND E., SCHEIDEGGER A. M. (2005)
Speciation of heavy metals in cement-stabilized waste forms: A micro-spectroscopic study. Poster presentation, GES-7 (Seventh International Symposium on the Geochemistry of the Earth Surface), Aix-en-Provence, France, August 23-27, 2005.

WIELAND E., TITS J., BONHOURE I.[1], VESPA M., SCHEIDEGGER A.M. (2004)
Radionuclide immobilization in cement systems. Oral presentation, 6th International Conference on Nuclear and Radiochemistry (NRC-6), Aachen, Germany, August 29-September 3, 2004.

[1] CTB-UPC, Manresa, Spain

WIELAND E., TITS J., STUMPF T.[1], FANGHÄNEL T.[1]
Uptake of lanthanides and trivalent actinides by cementitious materials. (Oral presentation) International Workshop on “Mechanisms and Modelling of Waste/Cement Interactions”, Meiringen, Switzerland, May 8-12, 2005.

[1] Forschungszentrum Karlsruhe, Karlsruhe, Germany

5.9.3 Review work for scientific journals

Environmental Science and Technology (3),
Geochimica et Cosmochimica Acta (2),
Waste Management (5).

6 COLLOID CHEMISTRY

C. Degueldre, R. Rossé, A. Kline

6.1 Introduction

The aim of the Colloid Chemistry sub-programme is to understand the role of colloids in the migration of radionuclides in the geosphere. Colloid studies focus predominantly on their properties (concentration, size distribution, nature) in the particular systems under investigation.

This report summarises the work carried out within the framework of the Grimsel colloid projects. Further activities include colloid studies such as the analytical tests on single particle analysis by ICP-MS.

6.2 Activities for the Grimsel Colloid Projects

The Colloid and Radionuclide Retardation (CRR) experiment was dedicated to the study of the in situ migration behaviour of selected actinides and fission products in the absence and presence of bentonite colloids in a water-conducting feature (shear zone) at the Grimsel Test Site (GTS).

In order to explain the colloidal behaviour of tri- and tetravalent actinides, in the absence and presence of bentonite colloids, ultracentrifugation and spectroscopic investigations were performed. It was found that up to 60 % of the Pu(IV) and Am(III) could be centrifuged out. Adding Cm(III) (5.10^{-8} mol L^{-1}) into the injection solutions instead of Am(III) allowed time resolved laser fluorescence spectroscopy (TRLFS) techniques to be employed. Peak position and fluorescence lifetime information together with the fact that a large fraction of the Cm(III) could be separated out by ultracentrifugation, suggested the existence of inner-sphere surface complexes on groundwater and bentonite colloids. Carbon K-edge XANES analysis of the bentonite colloids revealed the presence of significant amounts of natural organic constituents, mainly of an aliphatic nature containing high fractions of carboxylate groups. It is considered likely that these organic species contribute to the bentonite colloid stability and the sorption of actinides. A paper on this study has been published in Radiochim. Acta: GECKEIS et al. (2004). The Colloid and Radionuclide Retardation program was completed early in 2004.

The colloid work is continuing through participation in the project “Colloid Formation and Migration”, CFM, whose primary aim is to understand the generation of colloids at a bentonite block/groundwater interface under quasi-stagnant water flow conditions. The detailed goals of the CFM experiment are:

1. To examine the colloid generation rates and mechanisms at the engineered barrier system (EBS) – host rock boundary under *in-situ* conditions
2. To evaluate the long-distance migration behaviour of EBS-derived colloids in a water-conducting feature in a repository-relevant flow system (i.e. with a very low flow rate/water flux)
3. To study the long-term geochemical behaviour (mobility, mineralisation, colloid formation, etc) of radionuclides at the EBS-host rock boundary
4. To examine the influence of radionuclide-colloid interaction mechanisms on colloid-mediated radionuclide migration
5. To gain experience in long-term monitoring of radionuclide/colloid propagation near a repository
6. To apply the results to improve repository performance assessments, optimise EBS design and contribute to the "monitoring" debate.

Fig. 6.1 presents the experimental design with the key experimental locations indicated. The colloid size distribution in the FEBEX bentonite source powder was estimated from 1ppm suspensions measured immediately, and after allowing 24 hours settlement, Fig. 6.2. These results will be compared with the size distributions determined in the groundwater during the field experiment and with size distributions measured as a function of time in laboratory batch experiments using compacted discs of FEBEX bentonite.

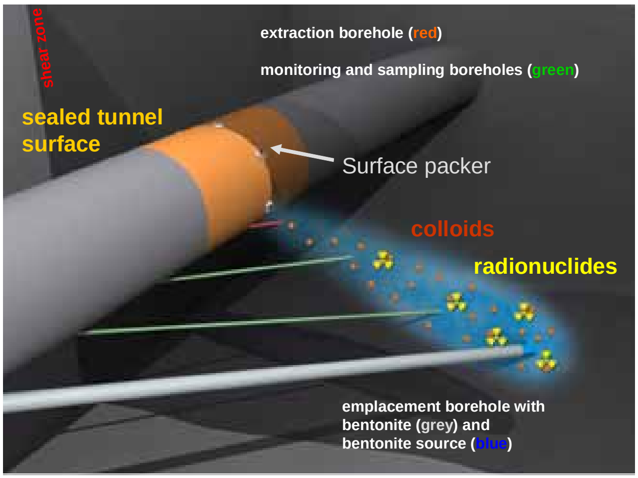


Fig. 6.1: *The design of the set up for the CFM experiment.*

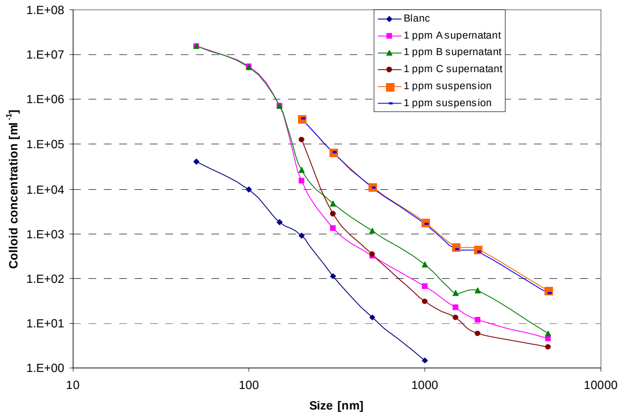


Fig. 6.2: *Colloid distribution in the FEBEX bentonite source material. The material was suspended in demineralised water. Conditions: 1 ppm FEBEX colloid suspensions measured immediately, and after a 24 hour settlement time (A,B&C 3 different tests).*

6.3 Other colloid activities

6.3.1 Colloid analytics

Uranium single particle analysis has been performed using inductively coupled plasma - mass spectrometry (ICP-MS) and the performance compared with results obtained from scanning electron microscopy (SEM) and single particle counting (SPC). The transient signal induced by the flash of ions due to the ionisation of a uranium colloidal particle in the plasma torch can be detected and measured for selected uranium ion masses ($^{238}U^+$, $^{235}U^+$ or $^{254}[^{238}U^{16}O]^+$) by the mass spectrometer. The signals recorded via time scanning are analysed as a function of particle size or fraction of the studied element or isotope in the colloid phase. The frequency of the flashes is directly proportional to the concentration of particles in the colloidal suspension. The basic equations for ICP-MS signal, s_A, analysis of a colloid of size d_{col} are:

$$s_A = \xi \, d_{\mathrm{col}}^3 \qquad (1)$$

(with $\xi = \pi \, \eta_A \, \eta_C \, \rho \, N_{\mathrm{Av}} / 6M_{\mathrm{MOx}}$, and with η_A the isotopic abundance, η_C the counting efficiency, ρ the colloid density N_{Av} Avogadro's number and M_{MOx} the molecular weight of the oxide). Equation (1) may be used for the size distribution evaluation using the colloid concentration N_{col} in the original suspension injected at a flow rate q_{col} and with the nebulisation fraction η_{neb} in argon. The colloid frequency detection f is then simply given by the product:

$$f = \eta_{neb} \, N_{col} \, q_{col} \qquad (2)$$

Equations (1) and (2) allow the metal size distribution (N_{col} vs d_{col}) to be calculated in the colloid phase on the basis of the signal distribution (f vs s_A) or vice versa.

The tests have been performed on uranium dioxide particles. The study, published in Talanta (DEGUELDRE et al. 2005) and presented at Actinide 2005 for U_3O_8 colloids, describes the experimental conditions and the reasons for choosing ^{238}U colloids for colloid counting in the single particle analysis mode.

Uranium dioxide colloid and particle distributions derived from SPC measurements are displayed in Fig. 6.3a. The material distribution is compared with a power law distribution fitted with an exponent $b = 4$. The larger sized colloid fraction, with a maximum population at $d_{col} = 700$ nm, is compared with results from counting a standard latex bead suspension with $d_{col} = 802$ nm. The ICP-MS signal for $^{238}U^+$, s_{238}, were recorded in time scan mode, see Fig. 6.3b. The scan was carried out over a 20 second period, and signal intensities recorded over 10 ms intervals. The signal analysis: f vs s_{238} (continuous line in Fig. 6.3c) was carried out under the following conditions: $\xi = 10^{-5}$ nm^{-3} and for 3 Gaussian distributions with maxima at $d_{col} = 160 \pm 90$ nm, $d_{col} = 300 \pm 50$ nm and $d_{col} = 700 \pm 130$ nm together with the concentrations corresponding to the “humps” in Fig. 6.3a.

Comparing the potentials of the different technique used for colloid analysis, it can be stated that SEM requires ~20 hours or so for a chemical analysis (colloid size >500 nm) and a morphological analysis (colloid size >50 nm). With SPC, counting colloids >30 nm requires only ~20 minutes. ICP-MS allows a colloid analysis isotope by isotopes in ~20 seconds for colloids in the range >50-100 nm with classical torch. This highlights the potential of this technique.

6.3.2 Actinide association on colloids

In a further study performed with a student (A. Kline), a model was developed to simulate metal surface precipitation by polymerization on colloids. The model took into account a reversible polymerization of the metal on the colloid, and used reversible surface complexation on one type of surface site. The model takes into account the correlation between hydrolysis and surface complexation constants to estimate all surface complexation constants. It is based on the metal adsorption on model sites as well as on already contaminated sites. In the model, the sorption coefficient (K_d) was calculated which is a measure of the amount of metal that sorbs onto the colloid particle.

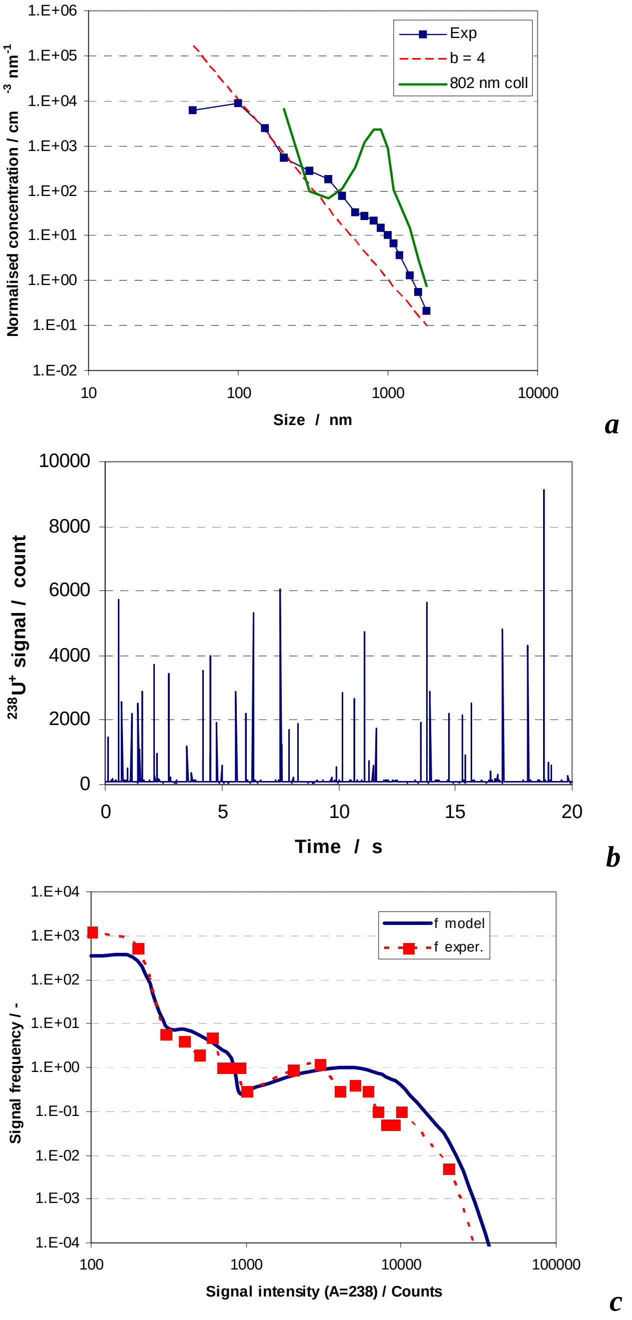


Fig. 6.3: *Analysis of uranium dioxide (UO_2) colloids by ICP-MS in a single particle mode.*

a*: Uranium colloid particle and volume distribution derived from SPC measurements. Conditions: uranium dioxide (UO_2) colloids; legend:* - - - *for the power law fit with b = 4,* —— *larger colloid fraction with a maximum population at d_{col} = 802 nm.*

b: *The signal s_{238} for $^{238}U^+$ was recorded over a 20 second period and the signal intensities recorded over 10 ms intervals.*

c: *Signal analysis: f vs s_{238}. Modelling conditions: $\xi = 10^{-5}$ nm^{-3} and for 3 Gaussian distributions with maxima at d_{col} = 160±90 nm, d_{col} = 300±50 nm and d_{col} = 700±130 nm together with the concentrations corresponding to the "humps" in Fig. 6.3 a.*

The model was applied to Th(IV), Pu(IV), and Am(III) onto Al_2O_3 colloids, and to Th(IV) onto TiO_2, FeOOH, and SiO_2 colloids. The calculations were performed for the effect of various polymer chain lengths, and pH e.g. Fig. 6.4, the radius of the colloids, and the concentration of both the metal and colloid. It was estimated that the highest sorption occurred at approximately neutral pH values for all of the tests. It was shown that at low metal concentrations polymerization did not significantly affect the sorption coefficient, but, as the metal concentrations reached the concentration of the surface sites, the sorption coefficients start to increase before tapering off at saturation for limited polymer sizes. As the size of the colloid particle decreased, the sorption coefficients increased as expected. The plot of the log K_d vs. log$[Th]_{tot}$ did not show any significant differences when the colloid concentration was increased up to 1 ppm. However above this concentration a peak in the K_d value was observed which was higher than would be estimated from the plot for 1ppm. When comparing the effect of colloid material, TiO_2 displayed the highest K_d values followed by Al_2O_3, FeOOH, and finally SiO_2. Since the polymerization is an effect associated with the metal and not with the type of colloid, once the polymerization began affecting the K_d, the K_d values for all four types of the colloids became similar as expected.

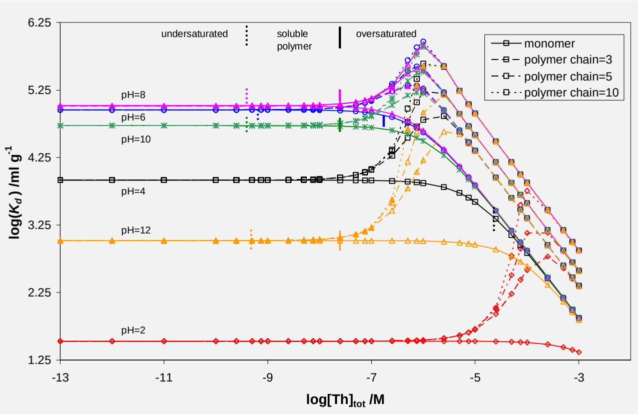


Fig. 6.4: *Distribution coefficient as a function of total thorium concentration for different pH values Conditions: Polymer Chain = Th atom number, Al_2O_3 colloid of radius 100 nm with [coll] = 10^{-6} g ml^{-1} and $[>SOH]_{tot} = 7.48x10^{-8}$ M at pH 7.*

6.4 Future work

Active participation in the Colloid Formation and Migration (CFM) at the Grimsel Test Site will continue. Analytical tests on single colloids by ICP-MS, carried out in collaboration with INE/FZK, will continue with clay and actinide colloids as well as with standard gold colloids.

The redox work has been completed as well as calculations dealing with polymerisation as a colloid generation mechanism. The work in future will focus on colloid generation from the bentonite block source in the CFM experiment.

6.5 Peer reviewed journals and reports

DEGUELDRE C., FAVARGER P.-Y.[1], ROSSÉ R., WOLD S.[2]
Uranium dioxide Colloid Analysis by Single Particle Inductively Coupled Plasma - Mass Spectrometry. Talanta (in press) (2005).

[1] Institut Forel, University of Geneva, Versoix, Switzerland
[2] Department of Chemistry, Royal Institute of Technology, Stockholm, Sweden

GECKEIS H.[1], SCHÄFER T.[1], HAUSER W.[1], RABUNG TH.[1], MISSANA T.[2], DEGUELDRE C.[3], MÖRI A.[4], EIKENBERG J.[3], FIERZ TH.[5], ALEXANDER W.R.[6]
Results of the Colloid and Radionuclide Retention experiment (CRR) at the Grimsel Test Site (GTS), Switzerland - Impact of Reaction Kinetics and Speciation on Radionuclide Migration. Radiochim. Acta 92 (2004) 765-774.

[1] Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung (INE), Postfach 3640, D-76021 Karlsruhe, Germany
[2] CIEMAT, Madrid, Spain
[3] Paul-Scherrer Institut, CH-5232 Villigen PSI, Switzerland
[4] Geotechnisches Institut, CH-3001 Bern, Switzerland
[5] Solexperts, CH-8603 Schwerzenbach, Switzerland
[6] NAGRA, CH-5430 Wettingen, Switzerland.

6.5.1 Internal reports

KLINE A.[1], DEGUELDRE C.
Metal Association with Colloids and Surface Precipitation: the Case of Actinides. PSI-LES, internal report: TM-44-04-02.

[1] University of Missouri-Columbia

6.6 Others

DEGUELDRE C., BOLEK M.
Modelling colloid generation with plutonium: the effect of pH and redox potential: Poster @ NRC6, Aachen, 31 Aug.- 3 Sept. 2004.

DEGUELDRE C.
Colloid Analysis by Single Particle Inductively Coupled Plasma - Mass Spectrometry (2005). SCM/CEA Seminary, April 1, 2005.

DEGUELDRE C., FAVARGER P.-Y.[1], ROSSÉ R., WOLD[2] S.
Uranium Colloid Analysis by Single Particle Inductively Coupled Plasma - Mass Spectrometry, Oral presentation, Actinide 2005, Manchester, 4-8 July 2005.

[1] Institut Forel, University of Geneva, Versoix, Switzerland
[2] Department of Chemistry, Royal Institute of Technology, Stockholm, Sweden

7 DIFFUSION PROCESSES

L.R. Van Loon, M.A. Glaus, F. González, A. Yaroshchuk, W. Müller, R. Rossé

7.1 General

The main goal of the group "Diffusion Processes" is to obtain a detailed understanding of the diffusion of radionuclides in compacted geological systems. The clay systems currently under investigation are Opalinus Clay, compacted bentonite (MX-80), and compacted clay minerals such as montmorillonite, illite and kaolinite.

In the framework of the field diffusion experiments at the Mont Terri Rock Laboratory (DI-A), diffusion experiments for $^{85}\mathrm{Sr}^{2+}$, $^{134}\mathrm{Cs}^{+}$, $^{60}\mathrm{Co}^{2+}$, $^{152}\mathrm{Eu}^{3+}$, I^- and Br^- in Opalinus Clay samples were performed and diffusion parameters (D_e and α) obtained.

The work on pure clay minerals was continued. The diffusion of $^{85}\mathrm{Sr}^{2+}$ in Na-montmorillonite was completed. New diffusion experiments with $^{85}\mathrm{Sr}^{2+}$ and $^{22}\mathrm{Na}^{+}$ in Na-montmorillonite, Na-illite and kaolinite were started.

New measurement times at the IN16 at ILL in France, at FOCUS at SINQ (PSI) and at the TOFTOF high resolution spectrometer at the Heinz Maier-Leibnitz neutron source in München were obtained.

The work for NF-PRO was focused mainly on calculating the pore water composition of compacted bentonite based on the methodology reported by BRADBURY & BAEYENS (2003). A recipe was developed and new systems were set up using the calculated pore water.

The FUNMIG project started at the beginning of 2005. For the first 18 month, experiments on the diffusion/retention of Cs are planned.

From January 1st to April 30th, a temporary collaborator, A. Rieser), performed experiments on the complexing behaviour of organic matter extracted from the Callovo-Oxfordian argillite obtained from the Bure site, France.

7.2 Diffusion in Opalinus Clay

Diffusion experiments in Opalinus Clay were continued. The through-diffusion experiments with $^{134}\mathrm{Cs}^{+}$ (in 10^{-3} M Cs in the source reservoir) started last year are still ongoing. The experiments on samples from Mont Terri reached steady state, and out-diffusion tests were started. The samples from Benken have still not reached steady state after 400 days. Because the concentration of the $^{134}\mathrm{Cs}$ in the source reservoir decreases during the experiments (Fig. 7.1), the diffusion model had to be modified to take this varying boundary condition into account. Moreover, the non-linear sorption behaviour of Cs, and the effect of the filters used in the experiment, had also to be taken into account (Fig. 7.2).

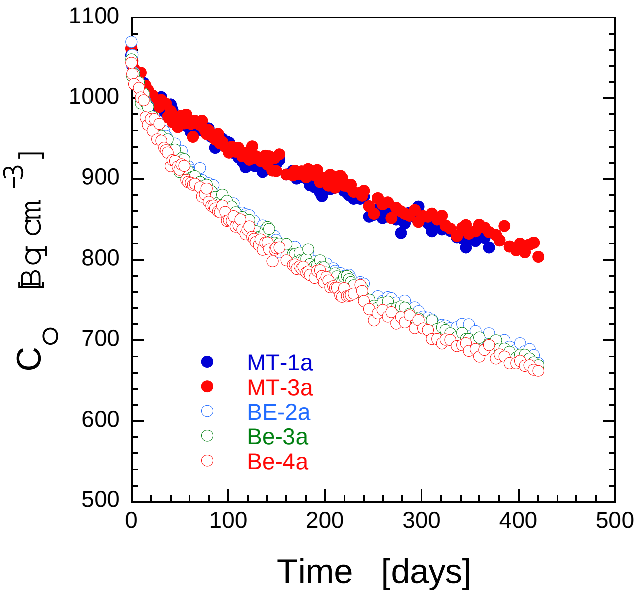


Fig. 7.1: *The evolution of the activity of $^{134}\mathrm{Cs}^{+}$ in the source reservoir during through-diffusion experiments in an Opalinus Clay sample from Mont Terri (MT) and Benken (BE).*

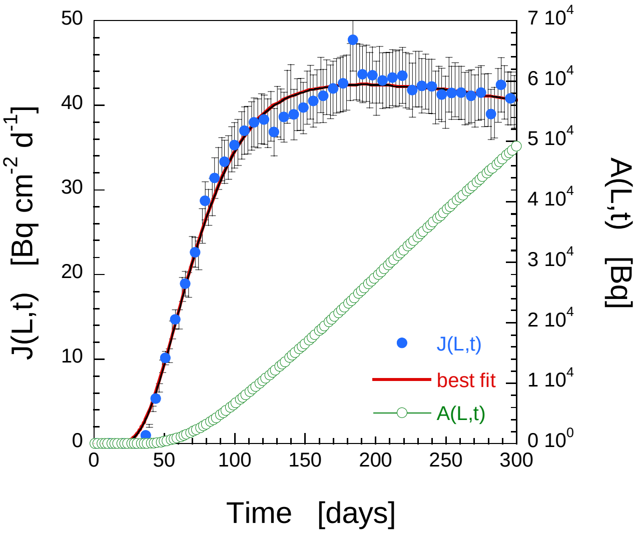


Fig. 7.2: *Break-through curve for the diffusion of $^{134}\mathrm{Cs}^{+}$ in an Opalinus Clay sample from Mont Terri (Cs_{tot} = 10^{-3} M). The best fit takes the decreasing concentration in the reservoir, the confining filters and the non-linear sorption of Cs into account. J(L,t) represents the flux at the downstream boundary (at x=L) and A(L,t) is the total diffused activity.*

The data for the in-diffusion of $^{134}Cs^+$ in Opalinus Clay at trace concentrations (VAN LOON & EIKENBERG, 2005) were re-evaluated. The influence of the filters used in the experiments was taken into account. This resulted in a better fit to the evolution of the concentration in the source reservoir. The values of the effective diffusion coefficient and the rock capacity factor were larger by a factor of 2. An interesting observation is that the effective diffusion coefficient of Cs^+ is a factor of 6 larger than that of HTO. Moreover, the values measured with a high background concentration of Cs^+ are lower than those measured at trace concentrations of Cs. So far, these results have not been explained.

In the framework of the DI-A experiment, the diffusion of I^-, Br^- and $^{134}Cs^+$ parallel to the bedding was studied. The diffusion parameters of Br^- and I^- were very similar to those measured for $^{36}Cl^-$ (VAN LOON et al. 2004). The diffusion of $^{134}Cs^+$ is still ongoing. Good sets of diffusion data for different cations and anions are now available for the Opalinus Clay from Mont Terri. Moreover, there is also good agreement between the data measured in the field experiments (mainly deduced from the decreasing concentration in the recirculation system) and the data measured in the laboratory on small samples.

Table 7.1: *Overview of the effective diffusion coefficients and rock capacity factors measured in the laboratory for different anions and cations in Opalinus Clay from Mont Terri.*

Isotope	D_e [m^2 s^{-1}] (23±2 °C)	α [-]
HTO	$(5.4 \pm 0.4)\times10^{-11}$	0.15 ± 0.03
$^{22}Na^+$	$(7.2 \pm 0.5)\times10^{-11}$	0.62 ± 0.05
$^{85}Sr^{2+}$	$(6.5 \pm 0.5)\times10^{-11}$	3.40 ± 0.20
$^{134}Cs^+$	$(2.6 \pm 0.1)\times10^{-10}$	isotherm
$^{36}Cl^-$	$(1.6 \pm 0.1)\times10^{-11}$	0.08 ± 0.01
Br^-	$(1.5 \pm 0.2)\times10^{-11}$	0.09 ± 0.03
I^-	$(1.4 \pm 0.1)\times10^{-11}$	0.12 ± 0.05

First scoping experiments on the diffusion of $^{60}Co^{2+}$ and $^{152}Eu^{3+}$ in Opalinus Clay were performed using in-diffusion combined with an abrasive peeling technique (ALBINSSON & ENGKVIST, 1989). This technique has been further developed and refined at PSI (VAN LOON & EIKENBERG, 2005) to abrade thin layers with typical thicknesses between 20 and 90 µm. Although the diffusion profiles could be measured with high resolution (Fig. 7.3), it turned out that only a small fraction of the activity which disappeared from the source reservoir could be found in the clay. The larger part was trapped by iron oxides precipitated on the porous filters used. The iron oxides are formed through the oxidation of pyrite in the Opalinus Clay. Future experiments will have to be performed under anoxic conditions. In the case of $^{60}Co^{2+}$ the profile in the Opalinus Clay showed an anomalous behaviour. Further experiments are planned to verify this observation.

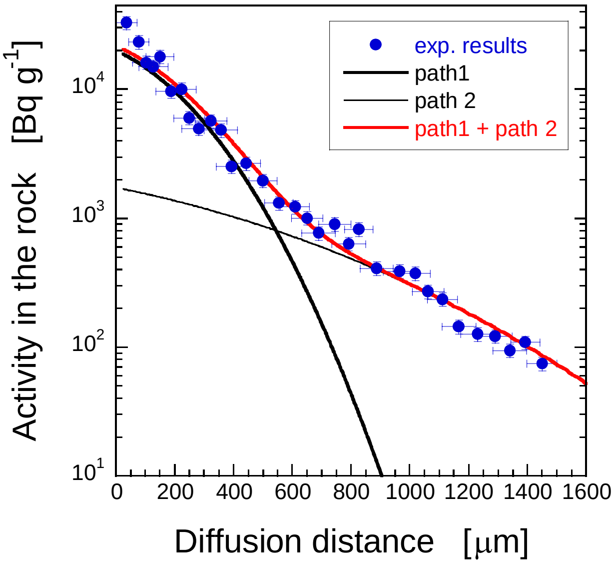


Fig. 7.3: *Diffusion profile of $^{60}Co^{2+}$ in Opalinus Clay after 15 days diffusion time. The profile cannot be described by a single diffusion process. At least two diffusion paths have to be used.*

7.3 Diffusion in compacted bentonite

Through-diffusion of $^{36}Cl^-$ was studied as a function of the dry density of the bentonite, and the chemical composition of the external water used in the experiments. The Cl-accessible porosity was found to be dependent on both the dry density of the clay and the ionic strength of the external water. The Cl-accessible porosity together with the cation surface loadings and the minerals present in the bentonite was used to calculate the composition of the bentonite porewater. A recipe for preparing the porewater was developed and distributed to the partners in the NF-PRO project. The results have been summarised in a report that is prepared as a deliverable defined in the project. (This work was carried out in close co-operation with the Clay Systems sub-programme using the methodology developed by BRADBURY & BAEYENS (2003)).

A new series of samples was prepared and saturated with the artificial porewater, and the diffusion of $^{22}Na^+$ and $^{85}Sr^{2+}$ started.

7.4 Transport phenomena in compacted clay mineral systems (TRAPHICCS)

The through-diffusion experiments of $^{85}Sr^{2+}$ across Na-montmorillonite, in which the effect of sample thickness and ionic strength was investigated at a dry density of ~1950 kg m^{-3}, were completed. Owing to the difficulties in interpreting the dependence of D_e values on ionic strength the general strategy had to be reassessed. It was decided to extend the investigations on the effect of ionic strength to other clay materials with differing swelling properties, viz. to kaolinite and illite. The issue of minimising the sample thickness was continued using sodium as a tracer, which has — owing to its weaker sorption properties — the advantages of a simpler chemistry and faster break-through times as compared to strontium. Thus the methodical and mechanistic questions have been decoupled. The past reporting period is thus mainly characterised by measuring experimental data. Modelling of these data will only be performed when all the information from through-diffusion, out-diffusion, filter diffusion and profile analysis are available. However, first attempts in this direction have already been undertaken. Time-dependent boundary conditions and the diffusive resistance of the filter plates have been included in the modelling.

The results obtained so far can be summarised as follows: i) The observation that D_e decreases with increasing ionic strength is most noticeable in the case of sodium montmorillonite. This finding has been established for all types of samples, i.e. for sample thicknesses between 1.4 and 10.4 mm. It is much less pronounced for illite and cannot be detected in the case of kaolinite. (Note that the interlayers in montmorillonite have the greatest tendency to swell.). It can thus be concluded that electrostatic phenomena are the reason for the dependence of D_e on ionic strength and that the diffusion of Sr across montmorillonite is mainly occurring through the interlayers. ii) First modelling calculations described in the last annual report suggested that the effect of the filter plates confining the clay samples needed to be considered in the evaluation of experimental data from diffusion experiments. This conclusion has now been corroborated by direct measurements of the diffusive properties of filter plates that have either been used "as received" from the manufacturer or previously used in through-diffusion experiments with montmorillonite.

Table 7.2: *Overview of diffusive properties of the filter plates used for confining the clay samples.*

l (mm) [a]	**$D_e \cdot 10^{10}$ [$m^2 s^{-1}$]**	**α [-]**	**n** [b]
— [c]	1.03 ± 0.1	0.23 ± 0.4	7
1.4	0.61 ± 0.04	0.59 ± 0.22	6
5.4	0.59 ± 0.03	0.77 ± 0.44	6
10.4	0.52 ± 0.04	0.29 ± 0.05	6

[a] Thickness of the clay sample in the through-diffusion experiment from which the filter plate was taken.

[b] Number of measurements.

[c] Unused filter plates.

Table 7.2 shows that the D_e values for filter plates originating from diffusion experiments are considerably lower than those for unused ones. Typical breakthrough curves are shown in Fig. 7.4. The reason for this difference may be found in changes of tortuosity or constrictivity of the filter plates, either caused by mechanical deformation of the filter pores owing to the large pressures, or by infiltration of clay particles into the filter plate during the through-diffusion experiment. In view of the observation that D_e values for used filter plates are more or less independent of the clay thickness used in the through-diffusion experiment, the second interpretation is rather more to be favoured. Note that the capacity factors (α) are poorly defined owing to the short diffusion length through the filter plates.

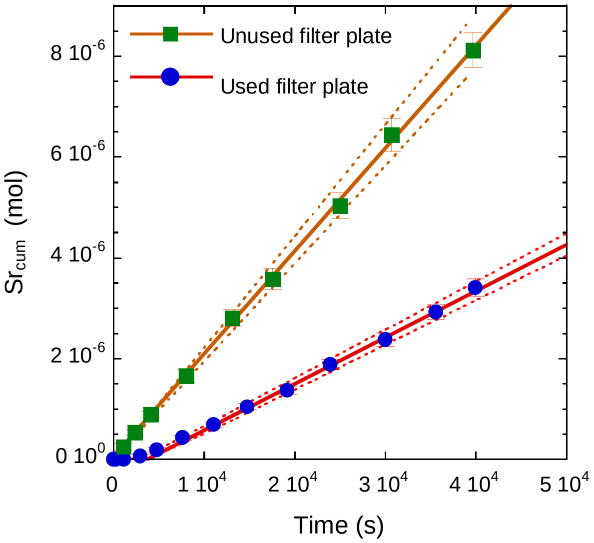


Fig. 7.4: *Comparison of breakthrough curves for Sr across unused filter plates and filter plates previously used in through-diffusion experiments with sodium montmorillonite compacted to dry densities of ~1950 kg m^{-3}.*

Note that the D_e values for filter plates originating from through-diffusion experiments with sodium montmorillonite (order of $6 \cdot 10^{-11}$ m^2 s^{-1}) are rather similar to those found for strontium diffusion in sodium montmorillonite (order of $4 \cdot 10^{-11}$ m^2 s^{-1}, at an ionic strength of 0.5 M; filter effects considered). Such a comparison makes clear that the diffusive resistance of the filter plates gains increasing importance with decreasing sample thickness. This conclusion was further corroborated by analyses of Sr concentration profiles (sum of Sr sorbed plus Sr in the pore space) across the direction of diffusion. The values found at the boundary between the clay sample and the filter plate on the high concentration side were much lower than expected from the Sr concentration in the feed reservoir.

7.5 Dynamics of water in compacted clay systems

Because water is the medium through which radionuclides are transported in compacted clay, it is important to know the structure and properties of confined porewater. The priority question is whether or not confined water has different (or similar) properties to bulk water. Pure clay minerals (montmorillonite, illite, kaolinite, and pyrophyllite) were chosen as model systems for studying the water behaviour in clays. The different clay systems were first characterised using several analytical methods (thermogravimetric analyses (TGA), differential thermal analyses (DTA), electron scanning microscopy (SEM), X-ray goniometry, chemical analysis).

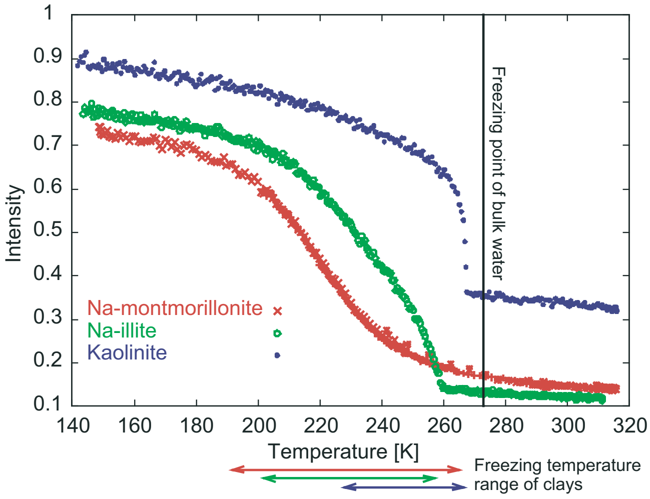


Fig. 7.5: *Freezing behaviour of water in different clay minerals compacted to a density of 1800 kg* m^{-3}. *The intensity of the elastically scattered neutrons is proportional to the amount of ice present in the system.*

Through-diffusion experiments with HTO were performed at different ionic strengths and at different temperatures. The temperature dependence of the effective diffusion coefficient gives information on the activation energy of the diffusion process and indirectly on the state of the pore water. So far measurements on two different clay systems (Na-illite and Ca-montmorillonite) were completed. New samples of Ca-illite, kaolinite and phyrophyllite were prepared and are ready to be used in further diffusion experiments. In the case of montmorillonite higher values of the activation energy than in bulk water were observed (Na-montmorillonite: 21 kJ mol^{-1}, Ca-mont-morillonite: 19 kJ mol^{-1}). In illite, the activation energy was significantly lower (Na-illite: 14 kJ mol^{-1}). The interpretation of the results is in progress.

Neutron scattering measurements on Na- and Ca-montmorillonite, Na- and Ca-illite, kaolinite and pyrophyllite were performed using the time-of-flight spectrometer FOCUS at PSI, and the IN10 and IN16 backscattering spectrometers at ILL. At FOCUS information on the local diffusion of water in the pores is gained, whereas the backscattering measurements gave information on the freezing behaviour of water in clays. Fig. 7.5 shows the elastic scattering of neutrons by the frozen water in three different clay materials. The more "ice-like" water present, the higher the intensity of the scattered neutrons. The figure clearly shows that the freezing behaviour of water in the pores depends strongly on the type of clay.

7.6 The use of ultra thin clay membranes in diffusion studies

A theoretical evaluation of the use of ultra thin clay membranes for studying the diffusion of strongly sorbing tracers was made. It could be shown that in the steady state phase of the through-diffusion, the filters used to confine the clay membranes dominate the diffusive flux and the contribution of the clay layer vanishes. In addition, it turned out that the production of thin compacted clay membranes is very difficult. The original idea of using membranes in through-diffusion experiments has therefore been abandoned. Alternatively, in-diffusion combined with tracer profile analysis has to be applied. Combined with analysis of the tracer evolution in the source reservoir, both the effective diffusion coefficient and the rock capacity factor can be determined. The profile in the rock gives the ratio of the effective diffusion coefficient, D_e, and the rock capacity factor, α. The evolution of the tracer in the source reservoir gives information on the product of both parameters. For the interpretation of the in-diffusion data, a novel theoretical approach has been developed taking into account the variation of radionuclide concentration in the feed reservoir and the presence of the filter. Its application to the interpretation of the in-diffusion of $^{134}Cs^+$ into the Mont Terri Opalinus Clay (VAN LOON & EIKENBERG, 2005) has enabled us to obtain reliable values of the sorption capacity and effective diffusion coefficient.

First steps on the application of electrochemical measurements on compacted clay systems have been carried out.

It has been shown that the self diffusion coefficients of the cations and anions of the dominant salt can be estimated from the integrated measurements of electric conductivity and of membrane potential with relatively thick layers of compacted clays confined by porous supports. As compared to the conventional diffusion measurements, the electrochemical techniques are very rapid, which makes the gathering of representative statistics and the studying of correlations with, for example, the ionic strength and the pH-value of the pore solution, relatively easy. On the other hand, the electrochemical measurements only provide data on the clay properties with respect to the dominant cations and anions. Therefore, the electrochemical measurements alone are not sufficient for our purposes and should be combined with reference diffusion measurements. The corresponding experimental programme is being worked out, and the test cell design is being developed.

The general methodology and the experimental approaches to the electrochemical characterization of nano-porous media have been described in YAROSHCHUK et al. (2005a, b).

7.7 Organic ligands

The focus of the experiments addressing the chemical stability of α-isosaccharinic acid (α-ISA) was on studying its reactivity at 90 °C in the presence of $Ca(OH)_2$. Previous experiments were carried out in an argon-filled vacuum oven, whereas the main experiments carried out in the present reporting period were performed in an oven housed in an inert atmosphere glove-box. Thus the possibility of oxygen contamination in the current experiments was significantly reduced. After an initial phase of rapid chemical transformation of α-ISA, the reactions slowed down unexpectedly, and no transformation of α-ISA could be detected in the subsequent observation time of more than 200 d. Note that in the test experiments in the argon-filled vacuum oven, the same amounts of α-ISA were transformed within a time period of less than 50 d. Owing to this unexpected behaviour it was agreed between the project partners (Nagra, Nirex, SKB, PSI) that the observation phase for the experiments should be prolonged, but without increasing the overall costs for the experiments. The time frame for finalising the project will, however, depend on the results of investigations on the stability of α-ISA in the presence of crushed hardened cement paste carried out in a glove box at room temperature. These will be available in the next months.

Another activity within the frame of organic ligands was the investigation of the complexing properties of organic matter extracted from Callovo Oxfordian clay from the French Rock Laboratory at Bure. Two types of extractions were tested: (i) Aqueous extraction and (ii) alkaline extraction after dissolution of calcite with nitric acid. After characterising the extracts using various ion chromatographic methods, carbon analysis and UV-VIS spectroscopy, they were tested for their influence on the sorption of Ni(II), Eu(III) and Th(IV) on a cation exchange resin. All of the steps in the rock preparation, extraction and sorption experiments were carried out under exclusion of air in a glove box in order to prevent any oxidative alterations of the organic material. It was observed that the sorption of the radionuclides tested did not differ significantly from the sorption observed in the presence of synthetic water with a similar composition as the extracts but containing no organic carbon. It can be concluded that only a minor part of the water soluble organic matter extracted may be composed of humic substances. This conclusion is further corroborated by analysis of the extracts with ion exclusion chromatography, which showed that a major part of the organic matter is composed of low-molecular weight carboxylic acids.

7.8 References

ANDERSSON K., TORSTENFELT B., ALLARD B. (1981)
Diffusion of cesium in concrete. In: Moore, J.G. (ed.) Scientific Basis for Nuclear Waste Management, Vol. 3. Plenum Publishers, New York, 235-242.

BRADBURY M.H., BAEYENS B. (2003)
Porewater chemistry in compacted re-saturated MX-80. Contaminant Hydrology 61, 329-338.

VAN LOON L.R., WERSIN P., SOLER J.M., EIKENBERG J., GIMMI TH., HERNÁN P., DEWONCK S., SAVOYE S. (2004)
In-situ Diffusion of HTO, $^{22}Na^+$, Cs^+ and I^- in Opalinus Clay at the Mont Terri Rock Laboratory. Radiochimica Acta 92, 757-763.

VAN LOON L.R., EIKENBERG J. (2005)
A High Resolution Abrasive Method for Determining Diffusion Profiles of Sorbing Radionuclides in Dense Argillaceous Rocks. Applied Radiation and Isotopes 63, 11-21.

Yaroshchuk A.E., Zhukova O.V., Ulbricht M., Ribitsch V. (2005a)
Electrochemical and other transport properties of nano-porous track-etched membranes studied by the current switch-off technique. Langmuir, 21, 6872-6882.

Yaroshchuk A.E., Boiko Yu.P., Makovetskiyx A.L. (2005b)
Some properties of electrolyte solutions in nano-confinement revealed by the measurements of transient filtration potential after pressure switch-off. Langmuir, in press.

7.9 Publications

7.9.1 Peer reviewed journals and reports

Glaus M.A., Baeyens B., Lauber M., Rabung T.[1], Van Loon L.R. (2005)
Influence of water-extractable organic matter from Opalinus Clay on the sorption and speciation of Ni(II), Eu(III) and Th(IV). Applied Geochemistry 20, 443-451.
[1] FZK, Karlsruhe, Germany

Tevissen E.[1], Soler J.M.[2], Montarnal P.[1], Gautschi A.[3], Van Loon L.R. (2004)
Comparison between *in situ* and laboratory diffusion studies of HTO and halides in Opalinus Clay from the Mont Terri. Radiochimica Acta 92, 781-786.
[1] CEA Saclay, Gif-sur-Yvette, France
[2] CSIC-IJA, Barcelona, Spain
[3] NAGRA, Wettingen, Switzerland

Van Loon L.R., Eikenberg J. (2005)
A High Resolution Abrasive Method for Determining Diffusion Profiles of Sorbing Radionuclides in Dense Argillaceous Rocks. Applied Radiation and Isotopes 63, 11-21.

Van Loon L.R., Jakob J. (2005)
Evidence for a Second Transport Porosity for the Diffusion of Tritiated Water (HTO) in a Sedimentary Rock (Opalinus Clay, OPA): Application of Through- and Out-diffusion Techniques. Transport in Porous Media 61, 193-214.

Van Loon L.R., Wersin P.[1], Soler J.M.[2], Eikenberg J., Gimmi Th., Hernán P. [3], Dewonck S.[4], Savoye S.[5] (2004)
In-situ Diffusion of HTO, $^{22}Na^+$, Cs^+ and I^- in Opalinus Clay at the Mont Terri Rock Laboratory. Radiochimica Acta 92, 757-763.
[1] NAGRA, Wettingen, Switzerland
[2] CSIC-IJA, Barcelona, Spain
[3] ENRESA, Madrid, Spain
[4] ANDRA, Bure, France
[5] IRSN, Fontenay-aux-Roses, France

Van Loon L.R., Soler J.M.[1], Müller W., Bradbury M.H. (2004)
Anisotropic diffusion in layered argillaceous rocks : A case study with Opalinus Clay. Environ. Sci. Technol. 38, 5721-5728.
[1] CSIC-IJA, Barcelona, Spain

Van Loon L.R., Glaus M.A., Vercammen K. (2004)
Stability of the Ion Pair Between Ca^{2+} and 2-(Hydroxymethyl)-3-Deoxy-D-*erythro*-Pentonate (α-Isosaccharinate). J. Solution Chemistry 33, 1573-1583.

Van Loon L.R., Müller W., Iijima K.[1] (2005)
Activation Energies of the Self-Diffusion of HTO, $^{22}Na^+$ and $^{36}Cl^-$ in a Highly Compacted Argillaceous Rock (Opalinus Clay). Applied Geochemistry 20, 961-972.
[1] JNC, Japan

Yaroshchuk A.E., Zhukova O.V.[1], Ulbricht M.[1], Ribitsch V.[2] (2005a)
Electrochemical and other transport properties of nano-porous track-etched membranes studied by the current switch-off technique. Langmuir, 21, 6872-6882.
[1] Universität Duisburg-Essen, Essen, Germany
[2] Karl-Franzens-Universität, Graz, Austria

Yaroshchuk A.E., Boiko Yu.P.[1], Makovetskiyx A.L.[1] (2005b)
Some properties of electrolyte solutions in nano-confinement revealed by the measurements of transient filtration potential after pressure switch-off. Langmuir, in press.
[1] National Academy of Sciences of Ukraine, Kiev, Ukraine

Yaroshchuk A.E., Karpenko L.[1], Ribitsch V.[1] (2005)
Measurements of transient membrane potential after current switch-off as a tool to study the electrochemical properties of supported thin nano-porous layers, J. Phys. Chem. B 109, 7834-7842.
[1] Karl-Franzens-Universität, Graz, Austria

7.9.2 Conferences/Workshops/Presentations

Glaus M.A., Müller W., Van Loon L.R.
Separation of radiolabelled iodate and iodide by HPAEC. IICS'04, 17th Annual International Ion Chromatography Symposium, Trier, Germany, 20-23 September, 2004.

Glaus M.A., Van Loon L.R.
Cellulosehaltige Abfälle : Ein stör(rischer)-Faktor in der Sicherheitsanalyse? Co-ordination Meeting, Forschungszentrum Rossendorf, Germany, 24-26 October, 2004.

GLAUS M.A., VAN LOON L.R.
Reactivity of α-isosaccharinic acid in heterogeneous alkaline systems. Interim Meeting of the Project Technical Group, PSI, Villigen, Switzerland, 27 August, 2004.

GLAUS M.A., LAUBE A., VAN LOON L.R.
Safety Assessment and Concrete Admixtures: Can we treat them all the same? International Workshop on "Mechanisms and Modelling of Waste/Cement Interactions", Meiringen, Switzerland, May 8-12, 2005.

GONZÁLEZ F.
Dynamics of Confined Water in Compacted Clay Systems. PSI internal seminar, 18. January, 2005.

GONZÁLEZ F.
Dynamics of Confined Water in Compacted Clay Systems. University of Bern internal seminar, 24. January, 2005.

GONZÁLEZ F., JURÁNYI F.[1], GIMMI T., VAN LOON L.R.
Dynamics of Confined Water in Compacted Clay Systems. SINQ User meeting, Villigen, 27. January, 2005.

[1] Saarland University, Saarbrücken, Germany

GONZÁLEZ F.
Macro- and microscopical Studies of Water Dynamics in Compacted Clays. PSI-CEA coordination meeting, Saclay, France, 27.-28. June, 2005.

GONZÁLEZ F., JURÁNYI F.[1], GIMMI T., VAN LOON L.R.
Dynamics of Confined Water in Compacted Clay Systems. 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

[1] Saarland University, Saarbrücken, Germany

GROLIMUND D., VAN LOON L.R., BAEYENS B., SCHEIDEGGER A.M., BARMETTLER K.[1], WERSIN P.[2], HEALD S.M.[3]
Cs Migration in Complex Geological Media: new insights through micro-X-Ray Fluorescence imaging and EXAFS spectroscopy. 2nd International Meeting on Clays in Natural and Engineered Barriers for Radioactive Waste Confinement, Tours, France, 14-18 March, 2005.

[1] ETHZ, Zürich, Switzerland
[2] NAGRA, Wettingen, Switzerland
[3] Pacific Northwest National Laboratory, Argonne, USA

VAN LOON L.R., EIKENBERG J.
A high-resolution abrasive method for determining diffusion profiles of sorbing radionuclides in dense argillaceous rocks. Mont Terri long-term diffusion experiment (DI-A), Technical Meeting, Tournemire, France, 7-9 November 2004, and 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

VAN LOON L.R., GROLIMUND D., BAEYENS B., SCHEIDEGGER A.M., GÜNTHER D.[1], AESCHLIMANN B.[1], BARMETTLER K.[1], WERSIN P.[2]
Migration of reactive chemicals in heterogeneous geologic media: new insights through micro-imaging and micro-spectroscopy. Mont Terri long-term diffusion experiment (DI-A), Technical Meeting, Tournemire, France, 7-9 November 2004.

[1] ETHZ, Zürich, Switzerland
[2] NAGRA, Wettingen, Switzerland

VAN LOON L.R., JAKOB A., MÜLLER W.
Laboratory studies at PSI. Mont Terri long-term diffusion experiment (DI-A), Technical Meeting, Tournemire, France, 7-9 November 2004.

VAN LOON L.R., JAKOB A., MÜLLER W.
Laboratory diffusion studies at PSI. Technical meeting DI-A/DI-B/DR. Basel, 13-14 June, 2005.

VAN LOON L.R., JAKOB A., MÜLLER W.
Diffusion of strongly sorbing tracers in Opalinus Clay : first experiences at PSI. Technical meeting DI-A/DI-B/DR. Basel, 13-14 June, 2005.

WERSIN P.[1], DEWONCK S.[2], SAVOYE S.[3], HERNÁN P.[4], VAN LOON L.R., SOLER J.[5], GIMMI T., CARTALADE A.[6], YLLERA A.[7], EIKENBERG J., GROLIMUND D., BAEYENS B., VAN DORP F.[1]
Diffusion of HTO, Iodide, Sodium-22 and Caesium in Opalinus Clay: A combined field, laboratory and modelling study. 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

[1] NAGRA, Wettingen, Switzerland
[2] ANDRA, Bure, France
[3] IRSN, Fontenay-aux-Roses, France
[4] ENRESA, Madrid, Spain
[5] CSIC-IJA, Barcelona, Spain
[6] CEA, Gif-sur-Yvette, France
[7] CIEMAT, Madrid, Spain

7.9.3 Internal reports

GLAUS M.A., LAUBE A., VAN LOON L.R. (2004)
A Generic Procedure for the Assessment of the Effect of Concrete Admixtures on the Sorption of Radionuclides on Cement : Concept and Selected Results. PSI Scientific Report 2003 / Volume IV. Paul Scherrer Institut, Villigen, Switzerland.

8 THE MICROXAS BEAMLINE PROJECT: STATUS AND MICROXAS RESULTS

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8.1 Overview

Within this report a brief description of the project status and important commissioning results as well as conceptual details concerning the measurements of radioactive samples is presented. The report is completed with an illustrative example of microXAS research related to the field of nuclear waste management.

8.2 Project status and commissioning results

During the past few months, the main emphases of the microXAS project were (i) *beamline commissioning* and (ii) *experimental feasibility studies*. Shortly after an initial period with remarkable high success rates – as documented in previous reports (GROLIMUND et al. 2004, 2005) – the microXAS project team was confronted with the harsh truth of beamline commissioning reality. Considerable progress was (too) often counter-balanced by the unexpected occurrence of subtle technical problems. In the following subsections, a short summary of the progress achieved as well as a description of the more severe difficulties is given.

8.2.1 Machine beamline interface and front-end

Early commissioning was considerably impeded by ambiguities concerning x-ray beam path. The x-ray beam could not be guided through all the front-end component as designed. The problem became most pronounced in the case of the diaphragm, the limiting aperture of the first beamline part. The diaphragm corresponds to a key component of the heatload management scheme. With anxiety coupled with appropriate care, the diaphragm had to be operated in a manner resulting in a considerably higher heat load on the downstream optical components. Joint efforts by the SLS Front-End Group (lead by Q. Chen), the PSI Surveying and Alignment Group (K. Dreyer, T. Schaarschmidt), the SLS Machine Group (M. Boege) as well as the SLS Alignment Group (F. Wei) allowed this complex problem to be resolved. An asymmetric dynamic range of the diaphragm positioning system (not conform with the engineering specifications) prevented any unexpected divergence of the x-ray beam trajectory to be compensated for. The mentioned divergence is due to electron beam orbit deviations which can be traced to post-construction settling of the storage ring facility. For example, in case of the last girder system before the X05LA straight section, positional changes – relative to the initial alignment – of a few tens of micrometers were established by repeated survying campaigns. As a result, angular deviations of the x-ray beam of the order of a few tens of μrads are observed at the X05LA beamline.

Specific to undulator beamlines, the characterization of the insertion device corresponds to one of the most crucial commissioning tasks. The spectral radiation characteristic of an undulator is dominated by sharp, high intensity peaks (WILLE, 1996). These so-called 'harmonics' correspond to different resonance conditions. (In the hard x-ray regime they are approximately integer multiples of the fundamental wavelength). The typical width of odd harmics is in the order of a few tens of eVs. In comparison, however, typical x-ray absorption spectroscopic scans extend over up to 1000eV. Without counter measures, dramatic variations in the photon flux would considerably limit most XAS techniques. However, by changing the magnetic field strength by changing the gap of the undulator, the fundamental wavelength and the corresponding harmonics can be shifted in energy space. As an example, Fig. 8.1 shows the measured photon flux as a function of energy and undulator gap opening. In order to maintain maximum photon flux conditions over an extended energy range, the gap opening has to be synchronized to the energy selected by the monochromator. First efforts to determine and to implement such a gap-monochromator synchronization yielded promising results for maintaining high and almost constant photon flux conditions. Fig. 8.2 depicts the measured location in energy space of the intensity maxima for the first 9 harmonics as a function of the gap setting. Solid lines correspond to respresentations based on semi-empirical functions (SCHMIDT, 2005; MOREIRA, 2005).

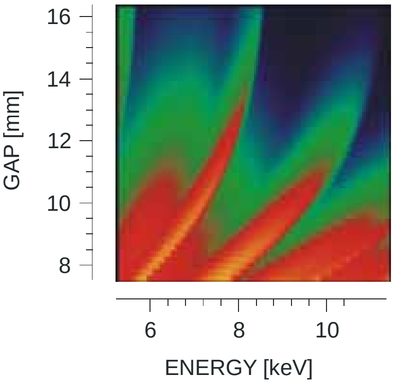

Fig. 8.1: *Roving of the undulator harmonics in energy space due to gap changes. Monochromatic photon flux shown is the energy range covered by the 3^rd^, 4^th^, and 5^th^ harmonic.*

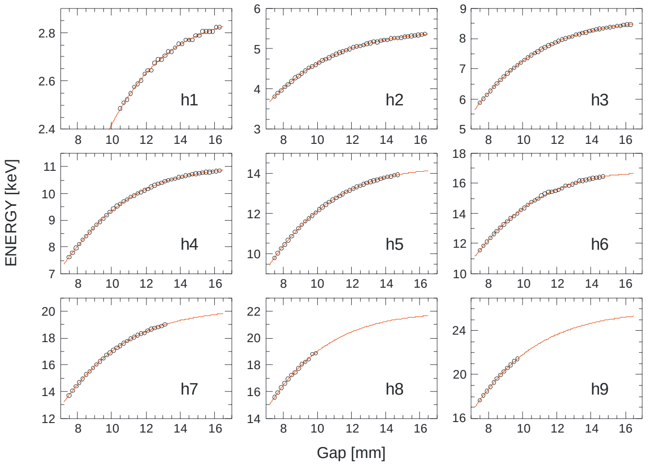

Fig. 8.2: *Gap-Energy relation of the first nine harmonics. Solid lines correspond to representations based on semi-empirical functions (SCHMIDT, 2005; MOREIRA, 2005).*

8.2.2 Beamline optics

Key optical components are (i) the pre-focusing mirror unit, (ii) the monochromator, and (iii) the micro-focusing unit. Concerning the pre-focusing mirror, considerable progress was achieved over the past few weeks in terms of alignment using the x-ray beam. For example, reflectivity techniques were employed to determine the incident angle. Further, beam shape analyses at in- and out-of-focus positions were used to optimize roll and yaw angular positions. At present, the mirror surface figure (dynamic toroid bent out of a static cylinder) and the resulting focusing properties of the mirror have been optimized.

Details concerning the monochromator and the microfocusing unit are provided below (sections 8.2.4 and 8.2.5)

8.2.3 Beamline and experimental infrastructure

The experimental and beamline infrastructure includes a broad variety of complex equipment including various detectors, the detector portal (see Fig. 8.4, bottom panel), sample stages, experimental tables, remote controlled x-ray eyes and microscopes.

At present, functionality tests and the integration of all these devices into the beamline control system is in progress. In most cases the beamline engineering and control team has to work out pioneering solutions. Consequently, the open tasks are extraordinary challenging and demanding in terms of skills and man-power. A considerable knowledge base has to be developed.

The implementation of a state-of-the-art data acquisition system for XAS scanning, XRF mapping, and XRD measurements represents an additional prominent and complex task in the context of experimental infrastructure. Present efforts are directed towards overcoming current limitations regarding deadtime, data through-put, and noise-levels. With the steadily increasing number of pilot experiments scheduled, the availability of a user-friendly interface becomes a more and more critical issue.

8.2.4 Low-light

The commissioning of the beamline was very severely interrupted by a major failure of the monochromator unit. The major parts having to be replaced include the main rotation axis, the vacuum feed through system, the linear translation stages of the second crystal holder, as well as the entire double cam system. While further investigations led by the manufacturer are still ongoing, the collapse of the entire unit was most likely due to the failure of a ball bearing unit resulting in the cam mechanics becoming stuck with resulting damage to the components listed above.

8.2.5 High-light

Shortly after the (considerably delayed) delivery of the microfocusing unit – a system consisting of two reflective mirrors combined in a classic Kirkpatrick-Baez arrangement – we have been able to produce the first x-ray beam focused by the KB-mirror unit. A few impressions are shown in Fig. 8.3. Without optimization of the preceding beam line optics (in particular mirror unit 1) and without optimization of either one of the elliptical figures of the two KB mirrors we have achieved a spot size of less than 13x13 μm^2 (2σ value). One-dimensional focusing in the vertical direction yielded a spot size of ~6 micrometers (!). These results have to be regarded as very exceptional. During this first try without mirror figure optimization, we are only a factor of 2.5 (horizontal) and about a factor of 5 (vertical) off the specified design goal.

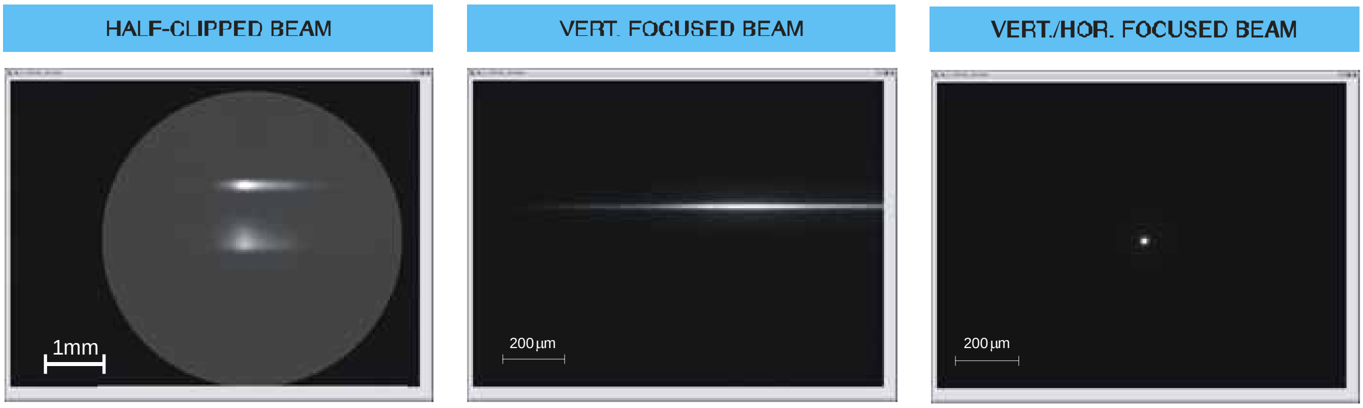

Fig. 8.3: *First observations of 'micro'-focused x-ray beams. Left: Beam splitting due to the partial clipping during the insertion of the first KB mirror. Middle: Vertically focused beam with a width of 6μm (2σ). Right: Beam focused in both dimensions yielding a beam size of 13x13 μm^2 (2σ).*

8.2.6 Feasability studies

Despite the challenging technical problems emerging during the ongoing commissioning phase, the project team have striven to reach operational conditions allowing for basic feasibility studies. A number of fruitful collaborations with internal and external research groups resulted from this endeavour. Subjects of such feasibility studies included, among others, XAS studies on cement phases (PSI-NES; M. Vespa, R. Dähn), EXAFS studies related to nuclear waste storage (CEA, France; M. Schlegel), trace metal – rock interactions (NAGRA, P. Wersin; PSI, D. Grolimund), low energy XAS and (ultra-)fast EXAFS (ETH Lausanne; Ch. Bressler), XRF using an energy dispersive detector system (PSI-ENE; N. Bukowiecki), XRF mapping (PSI-SYN, R. Abela) and time-resolved diffraction (PSI-SYN; S. Johnson). In the immediate future the following feasibility studies are scheduled: Material characterization by EXAFS (PSI-NES; G. Kuri, G. Bart), catalytic phenomena elucidated by fast XANES and EXAFS (ETH Zuerich; J.D. Grunwaldt), metal-organo complexes (Univerity Geneva, M. Borkovec, K. Wojciechowski; PSI, D. Grolimund), and time-resolved EXAFS (ETH Lausanne: Ch. Bressler, W. Gawelda; PSI: S. Johnson, D. Grolimund).

8.3 Micro-beam experiments with radioactive samples

As a special feature of the microXAS beamline, radioactive samples can be measured. Since the SLS is a low-hazard, non-nuclear facility, strict regulations must be complied with and the experimental hutch will be temporally declared as a "zone 1" when radioactive samples are measured. In such a case, a hand and foot monitor must be available at the entrance to the hutch. Furthermore, no sample manipulation will be allowed at the beamline at any time and the samples must be encapsulated (closed samples). One critical issue for experiments with radioactive samples is the fact that the dose rate will be limited to 20 microSv/week at a distance of 2 meters from the sample (hutch wall). Consequently, the thickness of the Pb shielding required will vary strongly. For example, in addition to the existing shielding provided by the experimental hutch, a few cm of Pb will be mandatory for investigations of highly radioactive samples, while no additional shielding is required for samples containing only natural actinides (Th, U).

Based on the above-mentioned restrictions, a modular and local shielding concept has been devised and a *specimen containment system* for radioactive samples has been built (Fig. 8.5). The *specimen holder for radioactive samplers* consists of an air tight container holding up to three specimens with one layer of a Kapton window. (Fig. 8.4 top panel) The *specimen holder* is encapsulated in a safety case, again air tight, with a single or double layer of Kapton windows (for an overall double or triple encapsulation) to insure a contamination free analysis of the specimens at the beamline. The Kapton windows allow good transmission of the x-ray beam and insure the containment of the specimens. The *specimen holder* also contains a reference substrate (fluorescence screen) which is used for beam alignment by an optical microscope. A dedicated detector portal (Fig. 8.4, bottom) has been designed to exchange and position the different detector systems (e.g. 32-element Ge-detector for fluorescence and CCD detector for x-ray diffraction) around the tight containment system with the Pb-shielding. During the measurements of radioactive samples, the Ge-detector is mounted vertically above the *specimen containment system* (Fig. 8.5). In the rear rail system of the detector portal a CCD detector can be mounted to allow the monitoring of diffraction patterns at different positions.

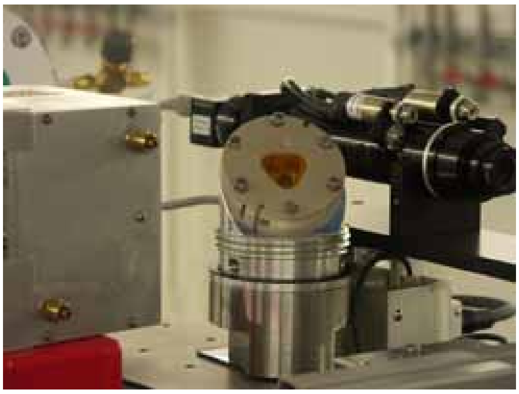

Fig. 8.4: *Top: Specimen holder for radioactive samples. Bottom: Detector portal suited for (micro) x-ray beam experiments with radioactive samples.*

Radioactive specimens will be encapsulated in the above outlined specimen holder system in the 'Hot Laboratory' which will be available for the storage and loading of radioactive XAS samples. Dedicated loading boxes at the 'Hot Laboratory' are foreseen. The details of the specimen holder are described in a safety concept (GAVILLET et al. 2005) which was submitted to the 'Bundesamt für Gesundheit' (BAG, regulatory agency for the SLS) in the summer of 2005. In the safety concept the procedure on how to load the samples in the 'Hot Laboratory', decontamination issues, and the measurement protocol at the beamline are defined. According to the defined transport procedure, the specimen containment system will be brought to the microXAS beamline at the SLS with a certified type A transport container. Prior to mounting the containment system containing radioactive samples, all measurement and safety relevant components will be securely in place. The safety concept for the measurements of radioactive samples at the microXAS beamline has been developed in order to minimize manual sample handling. Thus the time that users are (potentially) exposed to radiation will also minimized. In a first step the specimen containment system will be removed from the transport container and fixed on the sample manipulator. If shielding is required, the sample manipulator will be surrounded by an 80 mm thick Pb-shielding (Fig. 8.5a). In a next step the transport cover of the specimen containment system will be removed (Fig. 8.5b). Finally, the motorized sample manipulator will be used to move the specimen containment system containing a fluorescence screen to the focal point of the x-ray beam (Fig. 8.5c).

First XAS test experiments in transmission and fluorescence mode have been conducted using the specimen holder for radioactive samples. In a next step such experiments will be repeated in the presence of BAG representatives using the entire specimen containment system. The experiments in the presence of BAG representatives will also be used for testing the entire experimental procedure, including transport and sample manipulation. Thereafter, the first experiments with weakly active samples will be initiated. In agreement with BAG, there will be a step-wise extension of the measurements towards experiments with hot samples. Within the context of ACTINET-6 Pooled Facilities (EU project), the microXAS beamline will be available for external user experiments with radioactive samples in the framework of the 6th EU ACTINET-6 call for proposals.

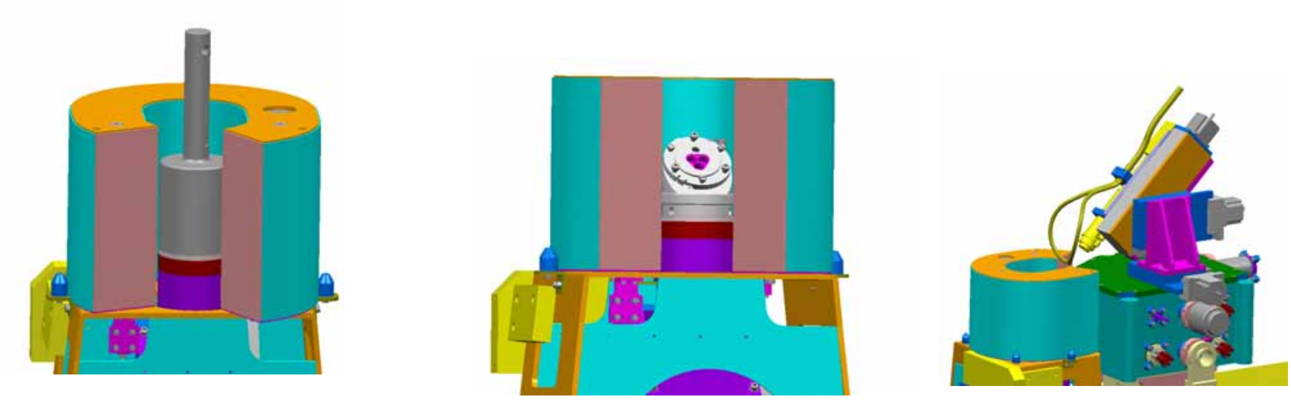

Fig. 8.5: *Specimen containment system fixed on the sample manipulator (a) with, and (b) without, the transport cover. (c) gives an overview of the experimental set-up: A microscope mounted on the KB mirror box will be used to align the specimen containment system with respect to the x-ray beam.*

8.4 MicroXAS research

Besides our obligations to the microXAS beamline, the beamline team has developed an active microXAS research program over the course of the last few years. As an example of the contribution of microXAS activities to waste repository systems, we present a case study on "*Speciation of heavy metals in cement-stabilized waste forms: A micro-spectroscopic study*"[#].

8.4.1 Introduction

Assuring safe disposal and long-term storage of hazardous and radioactive wastes represents a primary environmental task of industrial societies. The long-term disposal of the hazardous wastes is associated with landfilling of cement-stabilized waste, whereas radioactive wastes are disposed of in cementitious underground repositories. For example, more than 90 wt% of the near-field material of the planned deep underground repository for intermediate-level waste consists of HCP and cementitious backfill materials. Therefore, HCP plays an important role in the immobilization of heavy metals. From a chemical standpoint, HCP is a very heterogeneous material with discrete particles typically in the size range of about 2-200 μm. Overall, the material consists of mainly calcium (aluminium) silicate hydrates, calcium hydroxide and calcium aluminates.

Co and Ni isotopes are important contaminants in waste materials resulting from a variety of industrial processes, and they are activation products in metallic structures of nuclear power plants. Previous experiments of Ni uptake by blended cement (ATKINS et al. 1994) and Ni sorption onto a powdered material prepared from a sulfate resisting cement (SCHEIDEGGER et al. 2000; 2001) indicate that within an alkaline environment such as the one in a compacted cement matrix (pH>12.5) poorly crystalline $Ni(OH)_2$ and Ni-Al LDH phases are formed. Co speciation has been extensively studied in clay systems (e.g. MANCEAU et al. 1999; SCHLEGEL et al. 1999; THOMPSON et al. 1999), but it is poorly known in cement systems.

In the present study we have combined microXAS with microXRF to gain micro-scale information on the chemical speciation and structural coordination environment of Co and Ni in cement. The micro-spectroscopic study was complemented with bulk XAS experiments to assess whether the locally observed Ni and Co phases are representative of the entire cement system.

8.4.2 Materials and methods

The cement samples were prepared from a commercial sulfate-resisting Portland cement (CEM I 52.5 N HTS, Lafarge, France) used to condition low- and intermediate-level waste in the Swiss radioactive waste management program. Metal doped HCP was prepared by mixing nitrate salt solutions of the Ni and Co metals to the unhydrated cement at a water-to-cement ratio (w/c) of 0.4. The final concentration of the metal in the cement matrix was 5000 ppm. After hydration times of 3, 30 and 150 days the hardened metal-doped cement paste was cut into several slices of ~1 cm thickness. Some of the slices were crushed to prepare a powder material for bulk XAS measurements. Other slices were used to prepare polished thin sections for synchrotron based microXAS and microXRF investigations.

The characterization was carried out by using bulk XAS and microXAS. MicroXRF/XAS measurements were performed on beamline 10.3.2 of the Advanced Light Source (ALS), Lawrence Berkley National Lab, Berkley, USA. The beam size was 5x5 μm^2 for both fluorescence mapping and the collected microXAS spectra. Co and Ni K-edge bulk XAS spectra of the powdered materials were collected at the Swiss Norwegian Beam Line (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.

Data reduction of both micro and bulk XAS data was performed using the WinXAS 3.1 software package following standard procedures. Theoretical scattering paths for the fit were calculated using FEFF 8.2. The amplitude reduction factor (S_0^2) was fixed at 0.85 for both Ni and Co (O'DAY et al. 1994).

8.4.3 Selected results

The study on the Ni speciation in the cement matrix revealed that Ni is highly heterogeneously distributed and forms Ni-rich "hot spots" (spot sizes up to ~50 μm^2). XAS spectra of the "hot spots" and the bulk XAS data show a distinctive beat pattern at ~8$Å^{-1}$. This characteristic feature indicates the formation of Ni-Al Layered Double Hydroxide (LDH) phases (SCHEINOST & SPARKS, 2000). For both bulk- and microXAS data, data analysis reveals Ni-Ni distances (R_{Ni-Ni}= 3.09-3.11 Å) longer than in pure Ni-Al LDH phases (3.06 Å). The longer R_{Ni-Ni} are caused by the presence of β-$Ni(OH)_2$ (R_{Ni-Ni}=3.12 Å) (SCHEIDEGGER et al. 2000). Linear least-square fitting (LSF) of the experimental XAS (bulk and micro) spectra with linear combinations of reference spectra (Ni-Al LDH,

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[#] This work is a part of the ongoing Ph. D. thesis of Marika Vespa and is based on a LES collaborative effort including Erich Wieland, Daniel Grolimund, Rainer Dähn, Messaoud Harfouche and André Scheidegger, Paul Scherrer Institut, Laboratory for Waste Management and the Swiss Light Source, Villigen PSI, Switzerland.

$Ni(OH)_2$ and Ni-Phyllosilicate) suggests that the sample is composed mainly of Ni-Al LDH (~60%) and some $Ni(OH)_2$ (~40%).

For the Co-doped cement system, the microXRF maps show that Co is also heterogeneously distributed in the cement matrix (Fig. 8.6a, b). On the one hand there are Co-rich spots up to ~50 μm^2 in size (as observed for Ni) but on the other, Co-rich ring-like structures with diameters up to ~200 µm were observed. Fig. 8.6c shows the normalized, background-subtracted and k^3-weighted spectra of bulk XAS and microXAS data of a Co-rich spot and a Co ring–like structure (3 days hydration time) together with reference compounds. The spectrum of spot 2 was collected on the ring-like structure and shows a clear shift of the first oscillation compared to spot 1 and the bulk data. From the comparison of the data with reference compounds it clearly appears that spot 1 and the bulk data exhibit similarities with respect to Co(II) speciation, whereas spot 2 shows more similarities to Co(III) compounds. For spot 1 and the bulk data, data analysis reveals longer Co-O (2.06 Å) and Co-Co (3.16 and 3.13 Å) distances than for spot 2 ($R_{Co\text{-}O}$= 1.90 Å; $R_{Co\text{-}Co}$= 2.80 Å). The longer distances are comparable to Co-O and Co-Co distances in Co(II) compounds such as Co(II) hydroxide-like phases ($(Co(OH)_2)$) ($R_{Co\text{-}O}$= 2.09 Å; $R_{Co\text{-}Co}$= 3.17 Å), Co-Al LDH ($R_{Co\text{-}O}$= 2.08 Å; $R_{Co\text{-}Co}$= 3.09 Å) or Co-phyllosilicates (e.g. Co-kerolite; $R_{Co\text{-}O}$= 2.09 Å, $R_{Co\text{-}Co}$= 3.13 Å (MANCEAU et al. 1999)). The shorter distances, observed for spot 2, suggest that Co is present as Co(III) incorporated into a Co(III)O(OH)-like phase ($R_{Co\text{-}O}$= 1.90 Å, $R_{Co\text{-}Co}$= 2.85 Å) or a Co-phyllomanganate (Co-asbolane and Co-buserite; $R_{Co\text{-}O}$= 1.89 Å, $R_{Co\text{-}Co}$= 2.80 Å (MANCEAU et al. 1987; 1997).

8.4.4 Conclusions

The micro-spectroscopy study shows a heterogeneous distribution of Ni in the metal-doped compacted cement matrix. Ni(II) predominantly forms Ni-Al LDH phases and to a lesser extent $Ni(OH)_2$. These results are consistent with XAS studies of Ni sorption on powdered HCP material (SCHEIDEGGER et al. 2000; 2001). For Co(II), the spectroscopic investigations reveal that part of the Co(II) was oxidized to Co(III) during the hydration process of HCP and accumulated at some Co-rich spots (ring-like structure). The oxidation process is possible due to the low redox potential of Co at pH>12.5. The microXAS data further suggest that Co(III) tends to be incorporated into a Co(III)O(OH)-like phase or a Co-phyllomanganate. At other spots of interest, however, Co(II) was not oxidized. Similarly to Ni(II), Co(II) is predominately incorporated into newly formed Co(II) hydroxide-like phases ($Co(OH)_2$), Co-Al LDH or Co-phyllosilicates.

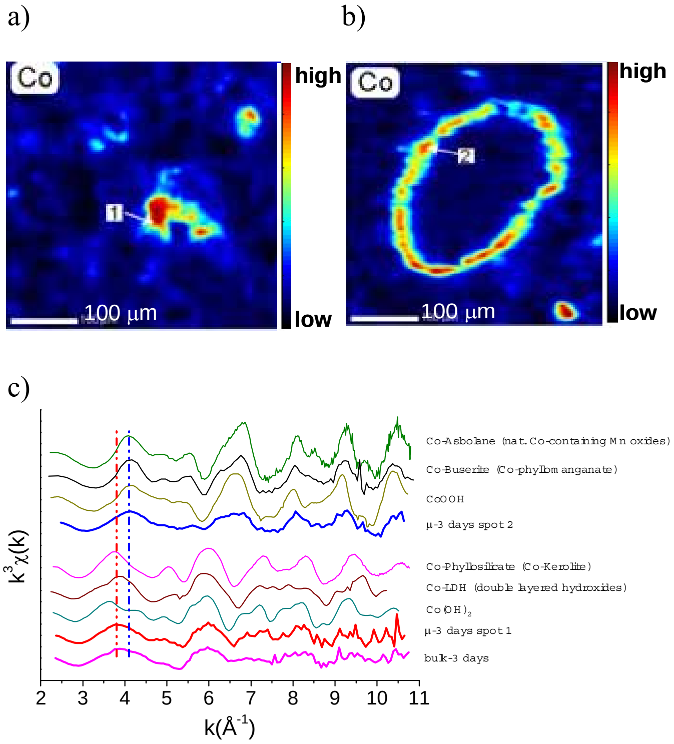

Fig. 8.6: *Element distribution map of Co after 3 days of hydration for a) Co-rich spot 1 and b) Co-rich spot 2; c) k^3-weighted, normalized, background-subtracted XAS spectra of Co enriched cement after 3 days of hydration, reference material and micro-XAS of Co-rich spots.*

The oxidation of Co is a locally occurring process. Future work will focus on the identification of the potential oxidizing agent, such as traces of O_2, Mn(IV) or Fe(III).

The findings from the micro-spectroscopic study indicate that Co and Ni react differently during the hydration of cement and that both became immobilized in specific cement minerals. These immobilization processes are expected to reduce the mobility of Co and Ni in the cement matrix. Furthermore, it illustrates that the immobilization potential of cement is element specific.

8.5 References

ATKINS M., GLASSER F.P., MORONI L.P., JACK J.J. (1994)
Thermodynamic modelling of blended cements at elevated temperatures (50°C to 90°C). DoE/UMIP/PR/94.011.

GAVILLET D., NICOLET M., SCHEIDEGGER A.M., RESTANI R. (2005)
Strahlenschutzplanung für Röntgenabsorptions-spektroskopie-Messungen mit radioaktiven Proben an der microXAS Strahllinie (SLS) AW-43-05-04, Paul Scherrer Institut, Villigen.

Grolimund D., Scheidegger A.M., Farges F., Harfouche M., Willimann M., Meyer B. (2005)
FIAT LUX – ET FACTA EST LUX. The micro-XAS Beamline Project at the Swiss Light Source (SLS). PSI Scientific Report 2004, IV, Paul Scherrer Institut, Villigen PSI, Switzerland.

Grolimund D., Scheidegger A.M., Harfouche M., Meyer B., Willimann M. (2004)
The micro-XAS Beamline Project: Status and microXAS Results. Laboratory for Waste Management Progress Report 2003/2004, 67-75.

Manceau A., Drits V., Silvester E., Bartoli C., Lanson B. (1997)
Structural mechanism of Co2+ oxidation by the phyllomanganate buserite. American Mineralogist 82, 1150-1175.

Manceau A., Llorca S., Galas G. (1987)
Crystal chemistry of cobalt and nickel in lithiophorite and asbolane from New Caledonia. Geochimica et Cosmochimica Acta, 51, 105-113.

Manceau A., Schlegel M., Nagy K.L., Charlet L. (1999)
Evidence for the formation of triochtahedral clay upon sorption of Co2+ on quartz. Journal of Colloid and Interface Science 220, 181-197.

Moreira O. (2005)
Beamline X05LA-μXAS Report Series, Swiss Light Source (SLS), Paul Scherrer Institut, Villigen, Switzerland.

O'Day P.A., Rehr J.J., Zabinsky S.I., Brown J.G.E. (1994)
Extended X-ray absorption fine structure (EXAFS) analysis of disorder and multiple-scattering in complex crystalline solids. Journal of the American Chemical Society 116, 2938-2949.

Scheidegger A., Wieland E., Dähn R., Spieler P. (2000)
Spectroscopic evidence for the formation of layered Ni-Al double hydroxides in cement. Environmental Science and Technology 34, 4545-4548.

Scheidegger A.M., Wieland E., Scheinost A.C., Dähn R., Tits J., Spieler P. (2001)
Ni phases formed in cement and cement systems under highly alkaline conditions: an XAFS study. Journal of Synchrotron Radiation 8, 916-918.

Scheinost A.C., Sparks D.L. (2000)
Formation of layered single- and double-metal hydroxide precipitates at the mineral/water interface: A multiple-scattering XAFS analysis. Journal of Colloid and Interface Science 223, 1-12.

Schlegel M.L., Manceau A., Chateigner D., Charlet L. (1999)
Sorption of metal ions on clay minerals. I. Polarized EXAFS evidence for the absorption of Co on the edges of hectorite particles. Journal of Colloid and Interface Science, 215, 140-158.

Schmidt T. (2005)
About APPLE II operation, Technical Note, SLS-SPC-TA-2005-268, Swiss Light Source (SLS), Paul Scherrer Institute, Villigen PSI, Switzerland.

Thompson H.A., Parks G.A., Brown J.G.E. (1999)
Dynamic interactions of dissolution, surface adsorption, and precipitation in an aging cobalt (II)-clay-water system. Geochemica et Cosmochemica Acta, 63, 1767-1779.

Wille K. (1996)
Physik der Teilchenbeschleuniger und Synchrotronstrahlungsquellen, 2nd ed., Teubner Studienbücher, Stuttgart.

8.6 Publications

8.6.1 Peer reviewed journals and reports

Bonhoure I.[1], Baur I.[2], Wieland E., Johnson C.A.[2], Scheidegger, A.M. (2005)
Se(IV/VI) oxyanion immobilization by cementitious systems: An X-ray absorption spectroscopy study. Cement and Concrete Research (in press)

[1] CTB-UPC, Manresa, Spain

[2] EAWAG, Dübendorf, Switzerland

Gawelda W.[1], Bressler Ch.[1], Saes M.[1], Kaiser M.[1], Tarnovsky A.N.[1], Grolimund D., Johnson S.L., Abela R., Chergui M.[1], (2005)
Picosecond Time-Resolved X-Ray Absorption Spectroscopy of Solvated Organometallic Complexes, Physica Scripta, T115, 102-106.

[1] Laboratoire de Spectroscopie Ultrarapide LSU, Institut des Sciences et Ingenierie Chimiques ISIC, Ecole Polytechnique Federale de Lausanne EPFL, Lausanne, Switzerland

Grolimund D., Borkovec M.[1] (2005)
Colloid-Facilitated Transport of Strongly Sorbing Contaminants in Natural Porous Media: Mathematical Modelling and Laboratory Column Experiments, Environmental Science Technology (in press).

[1] Department of Inorganic Analytical, and Applied Chemistry, University of Geneva, Geneva 4, Switzerland

Grolimund D., Borkovec M.[1] (2005)
Release of Colloidal Particles in Natural Porous Media by Monovalent and Divalent Cations. Journal of Contaminant Hydrology (submitted).

[1] Department of Inorganic Analytical, and Applied Chemistry, University of Geneva, Geneva 4, Switzerland

Grolimund D., Senn M.[1], Trottmann M.[1], Janousch M., Bonhoure I., Scheidegger A.M., Marcus M.[2] (2004)
Shedding new Light on Historical Metal Samples using Micro-focused Synchrotron X-Ray Fluorescence and Spectroscopy. Spectrochimica Acta Part B: Atomic Spectroscopy, 59, 1627-1635.

[1] EMPA, Dübendorf, Switzerland
[2] Advanced Light Source, Berkeley, CA, USA

Nachtegaal M., Scheidegger A.M., Dähn R., Chateigner D.[1], Furrer G.[1] (2005)
Immobilization of Ni by Al-modified Montmorillonite: A novel uptake mechanism. Geochimica Cosmochimica Acta (in press).

[1] Lab. Cristallograpie et science des Matériaux, ISMRA, F-14050 Caen, France.
[2] Inst. for Terrestrial Ecology, EHTZ, Schlieren, Switzerland

Scheidegger A.M., Grolimund D., Cheeseman C.R.[1], Rogers R.D.[2] (2005)
Micro-spectroscopic investigations of highly heterogeneous waste repository materials. Journal of Geochemical Exploration (in press).

[1] Centre for Environmental Control and Waste Management, Imperial College of Science, Medicine and Technology, London, England
[2] Idaho National Engineering and Environmental Laboratory (INEEL), Idaho Falls, USA

Scheidegger A.M., Vespa M., Grolimund D., Wieland E., Harfouche M., Bonhoure I.[1], Dähn R. (2005)
The use of (micro)-x-ray absorption spectroscopy in cement research. Waste Management (submitted).

[1] CTB-UPC, Manresa, Spain

Vespa M., Dähn R., Grolimund D., Harfouche M., Wieland E., Scheidegger A.M. (2005)
Speciation of heavy metals in cement-stabilized waste forms: A micro-spectroscopic study. Journal of Geochemical Exploration (submitted).

8.6.2 Conferences/Workshops/Presentations

Bonhoure I.[1], Wieland E., Tits J., Scheidegger A.M.
X-ray absorption spectroscopy (XAS) study of U(VI) immobilization by hardened cement paste. 6th International Conference on Nuclear and Radiochemistry (NRC-6), Aachen, Germany, August 29 - September 3, 2004.

[1] CTB-UPC, Manresa, Spain

Dähn R., Curti E., Grolimund D., Harfouche M., Scheidegger A.M., Vespa M., Wieland E.
XAS-Measurements at LES: Present and Future. Program Committee Meeting, Paul Scherrer Institut, Würenlingen, 21. September 2004.

Dähn R., Scheidegger A.M., Grolimund D., Harfouche M., Willimann M., Meyer B.
The Micro-XAS Beamline at The Swiss Light Source (SLS): A New Analytical Facility Dedicated to Micro-Beam Applications in the Environmental Sciences. 3rd Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources (Actinide-XAS-2004), Berkeley, USA, 14-16 September 2004.

Grolimund D.
Chemical Phenomena at the Colloid-Solution Interface: ‘Enlightenment’ through Synchrotron Radiation. Invited keynote lecture: KORESI: International Workshop on Colloids and Colloid Mediated Transport of Contaminants in Soils, Bad Herrenalb, Germany, June 2005.

Grolimund D.
microXAS: Milestones and Highlights, 5th SLS Users Meeting, Paul Scherrer Institute, Villigen PSI, Switzerland, October, 2004.

Grolimund D., Borkovec M.[1], Barmettler K.[2]
Colloid Facilitated Transport in Natural Porous Media: Phenomena and Modelling. Invited keynote lecture: KORESI: International Workshop on Colloids and Colloid Mediated Transport of Contaminants in Soils, Bad Herrenalb, Germany, June 2005.

[1] Department of Inorganic Analytical, and Applied Chemistry, University of Geneva, Geneva 4, Switzerland
[2] Institute of Terrestrial Ecology, Swiss Federal Institute of Technology, ETHZ, Zürich, Switzerland

Grolimund D., Günther D.[1], Scheidegger A.M., Aeschlimann B.[1], Wersin P.[2], Heald S.M.[3]
Cs migration in complex geological media: New insights through micro-imaging and micro-spectroscopy. (Oral presentation) 2nd International Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement, March 14-18, 2005, Tours, France.

[1] Inorganic Chemistry, Swiss Federal Institute of Technology, ETHZ, Zürich, Switzerland.
[2] NAGRA, Wettingen, Switzerland
[3] PNC-CAT, Advanced Photon Source, Chicago, USA

Scheidegger A.M.
The micro-XAS beamline at the Swiss Light Source (SLS): A new analytical facility dedicated to micro-beam applications. Invited lecture at the ‘Abteilung für Strahlenschutz und Sicherheit’, Paul Scherrer Institut, Villigen, Switzerland, December, 12, 2004.

Scheidegger A.M.
X-ray micro-spectroscopy: A new tool for investigating chemical reactivity and structural identity of trace elements in cement. Invited lecture at the International Workshop on “Mechanisms and Modelling of Waste/Cement Interactions”, Meiringen, Switzerland, May 8-12, 2005.

Scheidegger A. M., Grolimund D., Harfouche M., Vespa M., Dähn R., Wieland E., Cui, D.[1], Spahiu, K.[2], Wersin, P.[3]
Metal speciation in heterogeneous waste repository materials using XAS. Invited lecture at the International Conference 'Energy Technologies for a Sustainable Future', PSI, Switzerland, June 16-17, 2005.

[1] Studsvik Nuclear AB, Nyköping, Sweden
[2] SKB, Stockholm, Sweden
[3] Nagra, Wettingen, Switzerland

Vespa M., Wieland E., Dähn R., Grolimund D., Scheidegger A.M.
Immobilization of Ni and Co in cement-stabilized waste forms: A micro-spectroscopic study. 3rd Workshop on Speciation, Techniques, and Facilities for Radioactive Materials at Synchrotron Light Sources (Actinides-XAS-2004), Berkeley, USA, September 14-17, 2004

Vespa M., Wieland E., Dähn R., Grolimund D., harfouche M., Scheidegger A.M.
Immobilization of Ni and Co in cement-stabilized waste forms: A micro-spectroscopic study. NES Colloquium, PSI, Switzerland, November 11, 2004.

Vespa M., Dähn R., Grolimund D., Scheidegger A. M., Wieland E.
Spectroscopic investigation of the Ni speciation in hardened cement paste. International Workshop on "Mechanisms and Modelling of Waste/Cement Interactions", Meiringen, Switzerland, May 8-12, 2005.

Vespa M., Dähn R., Grolimund D., Harfouche H., Wieland E., Scheidegger A. M.
Speciation of heavy metals in cement-stabilized waste forms: A micro-spectrscopic study. GES-7 (Seventh International Symposium on the Geochemistry of the Earth Surface), Aix-en-Provence, France, August 23-27, 2005

Wieland E., Tits J., Bonhoure I.[1], Vespa M., Scheidegger A.M.
Radionuclide immobilization in cement systems. 6th International Conference on Nuclear and Radiochemistry (NRC-6), Aachen, Germany, August 29-September 3, 2004.

[1] CTB-UPC, Manresa, Spain

8.6.3 Internal reports

Gawelda W.[1], Sobanek B.[1], Chergui M.[1], Bressler Ch.[1], Grolimund D., Tarnovsky A.[1], Johnson S.L., Abela R. (2005)
Structural Analysis of Short-Lived Reaction Intermediates Measured via Time-Resolved X-ray Absorption Spectroscopy, PSI Scientific Report 2004, VII, Paul Scherrer Institute, Villigen PSI, Switzerland.

[1] Institute of Condensed Matter Physics, University of Lausanne, Lausanne, Switzerland

Grolimund D., Scheidegger A.M., Farges F.[1], Harfouche M., Willimann M., Meyer B. (2005)
FIAT LUX – ET FACTA EST LUX. The micro-XAS Beamline Project at the Swiss Light Source (SLS). PSI Scientific Report 2004, IV, Paul Scherrer Institute, Villigen PSI, Switzerland.

[1] Institute of Condensed Matter Physics, University of Lausanne, Lausanne, Switzerland

Grolimund D., Scheidegger A.M., Farges F.[1], Harfouche M., Willimann M., Meyer B. (2005)
FIAT LUX – ET FACTA EST LUX. The micro-XAS Beamline Project. PSI Scientific Report 2004, VII, Paul Scherrer Institute, Villigen PSI, Switzerland.

[1] Institute of Condensed Matter Physics, University of Lausanne, Lausanne, Switzerland

Ingold G., Abela R., Beaud P., Chen Q., Grolimund D., Johnson J.L., Rivkin L., Rohner M., Schlott V., Schmidt T., Schulz L., Streun A., van der Veen J.F., Wei F. Tarnovsky A.[1] (2005)
Status of the FEMTO Project, PSI Scientific Report 2004, VII, Paul Scherrer Institute, Villigen PSI, Switzerland.

[1] Institute of Condensed Matter Physics, University of Lausanne, Lausanne, Switzerland

Grolimund D., Scheidegger A.M., Harfouche M., Meyer B., Willimann M. (2005)
The micro-XAS Beamline Project: Status and microXAS Results. Laboratory for Waste Management Progress Report 2003/2004, (2004), 67-75.

Sobanek B.[1], Gawelda W.[1], Chergui M.[1], Bressler Ch.[1], Grolimund D., Tarnovsky A.[1], Johnson S.L., Abela R. (2005)
Kinetic Studies of Transient Chemical Species Measured via Time-Resolved X-ray Absorption Spectroscopy, PSI Scientific Report 2004, VII, Paul Scherrer Institute, Villigen PSI, Switzerland.

[1] Institute of Condensed Matter Physics, University of Lausanne, Lausanne, Switzerland

8.7 Others, Teaching

GROLIMUND D.
The future is bright: The microXAS beamline project at the Swiss Light Source. Invited lecture: EMPA Academy, EMPA, Duebendorf, Switzerland, December 2004.

SCHEIDEGGER A.M.
Privatdozent at the Swiss Federal Institute of Technology in Zürich (ETHT), lecture entitled 'Aplication of Synchrotron Radiation in Environmental Sciences, Chemistry, and Biology', WS04/05.