

Progress Report October 2006 to December 2007

Laboratory for Waste Management
Nuclear Energy and Safety Research Department

Cover Photo

Samples of Opalinus Clay (right) were obtained from the Mont Terri Underground Rock Laboratory at St. Ursanne, Switzerland (top). Each sample was mounted in a diffusion cell (left) and contacted with a porewater solution labeled with ^{60}Co . The diffusion profile in the clay sample (bottom) was measured using a micro abrasive grinding technique combined with gamma spectrometry; in this case after a 54 day in-diffusion time.

PAUL SCHERRER INSTITUT



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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 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 microXAS beamline.

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

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1 OVERVIEW

Mike Bradbury

1.1 Introduction

The period covered by this report is from October 1, 2006 to December 31, 2007. This is a somewhat longer time span than in previous years. The reason is that the timing of the annual Programme Committee Meeting has been changed from autumn to spring so as to be in synchronism with the other Labs in the Nuclear Energy and Safety Division. Hence, in the future, the annual report will cover a calendar year January to December.

The progress made in the Laboratory for Waste Management (LES) over the past 15 months is summarised in the first part of the report. LES is organised into two projects. The first is the Waste Management Programme. This work is described in sections 2 to 7 according to each sub-programme. Although the topics covered in each sub-programme are either predominantly “experimental” or “modelling” in their nature, there are strong interactions between sub-programmes and between experimentalists and modellers. The results from the XAS sub-programme are integrated into the other activities.

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

Soon after the Bundesrat approved the Entsorgungsnachweis Bericht (Demonstration of Disposal Feasibility Report) in June 2006, confirming that the construction of a deep geological repository for Spent Fuel (SF), Vitrified High-Level Waste (HLW) and Long-lived Intermediate-Level Waste (ILW) is, in principle, practicable, the Federal Office of Energy (BFE) released a first draft of the guidelines for the site selection process defined in a “Sectoral Plan” (Sachplan Geologische Tiefenlagerung) within the framework of the existing land use planning legislation. Site selection will be based primarily on technical criteria, with the main emphasis on safety, but must also address socio-economic aspects. After a considerable consultation and revision process, it is expected that the Federal Government will issue the Sectoral Plan early in 2008.

Part 1 of the plan is concerned with the development of the concepts: aims, boundary conditions,

procedures (steps, role/responsibilities of stakeholders) and criteria (safety/feasibility, land use planning, and socio-economic issues). In Part 2 the implementation steps are described. A three step procedure is foreseen:

Step 1:

Identification of 5 potential regions for a low and intermediate level waste repository and 3 potential regions for HLW/SF and ILW repositories. (Note that regions suitable for combination repositories may be included).

Step 2:

The selection of at least 2 sites for each repository type within the potential regions.

Step 3:

The selection of 1 site for each repository type and the application for a general licence.

It is anticipated that the application for a general licence will take place in 2014/2016.

In connection with the site selection procedures for geological repositories for all categories of waste, Nagra is already compiling technical-scientific material (mainly geological information) for the upcoming site selection process.

In the previous annual report it was mentioned that Nagra was in the process of preparing an Entsorgungsprogramm (Disposal Programme) covering such issues as radionuclide inventories and their allocation to the different repository types, the required deep geological repositories and their layouts, repository realisation plans, costs and timescales, financial modalities etc. An advanced draft of this document is in circulation and the intention is to submit it to the Bundesrat for approval approximately 3 months after the Sectoral Plan has been approved. The Entsorgungsprogramm contains a section on the longer term R & D needs and it was this, amongst other reasons, that prompted LES to produce a long term (~10 years) research strategy paper divided into time periods of 3, 6 and 10 years. This strategy document has been widely discussed and commented upon, and it is anticipated that it will be ready for publication in the early part of 2008 and will then be generally available.

A further important development is that the new Nuclear Energy Law, which came into force on February 1, 2005, required that the supervisory body for nuclear facilities (HSK) be separated from the licensing authorities (Department of the Environment,

Transport, Energy and Communications). According to this requirement, HSK, which is currently part of BFE, will become an independent organisation called ENSI (Eidgenössisches Nuklear-Sicherheits-Inspektorat or Federal Nuclear Safety Inspectorate). The status of ENSI is defined in a new law which entered into force in September 2007.

The period covered by the present extended annual report includes the first full year of user operation of the microXAS beamline at the Swiss Light Source. This beamline is a high resolution hard X-ray microprobe where material and matter can be studied by means of high intensity X-ray beams with a spatial resolution down to approximately $1\mu\text{m}^2$. The station possesses two unique features allowing investigations of radioactive materials with micro focus capabilities and the performance of ultra fast X-ray science using X-ray pulses of ~ 100 femto-seconds duration. During the past year a wide diversity of different types of investigations have been performed, making full use of the versatility and breadth of possibilities offered by the beamline e.g. validation of the ring like structural shapes of gold nano-clusters consisting of only 10 to 40 atoms; contributions to elucidating the role of transition metals in carcinogenic processes by determining their elemental concentrations, spatial distribution and chemical speciation in tissues; nano-focusing of X-rays using Fresnel zone plates to resolve test structures as small as 200 nm; the use of X-ray micro-diffraction to map crystal structure, texture, and strain within micro domains.

Several investigations on radioactive samples were successfully carried out at the microXAS beamline including solidified radioactive waste, irradiated alloys, activated corrosion products (crud), and analogues of the next generation of fuel materials. In most cases elemental distribution maps were recorded by collecting two-dimensional micro-XRF data. Following such structural investigations, chemical information was gained by measuring the microXAS spectra at specific locations within the radioactive specimen.

LES has been participating within the 6th EU Framework Programme in two Integrated Projects. In NF-PRO, experimental and modelling studies on the influence of inorganic carbon on the sorption of Ni, Eu and U(VI) in montmorillonite/bentonite and diffusion measurements of selected anions (e.g. I⁻, Cl⁻) and cations (e.g. Na, Cs, Ni) in compacted bentonite are being carried out. A further activity includes XAS measurements of Se(VI) and Tc(VII) in contact with corroding canister components. In FUNMIG, a similar experimental programme of work is being performed but in the illite/Opalinus Clay (OPA) systems and in addition predictive and interpretive modelling in

connection with the “Diffusion Retardation “ (DR) experiments at Mont Terri are being performed. Also, the microXAS beamline is part of the pooled facilities within the ACTINET Network of Excellence. NF-PRO will finish at the end of 2007 and FUNMIG and ACTINET at the end of 2008.

A new project called “Redox Phenomena Controlling Systems” (ReCosy) is due to begin in 2008 as part of the 7th EU Framework Programme. The contribution of LES is focused on cementitious systems in WP4, Redox Reactions of Radionuclides, where LES is the work package leader.

The joint project between JAEA (Japan) and LES set up to investigate the partitioning of Ra(II) between aqueous solutions, bentonite and clay rocks, in the presence/absence of minor minerals (barite, calcite and witherite) which could act as sinks for this radionuclide, is continuing on schedule.

In May 2007 a guest scientist, Dr Kotaro Bessho, began a 10 month stay at PSI working in the Colloid sub-programme within LES. His stay is wholly financed by his home institute, the Inter University Research Institute Corporation, High Energy Accelerator Research Organisation (KEK), Japan.

Bilateral co-operations with external institutions and scientists have continued and are summarized in Table 1.1.

Table 1.1: National and international co-operations

Co-operations
Nagra Major financial contribution Various technical working groups
Multinational 6 th FP (NoE: ACTINET-6, IP: NF-PRO, FUNMIG), OECD/NEA TDB III (Fe), OECD/NEA TDB (solid solutions) Mont Terri Project (<u>D</u> iffusion <u>R</u> etardation) Grimsel Test Site (<u>C</u> olloid <u>F</u> ormation <u>M</u> igration)
Universities Bern, Switzerland (mineralogy, petrography) Irkutsk, Russia (speciation) UC London, UK (molecular modelling) Mainz, Germany (cement, montmorillonite) Strasbourg (glass) Tübingen (geosphere transport)
Research Centres CEA*, France (near and far field) CIEMAT*, Spain (clay systems) EAWAG, Switzerland (cement) EMPA*, Switzerland (cement) INE, FZK*, Germany (near and far field; TRLFS) JAEA, Japan (Ra in bentonite/argillaceous rocks) IFR, FZD*, Germany (XAS, TRLFS) SCK/CEN, Belgium (clays) VTT, Finland (pH in compacted bentonite) *formal co-operation agreements

New, is a general co-operation agreement between LES and the Department of Environmental Informatics at the "Helmholtz Centre for Environmental Research - UFZ" which has been set up in order to encourage co-operation for developing and applying coupled models on HPC (High Performance Computing) platforms, to facilitate common projects and the exchange of students and research personnel.

During 2006/2007 LES was particularly successful in its applications for Euratom Training Fellowships: Inter European Fellowships (Marie-Curie Euratom Fellowship). Such fellowships are fully financed by the EU over a 2-year period. Two fellowships began in November 2006 (INCA, "Influence of carbonate on actinide sorption on clay minerals" in co-operation with INE/FZK, and DINAPOR, "Diffusion of nanoparticles in argillaceous media: Assessment of pore structure", in co-operation with IFR/FZD.) A third Inter European Fellow took up her position in September 2007 to work on the MISUC project "Microscale investigations of the speciation and mobility of U(VI) in cementitious materials" being carried out in co-operation with CEA Saclay/DANS/DPC.

Two applications for post doc positions made by LES in 2007 were successful. The first was entitled "Crystallographic analysis of micro-diffraction images from heterogeneous, polycrystalline samples: A novel approach to determine the mineral composition in the cement matrix and at cement/Opalinus Clay interfaces". This project is fully financed by PSI via FoKo and aims at investigating the single minerals in the cement matrix and chemically disturbed zone at the cement/Opalinus Clay interface on the micro-scale (Mont Terri Project "Cement-Opalinus Clay Interaction", (CI)). In connection with the ACTINET pooled facility activities, a candidate is being sought who will contribute to and co-ordinate radioactive experiments carried out at the microXAS and superXAS beamlines at the SLS, support internal and external users and carry out his/her own research within LES. A third post doc proposal to implement and optimise the MCOTAC reactive transport code on the massively parallel computer XT3 and Merlin was unsuccessful. However, this activity is seen as an important one, and continued efforts will be made to seek financial support.

There are two further open positions within LES which have already been advertised. The first is for an assistant professor, tenure track, in Repository Geochemistry in the Department of Earth Sciences at the ETHZ. The aim is to create a joint position between PSI and the ETHZ to strengthen the collaborative research work and to establish joint

research and education programmes. The second position is for a group leader of the Sorption Mechanisms Group, which has been vacant for some considerable time.

As part of the continuing efforts to strengthen the contacts to universities, two LES co-workers, W. Hummel and G. Kosakowski, have been granted the *Venia Legendi* in the Department of Environmental Sciences ETHZ for Nuclear Environmental Chemistry, and the Faculty for Geosciences (University Tübingen, Germany) for Environmental Geology and Hydroinformatics, respectively. The former person is involved in two MSc programmes at the ETHZ, namely "Landfilling, Nuclear Repositories and Contaminated Sites", and "Nuclear Energy Systems". Strong connections also exist between LES and the Universities of Bern (T. Gimmi) and Geneva (C. Degueudre).

Of the three PhD students in LES, one defended her thesis successfully in November 2007. The two others have projected finishing dates in 2008 and 2010. Three further PhD proposals have been either accepted, "Iodide and selenium uptake on selected minerals", or are in the latter stages of evaluation, "High temperature thermodynamics and transport" (Geothermal Reservoir Processes Project within the Competence Centre Environment and Sustainability), and "Determination of narrow diffusion profiles: microXAS and laser ablation" (Swiss National Science Foundation).

On 19 and 20 October 2006, and 22 March 2007, the Waste Management Programme Committee (PCM) met for their annual meetings. As mentioned earlier, the intention of holding the meeting so early in 2007 was to synchronise the meeting time with the other Labs in the Nuclear Energy and Safety Division. The work performed within LES and the future plans were discussed as usual (AN-44-07-01, AN-44-07-02). The valuable help and input from the members of the committee, both at the meeting, and throughout the year are appreciated by the whole Lab.

Two long serving members retired from the PCM at the end of 2007, Professor Heino Nitsche (University of California) and Professor Wolfgang Kinzelbach (ETHZ). We would like to take this opportunity of thanking them both for their positive and constructive criticisms and contributions over the years. However, we feel ourselves very fortunate to have won two excellent replacements: Professor Bernhard Wehrli (ETHZ and EAWAG) and Dr. Jan van der Lee (Geosciences Centre, Ecole National Supérieure des Mines). We are very pleased to welcome them as members of the LES Programme Committee.

1.3 Performance assessment

Activities are now beginning within LES associated with the implementation of the Sectoral Plan for the deep geological disposal of low and intermediate level waste and HLW/SF/ILW. Such work is expected to increase over the years up to 2014/2016 by which time 2 sites will have been selected, one for each repository type, and the application for a general licence submitted. As time goes on, and this date gets nearer and nearer, it is anticipated that the level of detail involved in safety appraisals/evaluations will increase since the process will become more and more specific with respect to site evaluations.

Currently, we are in the early stages of the procedures involving the selection of potentially suitable regions for a radioactive waste repository. The key issues are the long-term safety and the geology, followed by land use planning and socio-economic issues. During the past year LES has contributed to this process by providing a generic study on the influences of mineralogy and water chemistry on sorption. Following this, a series of generic sorption databases for provisional performance assessment studies were produced. These sorption databases covered the range of water chemistries expected in Switzerland (pHs and ionic strengths) and major rock types such as calcareous rocks (one SDB), granite (four SDBs) and argillaceous rocks (four SDBs) as well as considering reducing and oxidising conditions.

Also in 2007 key issues for performance assessment such as the justification of high sorption values, the transfer of sorption data and models derived from dispersed systems to intact rock (OPA) and compacted systems (bentonite), Ra solubility (solid solution formation), have been pursued further. The goal of developing thermodynamic sorption databases founded on mechanistic sorption models and parameter values has been advanced by sorption experiments and modelling on the illite system and investigations within NF-PRO and FUNMIG on the influence of aqueous phase carbonate complexation on sorption. A potentially very interesting and exciting development for performance assessment was the incorporation of the two site protolysis non electrostatic surface complexation and cation exchange (2SPNE SC/CE) sorption model into the reactive transport code MCOTAC.

The focus on dose determining radionuclides has been continued in the last year with diffusion and sorption measurements of iodide and iodate on Opalinus Clay and compacted bentonite under atmospheric and anoxic conditions. It is anticipated that once reliable redox controlled conditions can be achieved in the lab, the sorption behaviour of selenium in clay rich and cementitious systems will be investigated.

The experimental/modelling task force set up in 2007 to investigate the speciation and transport properties of ^{14}C arising from anaerobic corrosion of carbon steels will propose ways and means of quantifying this problem in the coming year. Although the information existing in the literature on this topic is very sparse, the indications are that ^{14}C may be released in the form of small organic molecules which could be mobile. In the mean time, first diffusion experiments of ^{14}C labelled formic and acetic acids in Opalinus Clay have been performed in order to gain practical experience in measuring the transport properties of small organic molecules.

1.4 Foundations of repository chemistry

As in the reporting period 2005-2006, LES's commitment to the international reviews of thermodynamic data within the scope of the OECD/NEA Thermodynamic Data Base Project has continued. The "state-of-the-art" report on solid solutions has been published as Vol. 10 of the OECD/NEA "Chemical Thermodynamics" series. The NEA TDB review on iron (aqueous complexation of Fe(II)) is taking longer than anticipated and will continue on into 2008. The important problem of how to derive chloride complexation constants from osmotic coefficients in a consistent manner has been solved. The GEMS-PSI code, with the built-in Nagra/PSI TDB 01/01, is a tool for advanced modelling of chemically plausible redox-sensitive systems with aqueous speciation, surface complexation, co-precipitation and solid solution formation. Development is ongoing, with work on the "help system", documentation, test examples and tutorials of GEMS still being necessary. The GEM IPM numerical kernel has been performance-optimised, running now at up to 30 times faster than before. This gain in speed is crucial for applications in coupled code reactive transport modelling. The GEM approach to the thermodynamic modelling of systems relevant to radioactive waste disposal is now being applied, e.g. evaluation of new experimental data on the uptake of Sr in C-S-H phases, understanding the thermodynamics of hydrotalcite-pyroaurite solid solution systems, radium interaction with minor minerals such as barite, in clay systems.

Activities related to the long-term glass corrosion experiments at PSI are continuing. Current work is focussed on the spectroscopic characterisation of the corrosion products and their interaction with Ni and Ce(III/IV). The latter was introduced into the inactive MW glass as an analogue of Pu(III/IV).

Within the framework of the co-operation with the Japan Atomic Energy Agency (JAEA), kinetic experiments on the uptake of ^{133}Ba on barite are being

performed. The goal of these experiments is to determine barite re-crystallisation rates. This information is necessary in order to apply thermodynamic solid solution models to the uptake of Ra on barite.

1.5 Repository near field

1.5.1 Clay systems

Porewater is the medium through which radionuclides are transported in compacted clay, and it is important to know its structure and properties. Pure clay minerals (montmorillonite, illite, kaolinite, and pyrophyllite) were chosen as model systems for a PhD thesis on this topic which was completed successfully in November 2007.

The work on pure clay minerals was continued. A good set of diffusion data with $^{85}\text{Sr}^{2+}$, $^{22}\text{Na}^+$, $^{134}\text{Cs}^+$, $^{36}\text{Cl}^-$ and $^{35}\text{SO}_4^{2-}$ in Na-montmorillonite, Na-illite and kaolinite under different chemical conditions are now available and brings us a step forward to understanding diffusion in clays. The aim of the complementary DINAPOR project is to develop alternative methods for determining the pore size distribution in compacted argillaceous materials by studying the diffusive behaviour of ^{14}C labelled macromolecules of different sizes.

Monte Carlo and classical molecular dynamics methods have been used to investigate the state and dynamics of water and cations in pure and mixed Na-Cs-montmorillonite as a function of the interlayer water content. At low hydration levels the values for the diffusion coefficient of Cs^+ are lower than those for Na^+ , whereas at high hydration levels Cs^+ diffuses faster than Na^+ . It remains an open question as to why experimentally determined values for the relative diffusion coefficients of Cs^+ in the interlayer of clays are about 20 times smaller than those obtained by classical molecular dynamics studies.

One of the long-term goals of the clay related work is to answer the key question as to whether mechanistic sorption models, based on measurements in dispersed systems, are directly applicable to compacted systems. Cs sorption experiments on highly compacted montmorillonite in specially designed cells have been carried out. The conclusion drawn from the experiments is that Cs sorption on compacted clay (at a dry density of $\sim 1500 \text{ kg} \cdot \text{m}^{-3}$) is the same as the sorption measured in dispersed systems. COMSOL Multiphysics was used to model the measured decrease in caesium concentration in solution. The analyses showed that a simplified 1D and 2D modelling approach was not appropriate, and only a full 3D calculation could adequately describe the measurements.

In other experiments on highly compacted bentonite it was observed that for bulk dry densities $> 1600 \text{ kg} \cdot \text{m}^{-3}$, the sorption of $^{134}\text{Cs}^+$ increased with increasing compaction. This was interpreted in terms of an increase in the Cs-Na selectivity coefficient related to the lower availability of interlayer water for cation hydration.

The effect of charge on the diffusion behaviour of anions ($^{35}\text{SO}_4^{2-}$) was studied in compacted bentonite as a function of the dry density. The effective diffusion coefficient was found to depend strongly on the degree of compaction and there was evidence that the $^{35}\text{SO}_4^{2-}$ anions were sorbing.

The so called “bottom up” approach to predicting sorption in real systems, coupled with the development of thermodynamic sorption data bases, has been continued. The influence of carbonate complexation on the uptake characteristics of Ni(II), Eu(III) and U(VI) in the montmorillonite/bentonite system has been systematically studied and modelled using the 2SPNE SC/CE sorption model. The majority of this work has been carried out within the framework of the EU Integrated Project NF-PRO and the Marie-Curie Euratom Fellowship project INCA. Additionally, the Np(V)/montmorillonite system has been studied within an ACTINET project in cooperation with the Johannes Gutenberg-University Mainz and FZD (ROBL). EXAFS investigations have been performed in association with this work with the aim of identifying the sorbed surface species involved.

With the 2SPNE SC/CE sorption model now incorporated into MCOTAC, it was possible for the first time to investigate the potential influence of competition on sorption. As an initial example the transport of Ni(II) through bentonite with and without the inclusion of Fe(II) competition was calculated and compared with the results obtained using a simple “ K_d approach”.

1.5.2 Cement

Cement is an important component of the engineered barrier system in long-lived intermediate-level and low-level and short-lived intermediate-level radioactive waste and controls the release of radionuclides to the far field by a combination of solubility and sorption constraints. Wet chemistry and spectroscopic techniques are combined with solid solution and molecular modelling studies with the aim of gaining a fundamental understanding of the radionuclide retention processes in cementitious materials.

The “in house” C-S-H ideal solid solution model is capable of quantitatively describing the incorporation of divalent cations. The model was extended with new

Sr, Na and K end members using published and unpublished Sr uptake measurements on C-S-H phases in contact with various aqueous phase compositions. The DualTh (Dual-Thermodynamic) module in the GEMS-PSI code was used to evaluate new experimental data. The quality of the description of the experimental Sr uptake isotherms was good.

The programme on the interaction of actinides with cementitious materials has continued. 1.13 nm tobermorite and xonotlite are crystalline C-S-H phases which are considered to be appropriate model compounds for the development of a mechanistic understanding of actinide and lanthanide binding to C-S-H phases. A combined experimental/theoretical approach has been used to explore the structure and stability of the silicate tetrahedral double chain in xonotlite. The defect structures in xonotlite are being investigated via ab-initio calculations based on density functional theory since they are believed to facilitate the incorporation and diffusion of radionuclides in the mineral structure. The uptake of Nd(III) and Eu(III) is being measured within the framework of a PhD project which has the further aim of substantiating the high sorption values previously determined and subsequently used in performance assessment calculations. X-ray diffraction studies coupled with Rietveld refinement are also being carried out on Nd(III) doped xonotlite and tobermorite to determine the crystallographic position of Nd(III) bound in the structures.

In an other project, the uptake of U(VI) in cementitious matrices is being addressed, in particular by the use of time resolved laser fluorescence spectroscopy (TRLFS) for U(VI) in co-operation with the Institut für Radiochemie at the Forschungszentrum Dresden.

In general, the uptake of redox sensitive actinides under the reducing conditions existing in a cementitious near field is poorly characterised. Th(IV) is commonly used as a chemical analogue for tetravalent actinides. In order to corroborate this assumption and to obtain actinide specific sorption values, a study on the uptake of Np(IV) and Np(V) by cement and C-S-H phases under reducing conditions has been started. Measurements under reducing conditions in alkaline media require the development of procedures to determine the chemical speciation of Np under these conditions and to establish stable and known redox conditions in the experiments.

A first series of experimental studies on the uptake of ^{129}I and ^{36}Cl by hardened cement paste (HCP) were carried out using the "modified HTS cement" currently being sold. The sorption values will be compared to those obtained from earlier studies with the "older HTS cement". Investigations on the

interaction of dose-determining radionuclides such as ^{79}Se , ^{129}I , ^{36}Cl and ^{14}C in cementitious systems will be at the focus of future research. In this context a PhD study aimed at understanding the thermodynamics of hydrotalcite – pyroaurite solid solution systems was re-started in January 2007. Such compounds are known to exchange and take up anions such as TcO_4^- , SeO_3^{2-} etc. which are relevant to Performance Assessment.

Within the framework of the Cement Interaction (CI) field experiment at the Mont Terri Underground Research Laboratory, the hydration processes of three cements (OPC, LAC, ESDRED shotcrete) are being investigated in co-operation with Empa. Sample preparation and porewater sampling, using the steel die method, were carried out at Empa with LES support. ICP-OES analyses were carried out at PSI to determine the concentration of the main elements, i.e., Ca, Si, Na, K, Al, S.

A short-term study was carried out in conjunction with Nagra's contribution to a joint Nagra-NUMO-SKB-Posiva project on the long-term safety aspects of superplasticizers and other organic cement admixtures.

1.6 Repository far field

In 2007 the focus of the far field work has remained on Opalinus Clay (OPA).

In order to avoid the problems associated with sorption on equipment, in-diffusion experiments of ^{152}Eu in Opalinus Clay were repeated by applying the tracer directly to the surface of the rock. Results are expected during the course of 2008.

The experiments in which the diffusion of $^{125}\text{I}^-$ and $^{125}\text{IO}_3^-$ in Opalinus Clay were studied separately and in which the iodine speciation was monitored by high performance anion exchange chromatography, were completed. No sorption of $^{125}\text{I}^-$ took place on Opalinus Clay and $^{125}\text{IO}_3^-$ was rapidly converted to $^{125}\text{I}^-$ upon contact with the rock.

The first experiments on the diffusion of $^{14}\text{CH}_3\text{COO}^-$ (OAc) in Opalinus Clay from Mont Terri revealed that $^{14}\text{CH}_3\text{COO}^-$ diffuses unretarded through Opalinus Clay with a diffusion coefficient lower than that of Cl^- .

Illite is one of the principal sorbing mineral phases in the Opalinus Clay and in most cases is considered to determine the sorption of many radionuclides. The influence of carbonate complexation on the uptake characteristics of Ni(II), U(VI) and Eu(III) on Na-illite is being investigated within the 6th EU project FUNMIG with a view to using the 2SPNE SC/CE sorption model to predict the uptake in Opalinus Clay.

In a first attempt to reproduce a U(VI) isotherm measured on Opalinus Clay, the model over predicted the sorption. Although there is convincing evidence in the open literature for the formation of an uncharged $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq.})$ complex, a stability constant was not contained in the selected NEA TDB data for U(VI). Once this complex was included in the modelling a good fit to the U(VI) isotherm was found.

The “in house” Cs sorption model has been incorporated into MCOTAC. Cs diffusion data in Opalinus Clay have been modelled with MCOTAC-Cs and compared with results from conventional modelling using a Cs isotherm. In the case of reactive transport calculations the potassium ion concentration in the clay porewater increased through the displacement of K by Cs via cation exchange reactions, and this in turn influenced the sorption of Cs. Such an effect is not captured when a non-linear sorption isotherm is used.

Thermodynamic modelling of Eu-calcite solid solutions and laser fluorescence data suggest the existence of distinct co-ordination environments for trivalent actinides and lanthanides incorporated in calcites, depending on the rate of precipitation, pH and pCO_2 conditions. In an effort to define bond distances and co-ordination numbers of such species, EXAFS spectra of Nd-doped calcites, synthesised under well-defined pH- pCO_2 and kinetic conditions, were measured at the DUBBLE beamline (ESRF, Grenoble). The measurements were successful and will be evaluated during the coming year.

In the framework of the long-term diffusion/retention experiment (DR) in Mont Terri, a new set of 5 samples was prepared for radial diffusion experiments. The diffusion of HTO showed very good agreement with previously measured values on samples obtained from another location at Mont Terri (DI site). Diffusion of I^- , Br^- , $^{36}\text{Cl}^-$, $^{22}\text{Na}^+$, D_2O and H_2^{18}O are ongoing and will be finished in early 2008. In February 2007, Eu was added to the DI test as an additional tracer. In order to design the sampling strategy, various scoping simulations were performed using a modified version of the code FLOTRAN. Modifications were necessary because in a previous version there were problems with anisotropic diffusion in radial co-ordinates.

Because clay formations have very low permeabilities, they are attractive as potential host rocks for radioactive waste repositories.

However, very low permeabilities imply that it is exceedingly difficult to obtain representative water samples. Since several parameters that constrain the geochemical modelling are not very well known (e.g., pCO_2 and the exchangeable cation populations) it is important to assess the effect of the uncertainties which these input values may have on the calculated water chemistries. Within the framework of the “Analysis of Geochemical Data (GD)” task for Phase 12 of the Mont Terri Project, LES is participating in the subtask “Parameter Uncertainty”. Monte Carlo methods are being used. The method consists of repeated calculations with a geochemical model in which all uncertain input data are changed randomly and simultaneously within the stated uncertainty limits from calculation to calculation. Statistical evaluation of the variation in the resulting output parameters yields their uncertainty. Sources of uncertainty in the input can be thermodynamic data or the analytical data needed to constrain the geochemical model.

Colloid investigations are being carried out within the framework of the “Colloid Formation and Migration” (CFM) project at the Grimsel Test Site. The focus remains on colloid generation and on colloid characterisation using combinations of single particle counting techniques and electron energy loss spectroscopy coupled to a transmission electron microscope. A mathematical model describing the changes of colloidal suspension properties over a colloid bed in batch experiments was developed and tested. In September 2008 a celebration of the 20th anniversary of the Grimsel Colloid Exercise will take place.

In order to gain confidence in the use of, and reliability of, various reactive transport codes being used in house, a number of benchmarking exercises are underway or planned. A benchmarking co-operation has started with HSK in which a set of test cases has been agreed. The tests will be performed using the different codes available to LES and HSK e.g. MCOTAC, ROCKFLOW, TOUGH2, COMSOL etc. A recent comparison carried out by CEA showed that the codes CRUNCH, HYTEC and ALLIANCES showed different front developments, porosity distributions and flow field changes when modelling high-pH water induced mineral reaction fronts. A comparison with results from MCOTAC and ROCKFLOW are planned.

Table 1.2: LES Organigram (December 2007)

2 GEOCHEMICAL MODELLING

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

2.1 Overview

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

- The NEA TDB state-of-the-art report on solid solution systems was completed and the book published as Vol. 10 of the OECD/NEA “Chemical Thermodynamics” series.
- Within the scope of the ongoing NEA iron review, the problem of how to derive chloride complexation constants from osmotic coefficients in a consistent manner has now been solved.
- The GEMS-PSI code was enhanced with new functionality, especially with several built-in non-ideal solution models. The GEM IPM numerical kernel has been performance-optimised, running now up to 30 times faster than before. This gain in speed is crucial for coupled modelling efforts.

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

- The GEM DualTh (Dual-Thermodynamic) approach has been used to evaluate new experimental data on the uptake of Sr in C-S-H phases. The solid solution model describes well the co-precipitation of Sr with C-S-H prepared in artificial cement porewater.
- A PhD study aimed at understanding the thermodynamics of hydroxalite – pyroaurite solid solution systems started in January 2007 with the syntheses of solid phases and their characterisation by XRD and Raman spectra.
- Within the scope of the joint JAEA – LES project on radium interaction with clays and minor minerals, barite re-crystallisation rates have been determined.

A detailed Monte Carlo analysis of the uncertainties in the geochemical modelling results of porewater compositions arising from the uncertainties in the input parameters has been carried out in the framework of the Mont Terri Project “Analysis of Geochemical Data (GD)”.

Activities related to the long-term glass corrosion experiments running at PSI focussed on the spectroscopic characterisation of the corrosion products.

W. Hummel received the “Venia Legendi” as Privatdozent (PD) at the ETH Zurich. Teaching started in the Autumn Semester of 2007 with a new course “Landfilling, nuclear repositories and contaminated sites”.

2.2 Thermodynamic databases and software

2.2.1 OECD/NEA TDB solid solution report

The work on the NEA TDB state-of-the-art report “Chemical Thermodynamics of Solid Solutions of Interest in Nuclear Waste Management” was completed and the book published by OECD (Paris) as Vol. 10 of the “Chemical Thermodynamics” series. This effort, which started in June 2005, should promote the consideration and possible inclusion of advanced concepts of solid solution immobilization of hazardous elements into future research related to nuclear waste disposal.

2.2.2 OECD/NEA TDB iron review

Fe(II)-chloride complexes

Formation constants and SIT coefficients of Fe(II) chloride complexes based on the analysis of osmotic coefficients were reported in the last annual report. In the meantime, part of the work has been substantially revised and the corrected parameters are reported here. The formation constant $\log_{10}\beta_1^0(\text{FeCl}^+) = (-0.111 \pm 0.027)$, as derived from HEINRICH & SEWARD (1990), was no longer assumed a priori to be valid. All three unknown parameters were now simultaneously fitted to the available osmotic coefficient data. The good news is that with $\varepsilon(\text{Fe}^{2+}, \text{Cl}^-)$ equal to $(0.17 \pm 0.01) [\text{kg} \cdot \text{mol}^{-1}]$, the most relevant parameter extractable from the data is nearly the same as given previously, $(0.165 \pm 0.002) [\text{kg} \cdot \text{mol}^{-1}]$. The interaction coefficient $\varepsilon(\text{FeCl}^+, \text{Cl}^-)$ changed from (0.370 ± 0.002) to $(0.16 \pm 0.01) [\text{kg} \cdot \text{mol}^{-1}]$ and with $\log_{10}\beta_1^0 = (-2.05 \pm 0.15)$ the formation constant decreased by two orders of magnitude, suggesting that the complex FeCl^+ is de facto non-existent at ambient temperature below ~ 5 molal Cl^- .

Fe(III) chloride complexes

In contrast to Fe(II), Fe(III) chloride complexes are much stronger. The most reliable literature values for the simplest complex, FeCl^{2+} are in the range $1.2 < \log_{10}\beta_1^0 < 1.7$, with a medium value of 1.4 to 1.5.

Similar to the FeCl_2 system mentioned above, osmotic data of FeCl_3 solutions were evaluated assuming a very simple speciation model which included the species Fe^{3+} , Cl^- and FeCl^{2+} . Hydrolysis products, higher order complexes and mixed hydroxide-chloride complexes were not included in the model because an estimate showed that they remain minor species in the

systems considered here. Activity coefficients were calculated using the specific ion interaction theory (SIT) model¹. Hence, the evaluation required the simultaneous determination of the three parameters $\log_{10}\beta_1^0(\text{FeCl}^{2+})$, $\varepsilon(\text{Fe}^{3+}, \text{Cl}^-)$ and $\varepsilon(\text{FeCl}^{2+}, \text{Cl}^-)$. A major problem in this evaluation is related to the osmotic data themselves, because the osmotic coefficient is a model-dependent entity which is calculated from the measured water activity and the sum of solutes according to

$$\Phi = \frac{-\log_{10} a_{H_2O} \cdot \ln(10) \cdot 55.5084}{\sum_k m_k} \quad (2.1)$$

A well defined value for this sum of solutes can only be calculated from the total molality of the electrolyte when the degree of dissociation is clearly defined i.e. when the electrolyte is completely dissociated or not dissociated. In order to provide actual values for the osmotic coefficient, it is usually assumed that the dissociation is complete. If the electrolyte forms complexes as indicated above (i.e. FeCl^{2+}), the sum of solutes decreases and becomes a complex function of the formation constant, the ionic strength and the interaction coefficients. In the framework of the SIT ionic strength correction model, osmotic coefficients at 25°C may be expressed according to a formula similar to that developed by LEWIS et al. (1961) (see also GRENTHE et al., 1997):

$$\frac{\Phi - 1}{\ln(10)} = -\frac{0.5091 \cdot |z_+ \cdot z_-| \cdot (t - 2 \ln(t) - \frac{1}{t})}{1.5^3 \cdot I_m} + \frac{1}{\sum_k m_k} \sum_c \sum_a \varepsilon_{(c,a)} m_a m_c \quad (2.2)$$

where z_+ , z_- denotes the charges of solutes, m denotes molalities, the subscripts a , c denote anions and cations, I_m is the ionic strength and t is a short hand notation for $(1+1.5\sqrt{I_m})$. Note that there is a problem with defining z_+ when several solutes with different charges are present. Here, z_+ is defined such that the known ionic strength I_m is reproduced by this z_+ and the sum of cationic solutes.

Provided that an appropriate model, a correct formation constant and sensible interaction coefficients have been selected, then both equations should produce identical osmotic coefficients. (Note that the osmotic coefficient deviates from the

¹ At 25 °C the activity coefficient of a ion i of charge z_i is

$$\text{given by } \gamma_i = \frac{0.5091 \cdot z_i^2 \cdot \sqrt{I_m}}{1 + 1.5 \cdot \sqrt{I_m}} + \sum_k \varepsilon(i, k) \cdot m_k$$

published values because the sum of dissolved species, $\sum m_k$ (Eq. 3.1) has now changed due to complex formation). The actual evaluation required a nested inverse and iterative calculation scheme which was performed with a spread-sheet. The sum of the squares of the Φ -differences was used to indicate the goodness of fit.

The parameters $\log_{10}\beta_1^0(\text{FeCl}^{2+}) = (1.38 \pm 0.02)$, $\varepsilon(\text{Fe}^{3+}, \text{Cl}^-) = (0.50 \pm 0.10) [\text{kg} \cdot \text{mol}^{-1}]$ and $\varepsilon(\text{FeCl}^{2+}, \text{Cl}^-) = (0.27 \pm 0.01) [\text{kg} \cdot \text{mol}^{-1}]$ were found to best describe osmotic coefficients in the range $0.2\text{m} < m(\text{FeCl}_3) < 2\text{m}$. Fig. 2.1 shows the excellent fit and demonstrates how osmotic coefficients change when the sum of the solutes, $\sum m_k$, decreases due to complex formation.

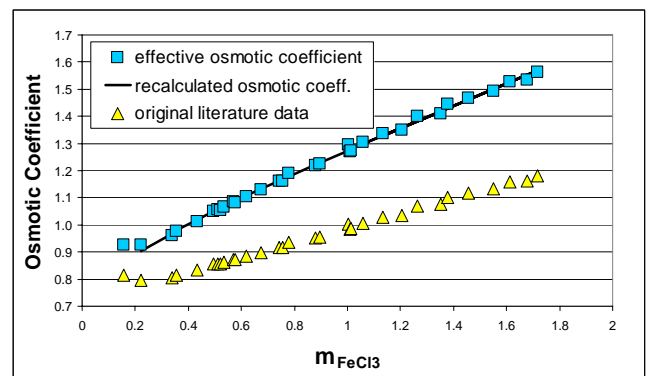


Fig. 2.1: Osmotic coefficients of FeCl_3 solutions, evaluated with Eq. 2.1 (blue squares) and Eq. 2.2 (solid line) using $\log_{10}\beta_1^0(\text{FeCl}^{2+}) = 1.38$ and the interaction coefficients given in the text. Yellow triangles are published values assuming that no complexes are formed. Concentrations are given in molality.

2.2.3 GEM-Selektor programme package v.2-PSI

The GEMS-PSI code has been under development in LES since June 2000. With the built-in Nagra/PSI TDB 01/01, it is a tool for advanced modelling of chemically plausible redox-sensitive systems with aqueous speciation, surface complexation, co-precipitation and solid solution formation. The GEMS-PSI package v. 2.2.0 (for Win32 and Linux) can be obtained from its new homepage <http://gems.web.psi.ch> (More than 800 downloads have been registered to date). There were important improvements and bug fixing carried out in 2007 (collaborators: S. Dmytrieva, Th.Wagner). Some work on the help system, documentation, test examples and tutorials of GEMS is still necessary.

Further work on testing and performance optimization of the GEMIPM2K code (Februar 2007) using the “node_gem” test example (500 calls of GEM IPM2) helped to identify loops in the code which slowed down the calculations. These loops involved the

stoichiometry matrix. After introducing index lists, and re-arranging these loops (S. Dmytriieva), the calculation time of GEM IPM2 decreased 1.2 and 14 times for the system with 6 and 41 independent components (IC), respectively. Using compiler optimization further increased the speed of test calculations by about a factor of 2 regardless of $n(\text{IC})$. Fig. 2.2 shows the achieved progress, with calculation times approximated using a simple power function.

This achievement brings the goal of coupling GEM with transport codes much closer than before because the performance of the chemical solver is a critical factor in coupled modelling in 2D and 3D space. Further, a 10 to 30 times increase in performance can be achieved by the clever use of previous GEM primal solutions for the node as initial approximations. Technical report(s) on the GEMIPM2K performance optimization, testing, and prediction of computing times are in preparation.

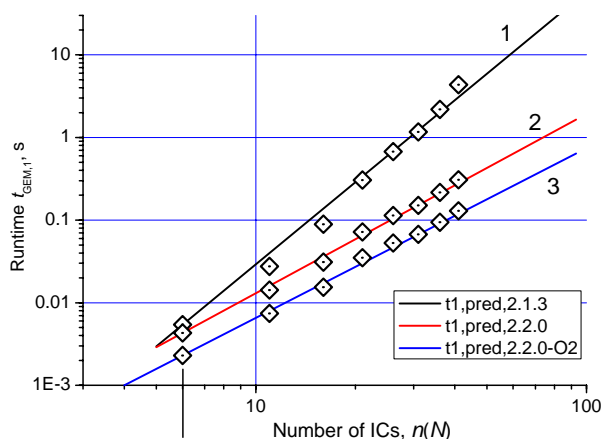


Fig. 2.2: Comparison of runtimes t , in seconds, per one GEM IPM2 call for the original GEMIPM2K version (1), the performance optimised version (2), and the further compiler optimised version (3). Diamonds indicate the respective “node_gem” test run times. Lines are approximations with simple functions.

An accelerated GEMIPM2K-MCOTAC prototype has also been produced (together with W. Pfingsten, S. Dmytriieva). The first coupling of GEMIPM2K with the ROCKFLOW transport code was achieved in November 2007 (with G. Kosakowski, and Hai-Bing Shao, UFZ Leipzig). Tests of these coupled prototypes showed again that the GEM chemical system formulation must be checked and tested carefully before starting any extensive coupled modelling.

Further progress was made in the development of a unified interaction parameter transfer data structure for non-ideal phases-solutions, implemented both in GEMS-PSI and GEMIPM2K codes (in collaboration

with Th. Wagner, Uni Tübingen). This allowed the improvement of some existing built-in models (SIT for aqueous electrolyte, Churakov-Gottschalk for mixed fluids) and to add several new ones (Peng-Robinson-Stryjek-Vera (PRSV) for mixed fluids; multicomponent regular, Van Laar and Redlich-Kister models for solid solutions). Using the new parameter transfer mechanism, some other important mixing models (e.g. Pitzer or Extended UNIQUAC for aqueous solutions) can be added with only a moderate effort in the future.

2.3 Solid solutions

2.3.1 Synthesis of Nd-calcites

Thermodynamic modelling of Eu-calcite solid solutions (CURTI et al., 2005) and laser fluorescence data suggest the existence of distinct co-ordination environments for trivalent actinides and lanthanides incorporated in calcites, depending on the rate of precipitation, pH and $p\text{CO}_2$ conditions. In an effort to define bond distances and co-ordination numbers of such species, EXAFS spectra of Nd-doped calcites, synthesised under well-defined pH- $p\text{CO}_2$ and kinetic conditions, were measured at the DUBBLE beamline (ESRF, Grenoble). The measurements were successful and will be evaluated during the coming year.

2.3.2 Extended C-S-H model

The bulk of hardened cement paste is composed of calcium silicate hydrate (C-S-H) phases which are capable of incorporating divalent cations such as Sr and Zn. Quantitative knowledge of the aqueous solubilities of C-S-H phases represented as solid solutions would be of advantage, both in studies of cement hydration and in PA studies for nuclear and toxic waste disposal. In this context, and in collaboration with J. Tits and E. Wieland, the aim was to extend our C-S-H ideal solid solution model (KULIK & KERSTEN, 2001, 2002) using new Sr, Na, and K end members. The DualTh (Dual-Thermodynamic) module in the GEMS-PSI code (KULIK, 2006) has been used to evaluate new experimental data on the uptake of Sr in C-S-H phases synthesised in solutions without Na and K (“Water”), and in artificial cement water, ACW (TITS et al., 2006 and unpublished data). DualTh is a form of inverse modelling which can, in particular, retrieve unknown stoichiometry and standard molar Gibbs energy G_m° of an ideal solid solution end member from experimental bulk compositions of the aqueous electrolyte and the co-existing solid solution phase.

Based on composition diagrams, 13 end member stoichiometries with the general formula $[(\text{Ca}(\text{OH})_2)_{n_{\text{Ca}}}(\text{Sr}(\text{OH})_2)_{n_{\text{Sr}}}(\text{KOH})_{n_{\text{K}}}(\text{NaOH})_{n_{\text{Na}}}\text{SiO}_2\text{H}_2\text{O}]_{n_{\text{Si}}}$ were used in DualTh runs, with stoichiometry

coefficients in the intervals $0.1 < n_{Si} < 2$; $0 < n_{Ca} < 1.6$; $0 < n_{Sr} < 2$; $0 < n_K < 2$; $0 < n_{Na} < 2$, to seek the smallest standard deviation σ of estimated mean $G_{m,298}^\circ$ values of end members over each set of experiments (C:S ratio in “Water” or ACW). In this way, the “optimal” stoichiometries of three hypothetical end members were determined: $[(\text{Sr}(\text{OH})_2)_{1.0}\text{SiO}_2\text{H}_2\text{O}]_{1.0}$ (SrSH); $[(\text{NaOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}]_{0.2}$ (NaSH); and $[(\text{KOH})_{2.5}\text{SiO}_2\text{H}_2\text{O}]_{0.2}$ (KSH), with their mean $G_{m,298}^\circ$ values and 2σ uncertainty intervals.

Table 2.1: C-S-H end members, in $\text{kJ} \cdot \text{mol}^{-1}$.

End member	$G_{m,298}^\circ$ DualTh	$G_{m,298}^\circ$ <i>fine-tuned</i>
Tob ($n_{Ca}=0.8333$)	-1863.60	-1863.60
Jen ($n_{Ca}=1.0$, “Water”)	-1570.15	-1569.05
JenCa ($n_{Ca}=1.0$, ACW)	-1568.02	-1567.05
SrSH (“Water”)	-2021.59	-2019.75
SrSH (ACW)	-2016.92	-2016.33
NaSH	-433.55	-433.55
KSH	-443.37	-443.37

These data were then fine-tuned in forward GEM modelling of the “in house” Sr uptake data (~90 experiments at ambient T,P). NaSH and KSH end members were fine-tuned in the modelling of literature data on Na and K uptake isotherms in C-S-H (HONG & GLASSER, 1999). The $G_{m,298}^\circ$ estimates are given in Table 2.1. The quality of the description of the experimental Sr uptake isotherms using the data in Table 2.1 in forward GEM calculations is seen from Figs. 2.3 and 2.4.

Note that for Sr uptake in C-S-H (especially with C:S $\sim 1.1 \pm 0.1$) prepared in “Water” and in ACW, different $G_{m,298}^\circ(\text{SrSH})$ values must be used (see Table 2.1). This is not an insignificant difference ($3.4 \text{ kJ} \cdot \text{mol}^{-1}$) and might be explained by the extent of $[\text{SiO}_4]$ tetrahedra polymerization in C-S-H during synthesis with and without alkali cations. Another possibility would be to test an ion-exchange model for C-S-H (not yet implemented in GEMS) in the hope that such a model will be more adequate. In this context, some more work is needed before the manuscript can be finalized.

2.3.3 Thermodynamics of hydrotalcites

A PhD study aiming at understanding the thermodynamics of hydrotalcite – pyroaurite solid solution systems was re-started in January 2007 (K. Rozov). Such solids are of interest because they are known to form crystalline iso-structural solid solutions by the exchange of trivalent cations (Al - Fe(III)) or bivalent cations (Mg – Ni). This class of compounds is further known to exchange and take up anions relevant to performance assessment, such as TcO_4^- , SeO_3^{2-} etc. A key point in understanding these phases is to characterise their thermodynamic and solubility properties. The study was re-started by precipitating solid phases with the composition $\text{Mg}_3\text{Al}_x\text{Fe}(\text{III})_{1-x}(\text{OH})_8(\text{CO}_3)_{0.5} \cdot z\text{H}_2\text{O}$ from sodium carbonate solutions at pH 11.4 according to well known procedures. Detailed elemental analyses of the solid phases and mother liquids are ongoing, but XRD analyses and Raman spectroscopy measurements have been brought forward in order to be sure that the correct phases have been produced. XRD spectra of both end members, i.e. hydrotalcite and pyroaurite, agree well with those in the literature. Rietveld analyses of solids with intermediate mole fractions ($x = 0.8, 0.6, 0.4, 0.2$) are ongoing and will hopefully confirm the expected trends in the lattice parameters.

Raman spectra of the solid solution series are shown in Fig. 2.5. The peak at about 1061 cm^{-1} corresponds to symmetric stretching modes of the carbonate anion. At $x > 0.5$ the intensity of this band seems to be related to the carbonate/water ratio of the solid phase.

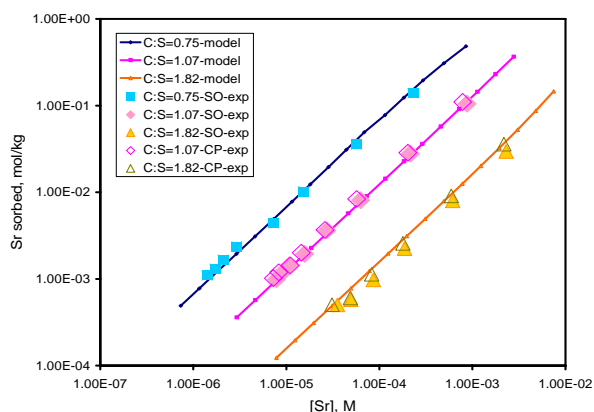


Fig. 2.3: Sr uptake on C-S-H in “Water” systems (without Na and K, pH 10 to 12.5), symbols: experimental data; lines: GEM Aq-SS model.

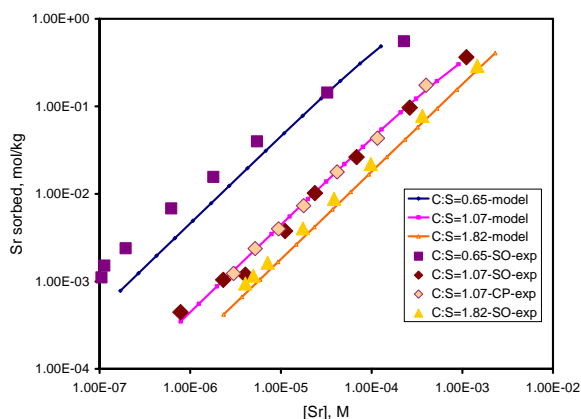


Fig. 2.4: Sr uptake on C-S-H in ACW systems, pH > 13.

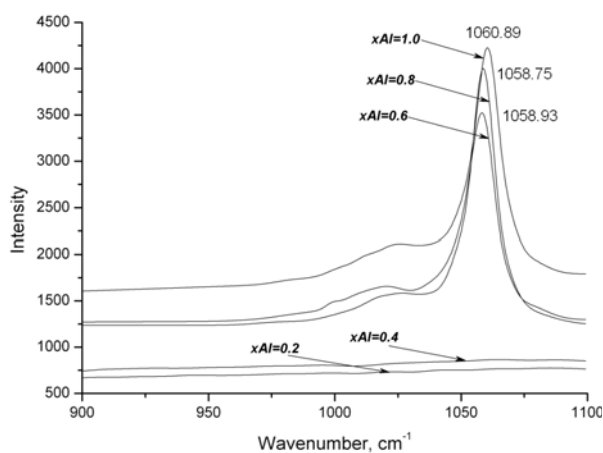


Fig. 2.5: Raman-spectra of the hydrotalcite – pyroaurite solid solution series with the general composition $Mg_3Al_xFe(III)_{1-x}(OH)_8(CO_3)_{0.5}zH_2O$. The peak at $\sim 1061\text{ cm}^{-1}$ corresponds to the symmetric stretching mode of the carbonate anion (FROST & REDDY, 2006) which disappears when the mole fraction of Fe(III) exceeds ~ 0.5 . Note that the peak intensity seems to depend on the carbonate/water ratio.

However, below $x < 0.5$ this band disappears, indicating a substantial impact of the Fe(III) which has entered into the structure. It is too early to make definitive conclusions, but, based on the available information it appears that the envisaged synthesis was successful.

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

In the framework of the co-operation started with the Japan Atomic Energy Agency (JAEA), the LES persons responsible for this project (E. Curti and J. Tits) visited JAEA at Tokai in March 2007, in order to plan the co-operation in detail. Although JAEA originally agreed to carry out all of the laboratory work, it was decided at the meeting that LES, in addition to the modelling work and the planning of the experiments, would contribute to the large experimental workload by carrying out ^{133}Ba kinetic sorption experiments with barite. The goal of these experiments is to determine barite re-crystallisation rates which need to be known in order to apply thermodynamic solid solution models to the uptake of Ra on barite. These experiments were started in July 2007 and were, to a large extent, carried out by a summer student (Clara Cuesta). They will continue to August 2008 (1 year). Preliminary data are encouraging, and indicate linear re-crystallisation rates of the order of $10^{-9}\text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, with little dependence on pH and solution composition.

2.4 Monte Carlo uncertainty analysis of clay porewater models

One of the main reasons why clay formations are chosen as potential host rocks for radioactive waste repositories is their very low permeability. This great advantage turns into a disadvantage when it comes to characterising the in situ clay porewater composition because it is exceedingly difficult to obtain representative water samples. PEARSON et al. (2003) compared water data from borehole samples taken at the Mont Terri Rock Laboratory, squeezed rock samples, and laboratory studies, and, combined with mineralogical data, developed a synthesis of all the data using geochemical modelling. Since several parameters that constrain the geochemical model are not very well known (e.g., $p\text{CO}_2$ and the exchangeable cation populations) it is important to assess the uncertainty of the modelling results due to uncertainties in the input values. In the framework of the “Analysis of Geochemical Data (GD)” task for Phase 12 of the Mont Terri Project, LES is participating in the subtask “Parameter Uncertainty”. “Classical” uncertainty analyses are typically conducted by varying one input parameter at a time and performing a separate calculation for each variation. While it is certainly possible to obtain the maximal range of output parameters in this way, the procedure is cumbersome if several input parameters are to be varied systematically. A more efficient and informative procedure is the Monte Carlo method which was introduced into the geological literature by ANDERSON (1976). The method consists of repeated calculations with a geochemical model, whereby all uncertain input data are changed randomly and simultaneously within the stated uncertainty limits from calculation to calculation. Statistical evaluation of the variation in the resulting output parameters yields their uncertainty. Sources of uncertainty in the input can be thermodynamic data or the analytical data needed to constrain the geochemical model.

In order to perform the uncertainty analysis we set up a simple Perl script is centred on the geochemical code PHREEQC, PARKHURST & APPELO (1999).

The Perl script

- (1) chooses random data for selected input parameters within specified limits using a specified probability distribution (uniform, Gaussian, etc.),
- (2) copies these parameters into the template of an input file,
- (3) runs a batch version of PHREEQC, and
- (4) writes specified output data to an output file.

Steps (1) to (4) are repeated until running averages of output parameters have stabilised to constant values (usually after about 1000 to 5000 iterations for the test cases discussed below). The resulting distributions of output parameters can be considered as a measure of their uncertainty.

We considered three test cases: (1) *Mont Terri BWS-A3*, the Opalinus Clay porewater model by PEARSON et al., (2003) for the BWS-A3 borehole at the Mont Terri Rock Laboratory, (2) *COX BRGM*, a porewater model by GAUCHER et al. (2007) for the Callovian-Oxfordian formation, and (3) *Mont Terri BRGM*, a model for the Mont Terri Opalinus Clay porewater by TOURNASSAT et al. (personal communication) based on the procedure developed by GAUCHER et al. (2007) for the Callovian-Oxfordian formation. The latter two cases were tested in collaboration with E. Gaucher and C. Tournassat from BRGM, Orléans.

In all three models it was assumed that, with the exception of certain fixed constituents (Cl^- , SO_4^{2-} , Br^- , or pCO_2), the porewater composition is controlled by saturation reactions with minerals and by cation exchange reactions with clay minerals. The following groups of input parameters were varied according to their estimated uncertainties:

- Concentrations (or activities or partial pressures) of fixed constituents
- Composition of the exchanger population on the clay minerals

These two groups represent the analytical constraints on the geochemical model. In addition, the following thermodynamic data were also varied:

- Equilibrium constants of saturation minerals
- Selectivity coefficients of cation exchange reactions

Results for *Mont Terri BWS-A3* are presented in Fig. 2.6. Input uncertainties were assumed to be distributed uniformly. The resulting parameter distributions are notably skewed (with the exception of Cl, whose distribution is practically not influenced by equilibria with minerals). For Mont Terri BRGM and for COX BRGM the largest influence on the output variability are due to uncertainties in the solubility constants of the minerals, followed by uncertainties in the selectivity coefficients of the exchanger, and by variations in the exchanger population. The uncertainties in the non-reactive constituents have only a minor influence.

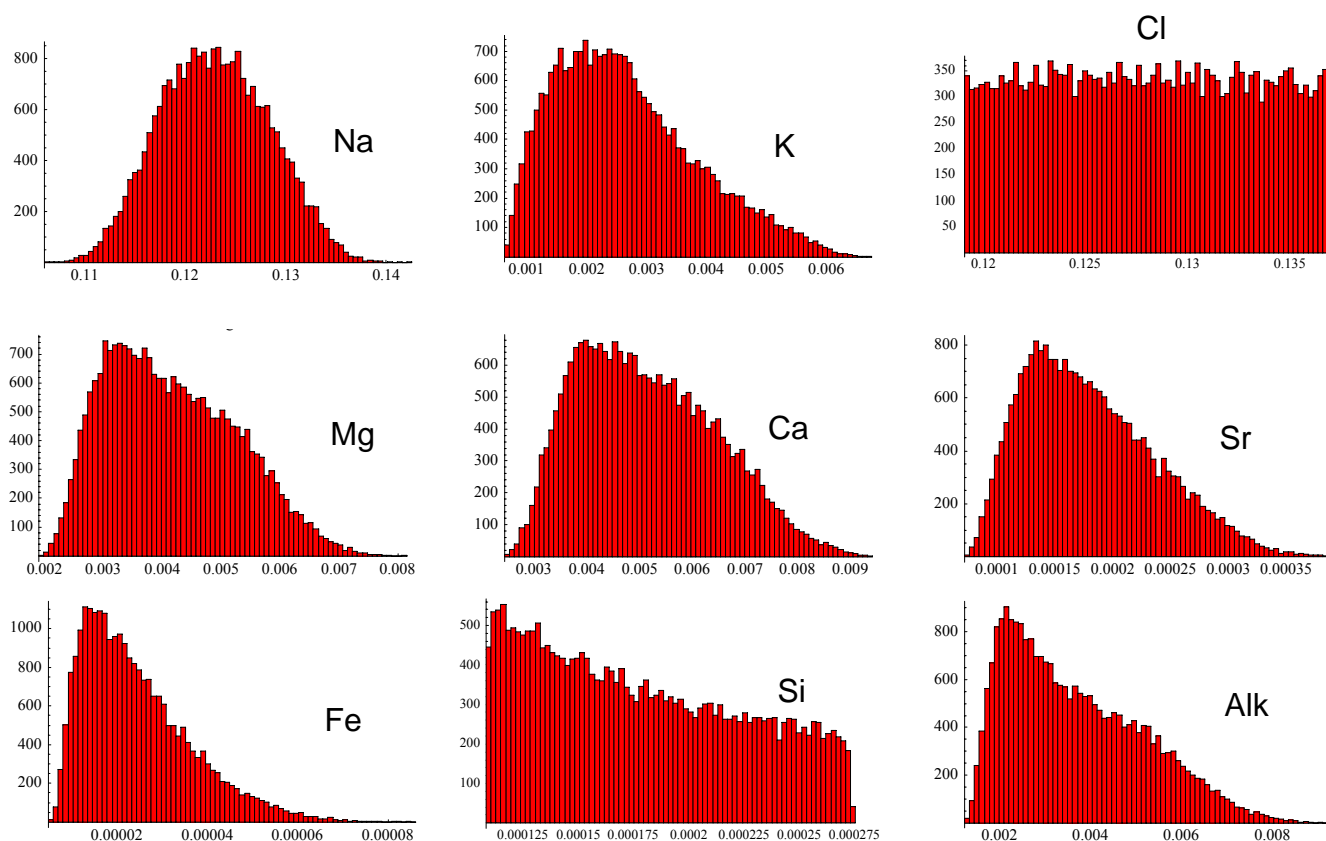


Fig. 2.6: Histograms showing uncertainties in output parameters of an Opalinus Clay porewater model for the Mont Terri Rock Laboratory. All concentrations are in $\text{mol} \cdot \text{kg}^{-1} \text{H}_2\text{O}$. The ordinate gives the number of runs resulting in the concentrations indicated on the abscissa.

This feasibility study has shown that the proposed Monte Carlo method is an efficient and computationally cheap way to assess the variability of output parameters due to uncertainties in the analytical input of a porewater model. In addition, the flexibility of the PHREEQC input file structure easily allowed the extension to uncertainties in thermodynamic data (e.g., cation selectivity coefficients and solubility constants).

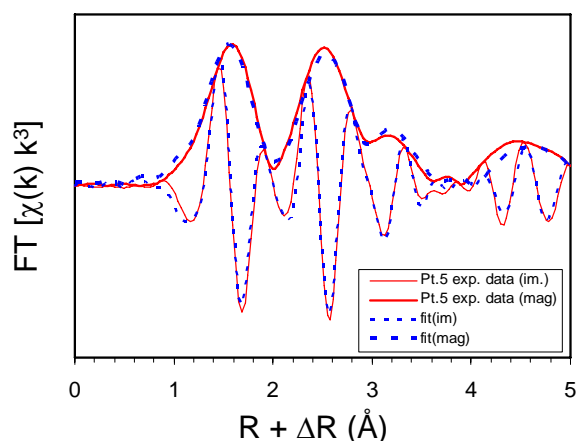
Further work will be devoted to a Monte Carlo-based sensitivity analysis aiming at the identification of those input parameters which have the largest influence on the output.

2.5 Glass corrosion, spectroscopy

Activities related to the long-term corrosion experiments running at PSI were focussed on the spectroscopic characterisation of the corrosion products of the MW glass. This glass is an inactive simulation of the vitrified glass produced at the Sellafield plants, U.K., after the reprocessing of Swiss high-level radioactive waste. Most of the work was devoted to the analysis and interpretation of the XAS/XRF data obtained during several measurement campaigns during the period 2005-2006. The evaluation basically confirmed the preliminary results. The majority of the analysed Ni spots indicated that Ni is associated with a major corrosion product, identified as a smectitic Mg-clay. The low Ni-Mg coordination number obtained in the EXAFS fits suggests that Ni is at least partly adsorbed on the clay surface. In addition, the XRF maps revealed the presence of tiny Ni-rich inclusions within the apparently uncorroded glass. Such inclusions (see Fig. 2.7) were identified beyond any doubt as trevorite particles (NiFe_2O_4), which may form as inhomogeneities during the fabrication of Ni-bearing glasses.

The presence of trevorite (also confirmed by micro-XRD analyses) implies that the initial distribution of Ni in the MW glass is heterogeneous. In a real vitrified waste, this situation would imply that the dissolution of ^{59}Ni from the waste cannot be described as the release from a single homogeneous source.

The last beamtime allocation (August 2007 at the microXAS beamline, SLS) was devoted to the mapping of redox-sensitive elements (Ce(III/IV), Fe(0/II/III), Cr(III/VI)) in the MW glass. The main goal was to detect changes in the oxidation state of cerium (introduced in the MW glass as an analogue of Pu(III/IV) during glass corrosion, and to correlate them with the fate of other redox sensitive elements (Fe, Cr) which could act as oxidants/reductants.



	σ^2	R	N	ΔE_0
Ni-O	0.005	2.03 ± 0.01	5.3 ± 0.4	2.8 ± 1.4
Ni-Ni	0.005	2.92 ± 0.01	3.9 ± 0.3	
Ni-Fe	0.007	3.47 ± 0.02	4.3 ± 0.7	S_0
Ni-Ni	0.011 ± 0.002	5.07 ± 0.03	12	0.85
Ni-Fe	0.021 ± 0.019	5.63 ± 0.14	8	
Ni-Fe	0.011 ± 0.004	6.07 ± 0.14	12	

Fig. 2.7: EXAFS analysis of a Ni-rich particle in the altered MW glass, showing an excellent fit to the mineral trevorite. Parameters in red were fixed in the fitting procedure. Those in blue were adjusted.

Fig. 2.8 shows an XRF map from which it appears that during glass corrosion Ce(IV) from the uncorroded parts of the glass (blue-violet regions) is reduced to Ce(III) and concentrated in the interstitial secondary phases (Mg-clays). This finding suggests that plutonium from the glass will re-precipitate in the insoluble Pu(III) form during the corrosion of vitrified high-level waste. The Fe and Cr data, which could act as potential reductants of Ce(IV), will be evaluated next year.

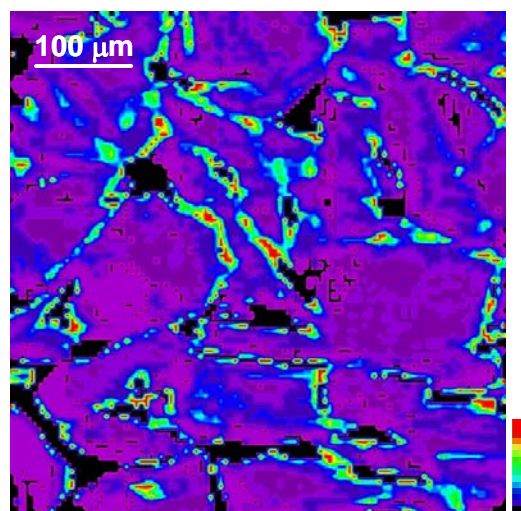


Fig. 2.8: Spatial distribution of Ce(III) (green to red) in the corroded MW glass.

2.6 Other Activities

2.6.1 Education activities

D. Kulik was invited to lecture on the GEM-Selektor Code Package, "History and perspectives in GEM chemical thermodynamic modelling", at the NANOCEM Workshop on "Chemical thermodynamic modelling in cement chemistry", held on 19-20 November 2007 at Empa, Dübendorf, Switzerland.

2.6.2 Teaching at university level

E. Curti gave a two hour lecture "Near field processes" at the University of Bern in the framework of a course "Disposal of radioactive waste" (Master in Erdwissenschaften) in the Summer Semester 2007.

On 1st April 2007, W. Hummel received the "Venia Legendi" for teaching "Nuclear Environmental Chemistry" as Privatdozent (PD) at the ETH Zurich, Department of Environmental Sciences, based on his Habilitation thesis "Radioactive Contaminants in the Subsurface: The Influence of Complexing Ligands on Trace Metal Speciation".

Teaching at ETH Zurich started in the Autumn Semester 2007 with the new course "Landfilling, nuclear repositories and contaminated sites" given by A. Johnson, W. Hummel and L.M. Plötze. These two hour per week lectures with student exercises and work on case studies is a "joint venture" of two different departments, i.e. it is eligible for credits for the Major in Biogeochemistry and Pollutant Dynamics (Master of Environmental Sciences) and compulsory for the Major in Ecological Systems Design and Waste Management (Master of Environmental Engineering). In the Autumn Semester 2007 the annual course was attended by 24 students.

Preparations have begun for lectures by W. Hummel on nuclear waste management within the scope of the planned course "Nuclear Energy Systems" (Prasser, Günther, Hirschberg, Hummel, Williams, Zuidema). This annual course will start in the Spring Semester of 2008 and it is foreseen as a compulsory course in the new "Master of Science in Nuclear Engineering".

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3 TRANSPORT MECHANISMS

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

3.1 Overview

Geosphere transport modelling is one of the key activities of the Laboratory for Waste Management and the activities in the group cover a wide range of scientific questions pertaining to performance assessment of geological repositories for radioactive waste.

Our main goal is to achieve an understanding of the most important transport mechanisms and processes and to quantify their effects on the mobility of migrating radionuclides. For this purpose, we use our own and commercial state-of-the-art models and computer codes 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 can be used for safety assessment purposes.

The main areas of investigations in the last twelve months were:

- analysis of laboratory experiments and modelling work related to the Mont Terri project;
- reactive transport modelling using an extended version of MCOTAC for analysing tracer diffusion through Opalinus Clay and bentonite;
- molecular modelling work investigating the mobility of selected radionuclides through the interlayer of montmorillonite and the details of the structure of xonotlite.

There are many in-house interactions, especially with the experimentalists in LES and the strong connections to the Mont Terri facility, universities and other research institutes worldwide have been maintained.

3.2 Analysing experiments on various scales

3.2.1 Modelling experiments at the laboratory scale

Analysing various small-scale laboratory diffusion experiments was again a major activity in the past year. For example, a single through-diffusion experiment using caesium as tracer was modelled extensively. The measured breakthrough data and also mass balance considerations revealed inconsistencies which appear to point to an unknown sink for the tracer in the Mont Terri Opalinus Clay sample

investigated. Sorption data measured on dispersed and on compacted clay samples were not able to describe the up-take adequately in the diffusion experiment. Neither by including a second type of transport porosity in the model, nor by including sorption kinetics, was it possible to improve the fit to the data. However, although the consideration of sorption competition and the co-transport of other cations released by the sorption of caesium did provide a better representation of the measurements, they could not resolve the problem of the observed early tracer breakthrough and the apparent reduced sorption capacity of caesium. These open questions regarding a chemically simple tracer such as caesium will certainly require further efforts next year.

An important question is whether sorption data measured on dispersed systems in batch type experiments can be applied in diffusion systems using highly compacted clay samples. In order to try to answer such a question, the first specially designed sorption experiments were carried out in the sub-programme "Clay Systems". Small, highly compacted montmorillonite samples, confined in a stainless steel sample holder, were exposed to a surrounding caesium tracers solution via a series of concentric holes for several months. (Further details can be found in section 4 "Clay Systems".) COMSOL Multiphysics was used to model the measured decrease in caesium concentration, Fig. 3.1. The analyses clearly showed that a simplified 1D and 2D modelling approach was not appropriate and only a full 3D calculation could adequately describe the measurements. Furthermore, the analysis confirmed the hypothesis that caesium sorption is consistent with the experimental and modelling results deduced from the dispersed system.

A literature survey concerning diffusion/sorption data of cations in clays (montmorillonite, bentonite, Opalinus Clay, Callovo Oxfordian Clay) was further extended. It appears that the surface mobility of sorbed cations is rather a property of the type of cation and sorption mechanism, and does not - or only weakly - depend on system conditions such as ionic strength, bulk density or mineralogy. A report describing this work is in preparation.

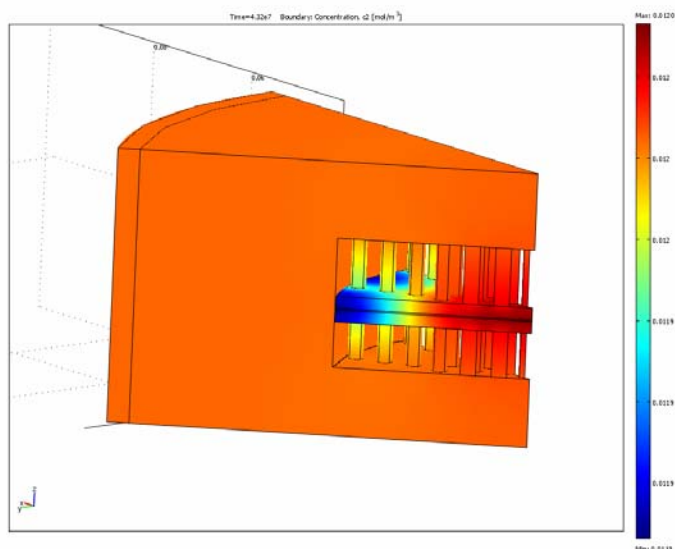


Fig. 3.1: Caesium distribution after 500 days exposure time. The colour bar designates the caesium concentrations in $\text{mol}\cdot\text{m}^{-3}$.

Due to symmetry considerations it was only necessary to model a 45 degree section of the diffusion/sorption system. The thin middle layer represents the montmorillonite layer (thickness ~ 0.2 mm) bounded above and below by porous steel filters (thickness ~ 1.58 mm); the dissolved tracer reaches the filters and the clay diffusively through a series of vertical holes drilled through stainless steel plates. The void volume in the figure represents the liquid-filled beaker.

As can be seen, the inhomogeneous tracer distribution in the filters and the montmorillonite sample points to an inadequate arrangement of the drilled holes (see blue areas in the figure where the caesium concentration are still far from equilibrium). The equipment is currently being improved for new experiments.

The water saturation state of a clay sample affects its hydraulic and mechanical properties. Neutron imaging can provide valuable information concerning the water distribution within a sample on the millimetre to micrometre scale. The work on this topic was performed in close co-operation with E. Lehmann and P. Vontobel from the Laboratory for Neutron Scattering, PSI. First results qualitatively show how a sample in an unsaturated atmosphere dries out from its surface. Additional experimental and theoretical work are required to make such measurements quantitative. These investigations will continue into next year.

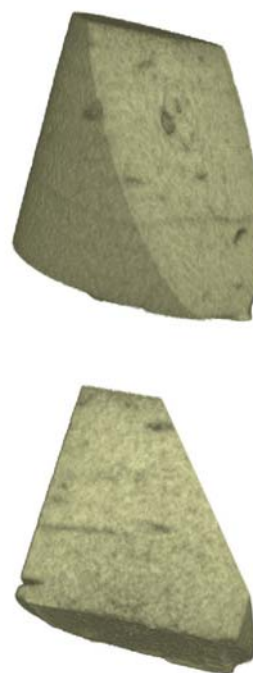


Fig. 3.2: Neutron tomography of a wet cylindrical Mont Terri Opalinus Clay sample with a diameter of 2.5 cm. The bright areas have a higher moisture content than the dark regions, indicating heterogeneities of the clay sample on the (sub-)millimetre scale.

3.2.2 Modelling work related to the Mont Terri project

The DR experiment at the Mont Terri Rock Laboratory was started in April 2006. In February 2007, Eu was added as an additional tracer. In order to design the sampling strategy, various scoping simulations were performed. A modified version of the code FLOTRAN was used because in a previous version there were problems with anisotropic diffusion in radial co-ordinates. We checked the new results with our own semi-analytical tool (radDiff), and found excellent agreement between the numerical results. We then performed a code comparison between FLOTRAN, CRUNCH (J. Soler, CSIC Barcelona), r3t (A. Rübél, GRS Braunschweig) and CORE2D (J. Samper und Q. Yang, UDC La Coruña) for a well-defined set of input parameters (HDO, Na, Sr, Cs). The agreement between FLOTRAN, CRUNCH, and CORE2D was good for the non- and weakly-sorbing tracers. The simulations with CORE2D for Cs and with r3t deviate from the rest; the underlying reasons for this are currently being investigated. The concentrations of the tracers measured in the borehole have up until now only decreased slightly, as intended, but the data show a considerable scatter. The scatter is so great that diffusion parameters cannot as yet be estimated reliably.

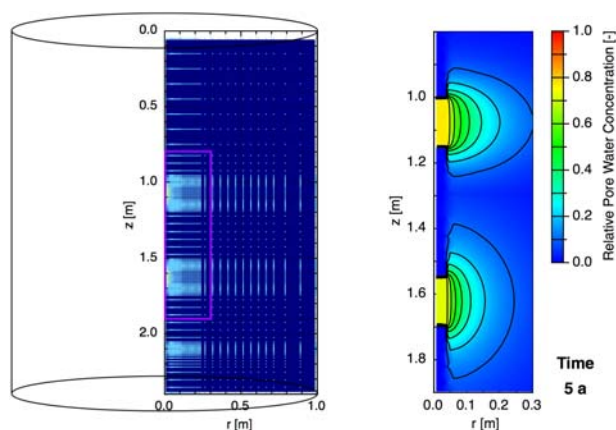


Fig. 3.3: The left sub-figure shows one of the grids used for the simulations of the DR field experiment with FLOTRAN. The size of the grid elements range from 0.001 m to 0.1 m. The purple line denotes the region shown in the right sub-figure including the two solute injection intervals.

In the right sub-figure normalised HDO concentrations calculated after five years are shown as indicated by the colour bar. The upper concentration distribution is based on an anisotropy ratio for the pore diffusion coefficients D_{rr}/D_{zz} of 4/1 and the lower concentration profile on a ratio of 4/4 (the r direction is parallel, the z direction perpendicular to the clay bedding).

In September 2006 the kick-off meeting for the Geochemical Data (GD) project took place. The details of the tasks have been defined in several meetings, and we contributed to a draft of a status report on the ongoing and past pore water and transport modelling.

Within the NEA-Claytrac project, additional modelling was performed for the natural tracer profiles at Benken, Mont Terri and some other locations. The simulations, as well as some generic considerations about tracer transport, notably $\delta^{37}\text{Cl}$, were documented in the manuscript.

The modelling results regarding the evolution of the stable water isotopes at Benken were finally published.

3.3 Reactive transport modelling

The modelling of a Cs diffusion experiment through an Opalinus Clay sample has been performed including the BRADBURY & BAEYENS (2000) 3-site cation exchange sorption model developed for illite which has been incorporated into MCOTAC. The results were compared to Cs diffusion modelling using a measured sorption isotherm. In order to obtain a reasonable fit to the experimental data the overall sorption of Cs had to be reduced. What this effectively meant was a reduction in the sorption sites in the Cs

sorption model. However, the necessary reduction in sorption site capacities in both cases was not the same. In the case of reactive transport calculations the potassium ion concentration in the clay porewater increased through the displacement of K by Cs through cation exchange reactions and this in turn influenced the sorption of Cs. Such an effect is not captured when a non-linear sorption isotherm is used (see Fig. 3.4). Hence, there is an intrinsic difference in modelling Cs diffusion using a measured sorption isotherm and a sorption model in a reactive transport code.

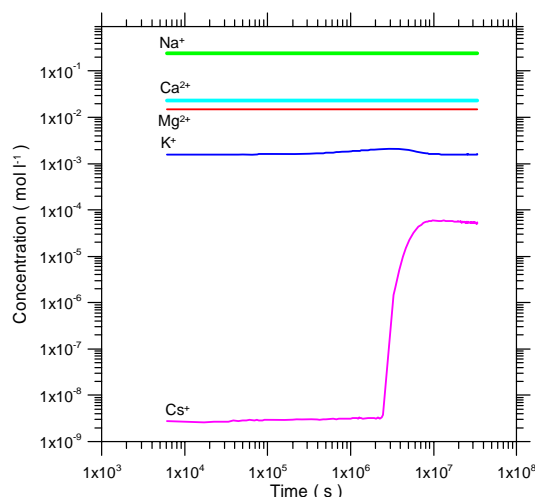


Fig. 3.4: The temporal evolution of various cation concentrations in solution during Cs diffusion through a compacted Mont Terri Opalinus Clay sample is shown. The concentrations of magnesium, calcium and sodium remain more or less constant in the time interval. Because K is displaced through cation exchange by Cs, potassium and caesium are competitive. Hence, any change in the K concentration in the porewater will also influence the uptake of Cs.

The modelling of Ni diffusion through bentonite taking into account competitive sorption reactions from other dissolved transition metals in the system has begun. The concentrations of Fe(II) and Mn(II) in the bentonite porewater have been measured in careful laboratory experiments. (Fe(II) concentrations are determined by the solubility limit of the mineral siderite contained in the bentonite). We have as yet not carried out any Fe(II) sorption tests, so the sorption parameters needed for Fe(II) in the 2SPNE SC/CE model of BRADBURY & BAEYENS (1997) were deduced using the Linear Free Energy Relationship (LFER) of BRADBURY & BAEYENS (2005). Ni diffusion profiles in compacted bentonite calculated using MCOTAC containing the 2SPNE SC/CE and including competition with Fe(II) and Mn(II) were compared to those in which simple K_d values from Nagra's safety report (NAGRA, 2002, Appendix B-16) were used.

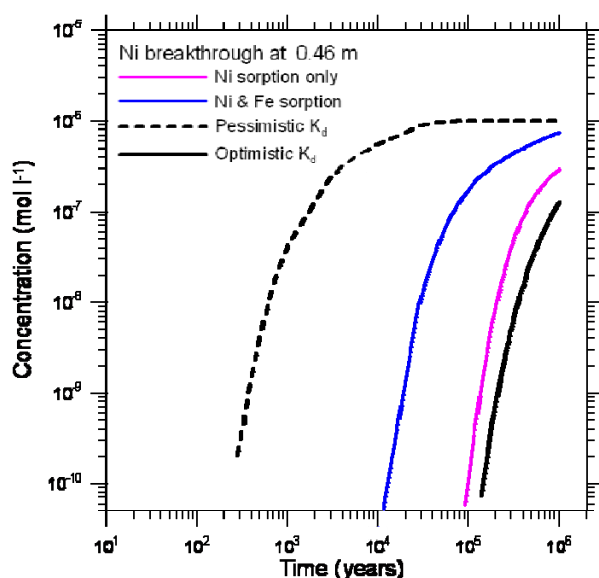


Fig. 3.5: Calculated Ni concentrations in the bentonite buffer 46 cm away from the canister surface.

The sorption of Ni is described in terms of the mechanistic sorption model of Bradbury and Baeyens. A second calculation accounts for the effects of sorption competition between Ni and Fe. For comparison, results from calculations based on the simple K_d approach using bounding pessimistic and optimistic K_d values for nickel (NAGRA, 2002) are also shown.

In order to reduce the long computing times in the foreseen future applications of MCOTAC, it is considered essential to parallelise the code. Unfortunately, no funding for this purpose could be obtained either from Nagra, nor from NES nor from PSI-FoKo. All applications for a postdoc position were rejected. A bilateral agreement with the PSI computing division has been made to get some support for this task. Since parallelisation of MCOTAC does not have the highest priority for the computing division, this procedure will need considerably more time.

A benchmarking co-operation was started with HSK with special emphasis on coupled reactive transport processes – a topic which is becoming increasingly important to HSK. A set of test cases with increasing complexity was discussed and finally agreed on. The tests will be performed applying the different codes available to LES and HSK e.g. MCOTAC, ROCKFLOW, TOUGH2, COMSOL etc. First results will be available by the end of the year.

The benchmarking activities with CEA-Cadarache are still ongoing.

Recent calculations by CEA using the CRUNCH, HYTEC and ALLIANCES codes, where high-pH water induced mineral reaction fronts, showed

different front developments, porosity distributions and flow field changes for the different codes. A comparison with results from MCOTAC and ROCKFLOW is planned.

3.3.1 Coupling of GEMS with ROCKFLOW/GEOSYS

In June 2007 a joint PhD project between the Department of Environmental Informatics at the Helmholtz Centre for Environmental Research – UFZ Halle-Leipzig, Germany (Prof. Kolditz) and LES started. It is the first joint project within the new general co-operation agreement between the Department of Environmental Informatics and LES. (A PhD student, Haibing Shao, is fully funded by a personal scholarship from the German Ministry of Education and Research.)

A main goal of the joint project is to develop a reactive transport model/code by coupling the UFZ THM-code “ROCKFLOW/GEOSYS” with LES’s GEMIPM2K code. Its computer performance, the free availability of the source codes and the possibility for extensive benchmarking with other codes such as MCOTAC etc. make it a valuable tool for future work. Presently, the new code is being modified so that it can run on high performance computers such as PSI’s Merlin3 cluster or on HORIZON (Cray XT3) in Manno for future complex 2D- and 3D studies relevant in radioactive waste management, geothermal energy or CO₂-sequestration. The first benchmarking results based on 1D reactive solute transport with dissolution of calcite and precipitation of dolomite show good agreement with the previous results from MCOTAC (PFINGSTEN et al., 2005; XIE et al., 2006).

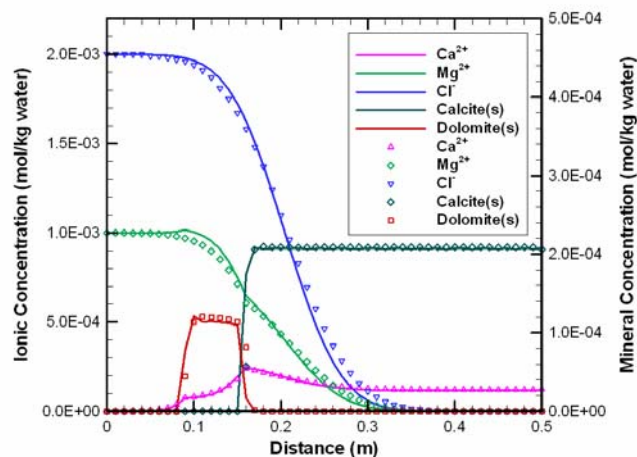


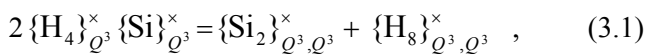
Fig. 3.6: Spatial concentration distributions for selected ions (left axis), and those for some minerals (right axis) in the mobile phase in the column after an elapsed time of 2.43 days as indicated in the legend. The solid lines represent results from the GEOSYS/ROCKFLOW-GEMS code and symbols represent those from MCOTAC-GEMS.

3.4 Molecular modelling

3.4.1 Structure of defects in tetrahedral double chain of xonotlite

Amongst the various calcium silicate hydrates (C-S-H), xonotlite $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ is formed as a product of the hardening of Portland cement. The basic structural unit of xonotlite is a Ca-polyhedra layer in which there are three different Ca sites. Two of them are seven-coordinated by oxygen while the third is a distorted octahedron. The silicate tetrahedra consist of a double chain with $2/m$ symmetry, and are formed by the condensation of two wollastonite chains (Fig. 3.7 A). The ideal xonotlite structure should contain only Q^2 and Q^3 types of the Si tetrahedral sites, where $Q^2/Q^3=2$ (in the Q^n notation “ n ” represents the number of bridging oxygen sites per tetrahedron Q) and only one type of OH group attached to the Ca layer similar to the portlandite structure. High resolution MAS NMR ^{29}Si and ^1H spectra of xonotlite (NOMA et al., 1998; HANSEN et al., 2003) revealed a minor presence of the Q^1 tetrahedra. The presence of the Q^1 tetrahedra is direct evidence for defects in the tetrahedral double chain of xonotlite. Such defects facilitate incorporation and diffusion of radionuclides in the mineral structure. A combined experimental/ theoretical approach has been used to investigate the structure and stability of the silicate tetrahedral double chain in xonotlite. The M2a2bc polytype of xonotlite was found to be dominant in the synthetic samples. This polytype was used in the ab-initio calculations based on density functional theory. The defects in the Q^3 sites were found to be energetically favourable compared to the Q^2 tetrahedra. Moreover, the paired substitutions (Fig. 3.7 B/C) in the silicate double chain at neighbouring Q^3 sites are more stable than the isolated Q^3 defects.

The relative abundance of isolated $\{\text{H}_4\}_{Q^3}^\times$ and coupled $\{\text{H}_8\}_{Q^3, Q^3}^\times$ defects was calculated from the reaction:



$$\frac{[\{\text{Si}_2\}_{Q^3, Q^3}^\times][\{\text{H}_8\}_{Q^3, Q^3}^\times]}{[\{\text{H}_4\}_{Q^3}^\times \{\text{Si}\}_{Q^3}^\times]^2} = \exp\left[-\frac{\Delta E}{RT}\right], \quad (3.2)$$

where $\{\text{Si}_2\}_{Q^3, Q^3}^\times$ is the concentration of undisturbed Q^3 pairs, $\{\text{H}_8\}_{Q^3, Q^3}^\times$ is the coupled defect in neighbouring Q^3 sites and $\{\text{H}_4\}_{Q^3}^\times \{\text{Si}\}_{Q^3}^\times$ is the Q^3 pair with a single substitution.

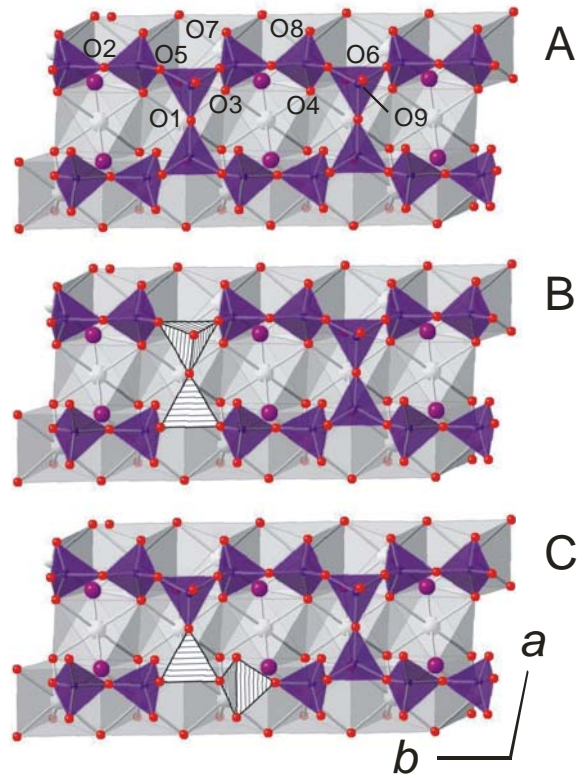


Fig. 3.7: Fragment of the ideal xonotlite structure (A). Gray octahedral polyhedra enclose Ca atoms. Silicate tetrahedra are black. The oxygen atoms are shown as small black spheres. The oxygen sites of O10H groups are shown as large black spheres. Possible tetrahedral defects in the silica double chain of xonotlite are shown as white hatched polyhedra: coupled Q^3Q^3 (B) and Q^2Q^3 (C) defects.

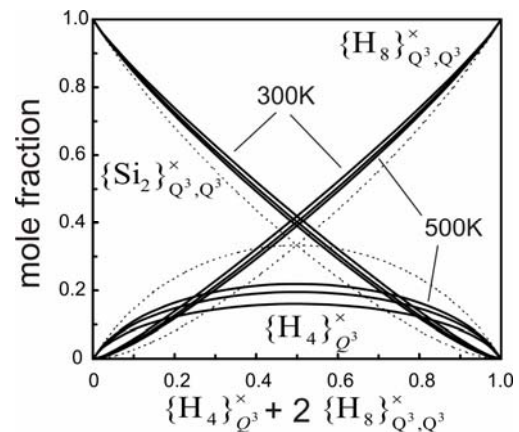


Fig. 3.8: The equilibrium distribution of doubly substituted Q^3 sites $\{\text{H}_8\}_{Q^3, Q^3}^\times$, isolated defects $\{\text{H}_4\}_{Q^3}^\times$ and undisturbed tetrahedral pairs $\{\text{Si}_2\}_{Q^3, Q^3}^\times$ as function of the total concentration of Q^3 substitutions for 300, 400 and 500 K (solid lines). The dotted line shows the ideal solution behaviour for $\Delta E = 0$ in equation Eq. 3.2.

The equilibrium distribution of coupled and isolated defects calculated with Eq. 3.1 is shown in Fig. 3.8 as a function of the total fraction of Q^3 substitutions. The diagram clearly illustrates that the double defect substitutions becomes more abundant compared to isolated Q^3 ones due to the difference in the formation energy. Similar to the xonotlite, 11.3 Å tobermorite – the crystalline phase used as the basic structural model for amorphous C-S-H phases – also contains bridging Q^3 and “paired” Q^2 sites. Based on the crystal-chemical similarities with xonotlite, we would suggest that similar defects are formed in C-S-H phases.

3.4.2 Diffusion of Cs and Na in the interlayer montmorillonite

We have investigated the state and dynamics of water and cations in pure and mixed Na-Cs-montmorillonite as a function of the interlayer water content using Monte Carlo and classical molecular dynamics methods. The study showed that the swelling behaviour of hetero-ionic Na-Cs-montmorillonite is comparable to that of a homo-ionic Na- or Cs-montmorillonite.

In addition, we found that at a low hydration levels the values for the diffusion coefficient of Cs^+ are lower than those for Na^+ , whereas at high hydration levels Cs^+ diffuses faster than Na^+ . For outer clay surfaces covered by several water layers, Na^+ ions preferentially form outer-sphere-complexes. The solute mobility perpendicular to the clay surface is

limited, and the diffusion is equivalent to 2D-solute diffusion in bulk water. In contrast to this, Cs^+ ions preferentially form inner-sphere-complexes at all hydration levels, and the value for the 2D diffusion coefficient is lower than in bulk water. The analysis of the data for the relative diffusion coefficients (the ratio between the diffusion coefficient of an ion in the interlayer and that in bulk water) revealed that water and Na^+ are less retarded than Cs^+ for all hydration states.

It remains an open question as to why experimentally determined values for the relative diffusion coefficients of Cs^+ in the interlayer of clays are about 20 times smaller than those obtained by classical molecular dynamics studies.

3.4.3 The evaluation of scattering functions for comparison purposes with results from neutron scattering experiments (QENS)

The exceptionally large incoherent scattering cross section of hydrogen atoms for neutrons makes neutron scattering an attractive experimental technique for investigating the dynamics of water in water-saturated clays. Typical energies used in such experiments correspond to a time resolution between ten and several hundred picoseconds. However, data for the diffusion coefficient of water can only be obtained indirectly by fitting a modelled spectrum with several freely adjustable parameters to experimental data.

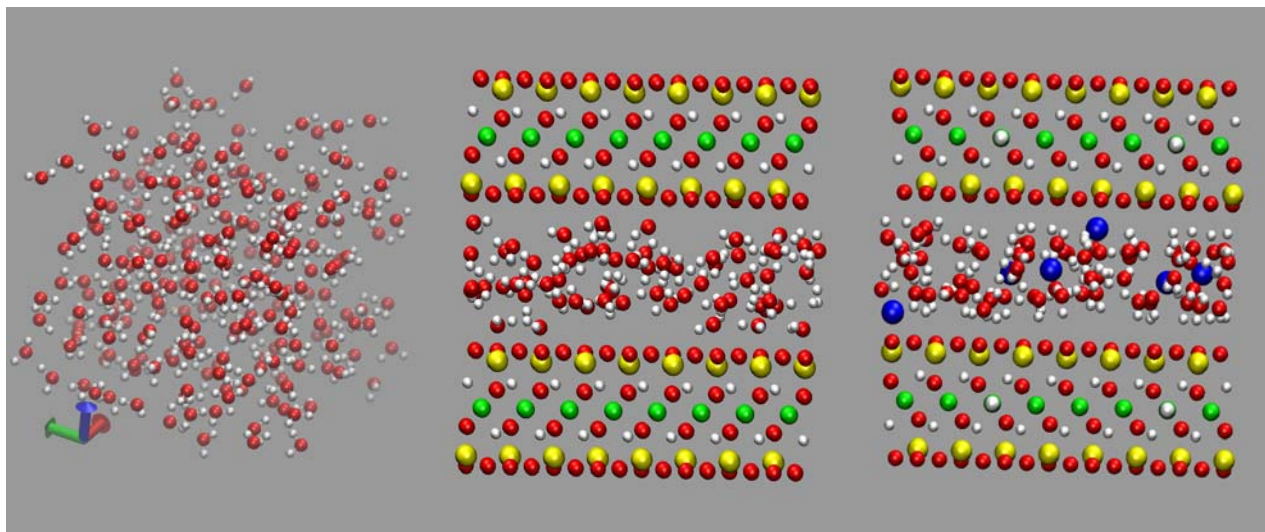


Fig. 3.9: Illustration of molecular dynamics calculations whose values for the diffusion coefficient were subsequently compared with QENS data. (Oxygen atoms are marked in red, hydrogen atoms in white, silicon atoms are denoted by yellow balls and aluminium atoms are green.)

Left sub-picture: The distribution of 256 TIP4P water molecules in a rectangular box.

Middle sub-figure: Water distribution in the interlayer of pyrophyllite as a model for water between uncharged surfaces (note: in reality there is no interlayer water in pyrophyllite).

Right sub-figure: Water molecules and Na-cations (blue) in the interlayer of montmorillonite. The large white spheres in the middle of the clay layers denote the isomorphous substitution of aluminium atoms by magnesium.

With classical molecular dynamics methods, the movement of water molecules in the interlayer of clays can be simulated for time scales similar to the experimental ones. The diffusion coefficient of each interlayer species can be directly calculated from the Einstein relation and used as a reference value. Additionally, it is possible to calculate the dynamic structure factor, the quantity measured in most neutron scattering experiments. In this study we investigated the diffusion of water on the molecular scale for three different systems: a) in bulk water, b) in the water between the uncharged interlayer surfaces in pyrophyllite and finally c) in the water between the negatively charged interlayer surfaces of montmorillonite (Fig. 3.9). The diffusion results were then compared with data from neutron scattering experiments. The main result was that the value for the diffusion coefficient was strongly dependent on the averaging procedure regarding time and space, especially for montmorillonite. In addition, in this latter case, the evaluation of the neutron scattering spectra required a much more complex procedure in order to account adequately for the diffusion dynamics in 2D. The results of the study will be published in 2008.

3.5 Varia

In order to acquire and increase the expertise in THMC-modelling, a NES-Seed-Action proposal was submitted. Since the necessary work would have been done by additional specialised manpower, and financed by Seed-Action money, such a task would have increased the manpower in the transport modelling group for the next two years. Unfortunately, we were not successful in the competition with the three other proposals.

In Autumn of 2007 Ralph Mettier successfully finished his PhD at the University of Tübingen (Germany) with "Magna cum laude". During the last three and a half years he had been involved in the evaluation of existing tracer test results from the Grimsel underground laboratory where a cocktail of radioactive tracers was injected in a bore hole. In his theoretical work he used - for the first time - several numerical models which incorporate a complex fracture network geometry based on documented field data (i.e. images of a bore core cut into thin slices), geostatistically generated apertures and the effects of matrix diffusion. His approach provided the basis for a new insight into the combined role of fracture heterogeneity and matrix diffusion (METTIER R., 2006).

In November 2007 Fátima González finished her PhD thesis. In her last year, the main emphasis of her work was on the discussion and interpretation of the

macroscopic and microscopic (neutron scattering) diffusion results at different temperatures (T. Gimmi and G. Kosakowski provided the necessary support). A manuscript is in preparation describing and analysing the differences in the behaviour of water in clays such as montmorillonite, illite, kaolinite and pyrophyllite. Also, in the Autumn of 2007 Georg Kosakowski received the 'Venia Legendi' for "Umweltgeologie und Hydroinformatik" at the University of Tübingen, thus strengthening our connections to universities abroad.

As part of the Master Course in Environmental and Resource Geochemistry at the University of Bern T. Gimmi prepared and delivered two new lecture courses with a subsequent examination of the students.

3.6 References

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4 CLAY SYSTEMS

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

4.1 Introduction

Within the framework of the "Sectoral Plan" (Sachplan Geologische Tiefenlagerung) important contributions were performed for planned performance assessments. These contributions consisted of the development of a number of generic sorption databases for argillaceous, crystalline and calcareous systems.

The clay minerals montmorillonite and illite are important minerals with respect to sorption on bentonite and Opalinus Clay, respectively. The main aim of the investigations into these major clay minerals is to elucidate their sorption properties and mechanisms, and develop sorption models which can quantitatively describe the uptake of radionuclides over a wide range of conditions (pH, Eh, water chemistry, radionuclide concentration). By understanding the sorption processes of the most important mineral phases, and developing models to describe them, quantitative predictions of the uptake of radionuclides in complex mineral/groundwater systems can be achieved. This so-called "bottom up approach" is a long-term activity within the clay systems sub-programme. At present these studies are entirely embedded in the EU 6th framework programme (i) Integrated Projects NF-PRO (Near Field Processes) and FUNMIG (Fundamental Processes of Radionuclide Migration) and (ii) Euratom Intra-European Fellowship project INCA (Influence of carbonate on actinides sorption on clay minerals).

The work in the two 6th EU Integrated Projects NF-PRO and FUNMIG was focussed on isotherm measurements of Ni(II), U(VI) and Eu(III) on MX-80 bentonite and Opalinus Clay in complex water chemistries.

Within the framework of the INCA project the influence of carbonate on the sorption of Eu(III) on clay minerals was investigated with macroscopic and microscopic methods such as Time Resolved Laser Fluorescence Spectroscopy (TRLFS).

Surface analysis (Extended X-ray Absorption Fine Structure Spectroscopy, EXAFS) activities within the sub-programme were focussed on Am(III) sorption studies on montmorillonite. An important finding was that the structural data obtained from EXAFS showed unambiguously that Am(III) forms inner-sphere complexes at the surface.

Two ACTINET projects (i) Np(V) sorption on montmorillonite and (ii) Eu(III)/Am(III) sorption on

clay minerals are on-going. TRLFS and EXAFS measurements were carried out at Forschungszentrum Karlsruhe (FZK) (at the facilities in INE (Institut für Nukleare Entsorgungstechnik) and ANKA (Angstroemquelle Karlsruhe respectively) and NpO_2^+ was studied at the Rossendorf Beamline (ROBL) at the ESRF (European Synchrotron Radiation Facilities, Grenoble).

The technician M. Binkert left the Clay Systems sub-programme in April 2007 and was replaced by V. Kalbermatter in August 2007.

4.2 Performance assessment

The sorption of radionuclides on materials in the near field (bentonite) and the far field (host rock formations) of a high-level waste repository is one of the main pillars upon which the safety case for a deep geological repository is founded (NAGRA, 2002). One of the primary tasks of the Clay Systems sub-programme is to ensure that near field and far field sorption data bases (SDBs) for performance assessment are "state of the art". From 2007 onwards NAGRA is planning to perform several safety analyses within the framework of the Sectoral Plan. Updates of existing SDBs, or the provision of new SDBs, will be required. This is clearly the task of the Clay Systems sub-programme.

In the current year a document was prepared in which a generic view on the influence of mineralogy and water chemistry on sorption was presented. Further, a number of generic SDBs for argillaceous, crystalline and calcareous systems were developed. These SDBs have been compiled for generic water compositions reflecting the range of conditions of pH and ionic strength found in the groundwaters in Switzerland. Sorption data bases for both reducing and oxidising conditions were developed.

4.3 Sorption on compacted montmorillonite

One of the long term goals of the sub-programme is to answer the key question whether mechanistic sorption models, based on measurements in dispersed systems, are directly applicable to compacted systems. Cs sorption experiments on highly compacted montmorillonite in specially designed cells have been carried out. The aim of the investigations was to compare sorption values measured in dispersed batch experiments (and predictions from sorption models) with those measured in compacted systems under the same well-defined chemical conditions. In the experiments

carried out, it is important to realise that the goal was not to deduce a sorption value from a diffusion experiment, but rather to carry out a sorption test on compacted montmorillonite. In order to keep the time scales of the experiments within reasonable bounds, the montmorillonite was compacted to a thickness of $2 \cdot 10^{-4}$ m at a dry density of $1500 \text{ kg} \cdot \text{m}^{-3}$. For thicknesses less than this the quality of the compacted montmorillonite deteriorated.

SWy-1 montmorillonite was purified and conditioned to the Na-form in 0.01 M NaClO_4 . The Cs sorption isotherm measured at low solid to liquid ratios ($\sim 1 \text{ g} \cdot \text{L}^{-1}$) in 0.01 M NaClO_4 is shown in Fig. 4.1. The solid line is the calculated curve modelled according to a cation exchange mechanism with a Cs-Na selectivity coefficient of 15.1 and a cation exchange capacity of $8.7 \cdot 10^{-1} \text{ equiv. kg}^{-1}$ for Na-SWy-1.

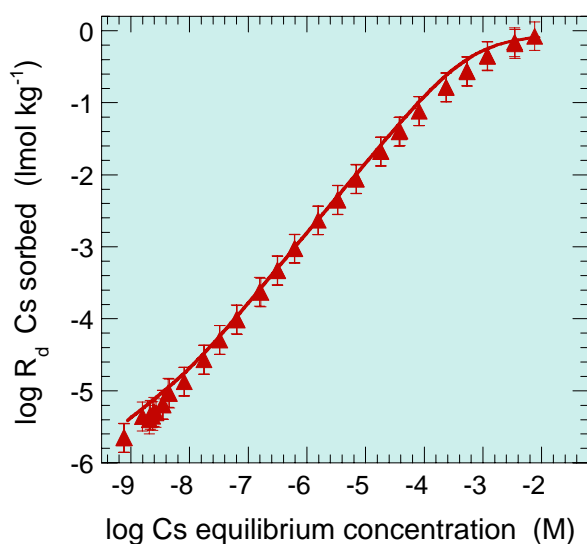


Fig. 4.1: Cs batch sorption isotherm on dispersed Na-SWy-1 in 0.01 M NaClO_4 at pH 7.

Freeze-dried Na-SWy-1 with a water content of $\sim 15 \text{ wt. } \%$ was used to make the compacted clay. The thin compacted montmorillonite sample (diameter $\sim 5 \cdot 10^{-2}$ m, $2 \cdot 10^{-4}$ m in thickness, dry weight $6.1 \cdot 10^{-4}$ kg) was confined between two porous SS316L steel filter frits in a stainless steel cell in which the ^{134}Cs containing solution had access to both large area faces. Separate experiments with the cell and porous frits showed no measurable Cs uptake on these materials. The initial conditions chosen for the sorption on compacted montmorillonite were $C_{\text{initial}} = 4.2 \cdot 10^{-5} \text{ M Cs}$ and a solid to liquid ratio of $2 \cdot 10^{-3} \text{ kg} \cdot \text{L}^{-1}$. From the isotherm/modelling, the predicted logarithm of the equilibrium distribution ratio was $3.1 \text{ L} \cdot \text{kg}^{-1}$. The conditions for the compacted montmorillonite experiment were chosen so that sorption was taking place in a linear sorption region of the isotherm far away from saturation and that the

predicted decrease in solution activity at equilibrium was approximately a factor of 5, which was easily and unambiguously measurable. Aliquots were taken as a function of time.

In Fig. 4.2 the results of the sorption measurements on the compacted clay as function of time are shown. As can be seen, the Cs sorption increases as function of time over a period of approximately 150 days and then remains constant at the predicted value of $\log R_d = 3.1 \text{ L} \cdot \text{kg}^{-1}$. The clear conclusion drawn from this experiment is that Cs sorption on compacted clay (at a dry density of $1500 \text{ kg} \cdot \text{m}^{-3}$) is the same as the sorption measured in dispersed systems.

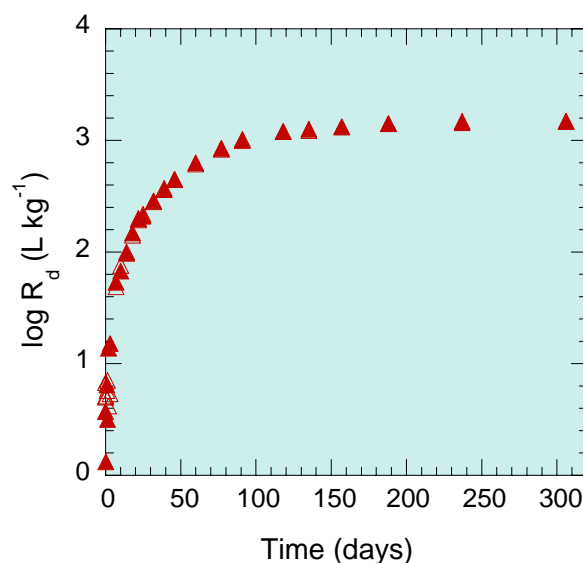


Fig. 4.2: Cs sorption measurements on compacted Na-SWy-1 in 0.01 M NaClO_4 at pH 7.

Similar experiments with Ni and Eu are ongoing. However, the initial results from these experiments are indicating that corrosion effects are playing a significant role. Contrary to Cs, the sorption of Ni and Eu on the iron corrosion products is important, and no definite conclusions can be drawn at the present time for these elements.

The results of these investigations were presented as an invited talk (M. Bradbury) at the International Conference "Clays in Natural and Engineered Barriers for Radioactive Waste Confinement", 2007 Lille.

4.4 Mechanistic sorption studies

Mechanistic sorption studies have been carried out predominantly within the framework of the EU Integrated Projects NF-PRO and FUNMIG and the Euratom Intra-European Fellowship project INCA, as discussed below.

4.4.1 NF-PRO

The Integrated Project NF-PRO started in January 2003 and finished at the end of 2007. The main objective of the work performed within this project was to investigate and quantify the influence of carbonate complexation on the uptake characteristics of Ni(II), Eu(III) and U(VI) on Na-montmorillonite (SWy-1) and bentonite. Carbonate is, together with hydroxide, one of the most important inorganic ligands for radionuclide complexation in natural groundwaters. The formation of strong carbonate complexes in the liquid phase can potentially lead to a decrease in metal ion sorption.

Sorption measurements of Ni(II), Eu(III) and U(VI) on Na-SWy-1 in the absence and presence of NaHCO_3 in the pH range ~ 7 to 9.5 have been made. The experimental data indicate that Ni(II) sorption onto montmorillonite is rather insensitive to the presence of inorganic carbon at levels up to ~ 0.02 M and pH values below 9, within the experimental uncertainties associated with the measurements. Only at very high inorganic carbon concentrations (0.1 M) was a more pronounced effect on sorption observable. On the other hand, a clear effect of the presence of inorganic carbon on Eu(III) sorption, and an even more pronounced effect on U(VI) sorption, on montmorillonite was measured. Model predictions using the two site protolysis non electrostatic surface complexation and cation exchange (2SPNE SC/CE) sorption model (BRADBURY & BAEYENS, 1997, 2006a) under the assumption that metal carbonate complexes do not sorb were carried out. The aqueous thermodynamic data were taken from HUMMEL et al. (2002) and NEA (2003).

In the case of Ni(II), the data and the model predictions agree within the uncertainty of the data. For Eu(III) and U(VI) the model predictions underestimated the measured data. This result could be an indication that (hydroxy)carbonate complexes could be taken up by the montmorillonite. On the other hand, such effects could, at least in part, be explained by the quality of the thermodynamic data *i.e.* carbonate complexation constants which are too strong. The wet chemistry investigations alone are not sufficient to resolve the question. Further investigations on the influence of inorganic carbonate using synchrotron radiation and pulsed laser-light spectroscopy methods are necessary. These measurements were taken up within the INCA project and are discussed below.

Finally, sorption isotherms for Ni(II), Eu(III) and U(VI) have been measured on MX-80 bentonite in the presence of a synthetic porewater composition. These measurements are of direct relevance to performance assessment studies.

4.4.2 FUNMIG

The objective in the FUNMIG programme was to investigate and quantify the influence of carbonate complexation on the uptake characteristics of Ni(II), U(VI) and Eu(III) on Na-illite and Opalinus Clay. Illite is one of the principal sorbing mineral phases in the Opalinus Clay which is being considered as a potential host formation for a high-level waste repository in Switzerland (NAGRA, 2002).

Sorption edge and isotherms for U(VI) on purified Na-illite (Illite du Puy) had already been measured and modelled previously using the 2SPNE SC/CE sorption model. This model, and the associated parameters, were subsequently used to predict the U(VI) isotherm data measured on Opalinus Clay samples under the assumptions that (i) illite is the main sorbing phase in the Opalinus Clay, and (ii) only the UO_2^{2+} and the hydrolysed species are sorbing.

A sorption isotherm at U(VI) equilibrium concentrations between $5 \cdot 10^{-9}$ and 10^{-6} M was determined in a synthetic porewater at pH 8 on an Opalinus Clay sample from Mont Terri. The results are shown in Fig. 4.3 as solid symbols.

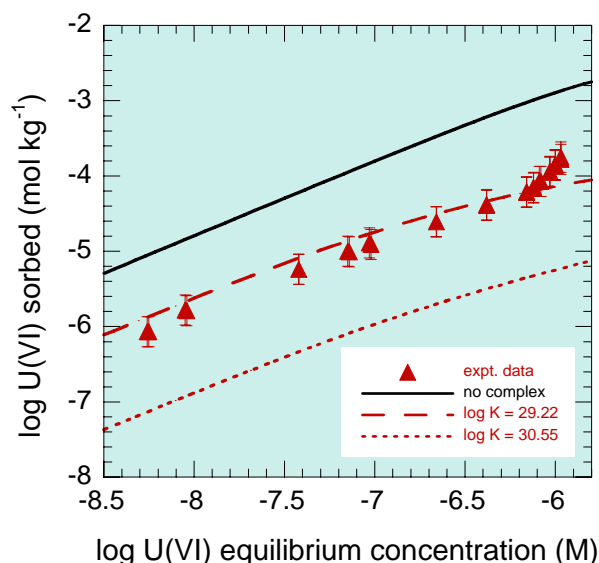
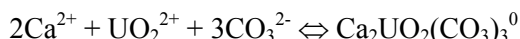


Fig. 4.3: Sorption isotherm of U(VI) on Opalinus Clay in a synthetic porewater (pH 8) measured under anoxic conditions (\blacktriangle). The curves are model calculations (see text for details).

In a first attempt to model this isotherm the same concept was used as in the case of illite *i.e.* U(VI) carbonate complexes were treated as being non-sorbing. The selected U(VI) NEA thermodynamic data (NEA, 2003) were used for these calculations. The results of this calculation are shown by the continuous curve in Fig. 4.3. As can be seen, the model over predict the sorption. Such a result is difficult to explain unless there is a missing aqueous

U(VI) complex which is non-sorbing and which is not contained in the selected NEA TDB data for U(VI).

BERNHARD et al. (2001) and GEIPEL et al. (1998) have studied the complex formation in the Ca(II)-U(VI)-CO₃²⁻-H₂O system. They present convincing evidence for the formation of an uncharged Ca₂UO₂(CO₃)_{3(aq.)} complex. Their studies were supported by time resolved laser fluorescence spectroscopic and EXAFS measurements. The equilibrium constant at zero ionic strength for the reaction:



was proposed to be $\log K^0 = (30.55 \pm 0.25)$. KALMYKOV & CHOPPIN (2000) have also studied the ionic strength dependence of the above reaction and used the SIT model to calculate an equilibrium constant of $\log K^0 = (29.22 \pm 0.25)$.

The influence of the presence of an uncharged Ca₂UO₂(CO₃)₃ aqueous complex on the calculations was tested using the range of $\log K^0$ values given above. In these model calculations the assumption was made that the Ca₂UO₂(CO₃)₃ complex did not sorb onto the Illite/Opalinus Clay. The results of these calculations are shown by the two sorption isotherms presented in Fig. 4.3 as broken and dotted red lines. The sorption isotherms calculated with the strongest complexation constant ($\log K^0 = 30.55$) leads to a significant underprediction of the experimental data, whereas the constant proposed by KALMYKOV & CHOPPIN (2000) fit the data well.

From the modelling evidence presented, it appears plausible that the Ca₂UO₂(CO₃)₃ complex exists in solution and is not taken up by illite in Opalinus Clay.

The results of these investigations will be published in the 3rd Annual Workshop Proceedings of FUNMIG.

4.4.3 Sorption of Eu(III) on Na-montmorillonite: Influence of carbonate complexation (INCA)

Sorption measurements for Eu(III) in the presence of various inorganic carbon concentrations have been measured for both illite and montmorillonite. Only the data for Na-montmorillonite are presented below. Table 4.1 summarizes the experimental conditions used in the Eu sorption edge measurements carried out in the presence of carbonate.

The uptake of Eu(III) at trace concentration as a function of pH on Na-montmorillonite in the absence and the presence of inorganic carbonate at a fixed pCO₂ (atmospheric conditions) and variable pCO₂ are shown as symbols in Fig. 4.4.

Table 4.1: Summary of experimental conditions of the Eu(III) sorption measurements on Na-montmorillonite and Na-illite in the presence of carbonate (TIC=total inorganic carbonate). Initial ¹⁵²Eu conc.: 2·10⁻⁹ M.

a) Fixed pCO ₂ , in equilibrium with the atmosphere 10 ^{-3.5} bar		
pH	TIC (mM)	Ionic Strength (M)
7.0	0.06	0.1
7.5	0.19	0.1
8.0	0.61	0.1
8.5	1.98	0.1
9.2	7.43	0.1
9.7	28.75	0.1
10.3	302.00	0.5 (not modelled)
b) Variable pCO ₂ (calculated)		
pH	TIC (mM)	pCO ₂ (bar)
7.4	20	10 ^{-1.4}
8.3	20	10 ^{-2.3}
9.3	20	10 ^{-3.4}

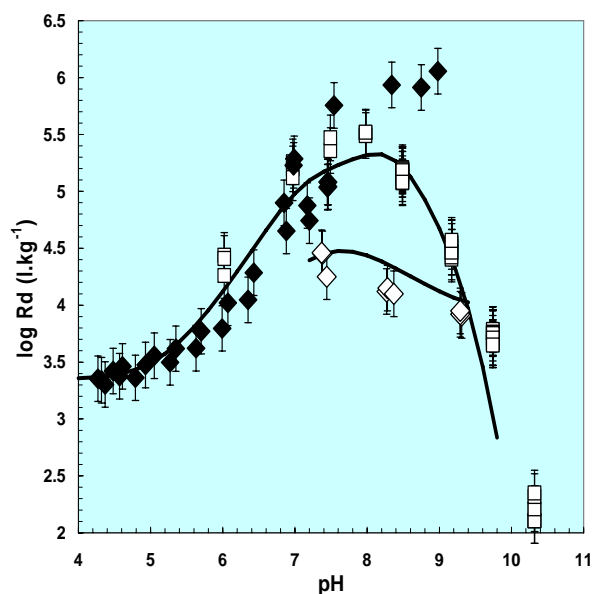


Fig. 4.4: Sorption edge for ¹⁵²Eu on Na-SWy-1 in 0.1 M NaClO₄ in the absence of carbonate (♦), at a fixed pCO₂=10^{-3.5} bar (□), Table 4.1a, and in the presence of 20 mM NaHCO₃ (◇). The continuous curves are calculated in the presence of carbonate using the 2SPNE SC/CE model with the parameters given in Table 4.2.

In the absence of inorganic carbonate the sorption of Eu increases as a function of pH and remains approximately constant above pH ~ 8 at a high value ($\log R_d = 6 \pm 0.2 \text{ L} \cdot \text{kg}^{-1}$). In both cases where carbonate is present there is a clear effect on Eu sorption. In the experiments at a constant pCO₂ of 10^{-3.5} bar (Fig. 4.4, Table 4.1), no influence of the presence of carbonate is observed up to pH ~ 8. The log R_d values are close to those measured in the carbonate-free system. However, at pH values greater than 8, a pronounced decrease in the Eu sorption is observed

with increasing pH and carbonate concentration (Table 4.1b and Fig. 4.4). The log R_d value decrease to $\sim 2.0 \pm 0.2 \text{ L} \cdot \text{kg}^{-1}$ at pH ~ 10.3 (Fig. 4.4). For levels of 20 mM, the effect on Eu sorption is already evident from pH 7.5 and higher. At pH 7.4 the log R_d is $\sim 4.5 \pm 0.2 \text{ L} \cdot \text{kg}^{-1}$, and decreases to $3.9 \pm 0.2 \text{ L} \cdot \text{kg}^{-1}$ at pH 9.3.

The sorption data were modelled using the 2SPNE SC/CE model (BRADBURY & BAEYENS, 1997, 2006a). The calculated aqueous speciation for Eu(III) under the investigated experimental conditions was used to guide the choice of the surface complexes. Both experimental data sets measured in the presence of inorganic carbon could be quantitatively modelled only by including two additional surface reactions forming $\equiv\text{S}^{\text{O}}\text{EuCO}_3^0$ and $\equiv\text{S}^{\text{O}}\text{EuOHCO}_3^-$ in the sorption model (Fig. 4.4). Table 4.2 summarizes the thermodynamic data used in the modelling procedure. The selected Am(III) data from the NEA compilation were used for Eu(III) since both elements are considered as excellent chemical analogues for one another (BRADBURY & BAEYENS, 2006b).

Table 4.2: Aqueous and major surface complexation reactions and constants for Eu(III) used in the sorption model calculations.

Aqueous complexation reactions: ^{*)}	Log K_0
$\text{Eu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{EuOH}^{2+} + \text{H}^+$	-7.2 ± 0.5
$\text{Eu}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_2^+ + 2\text{H}^+$	-15.1 ± 0.7
$\text{Eu}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_3^0 + 3\text{H}^+$	-26.2 ± 0.5
$\text{Eu}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{EuCO}_3^+$	8.0 ± 0.3
$\text{Eu}^{3+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Eu}(\text{CO}_3)_2^-$	12.9 ± 0.6
$\text{Eu}^{3+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{Eu}(\text{CO}_3)_3^{3-}$	15.0 ± 0.4
Surface complexation reactions:	Log K_{SC}
$\equiv\text{S}^{\text{O}}\text{OH} + \text{Eu}^{3+} \rightleftharpoons \equiv\text{S}^{\text{O}}\text{Eu}^{2+} + \text{H}^+$	1.6
$\equiv\text{S}^{\text{O}}\text{OH} + \text{Eu}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \equiv\text{S}^{\text{O}}\text{EuCO}_3^0 + \text{H}^+$	8.3
$\equiv\text{S}^{\text{O}}\text{OH} + \text{Eu}^{3+} + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \equiv\text{S}^{\text{O}}\text{EuOHCO}_3^- + 2\text{H}^+$	0.15
Cation exchange reactions:	K_{C}
$3 \text{ Na-clay} + \text{Eu}^{3+} \rightleftharpoons \text{Eu-clay} + 3 \text{ Na}^+$	29

^{*)} The aqueous hydrolysis and carbonate thermodynamic data were taken from the Am(III) NEA compilation (NEA, 2003).

In order to try to obtain a better molecular understanding of the structure of the main surface complexes formed on the clay minerals, and to check on the existence of the postulated surface complexes and thereby to gain a better understanding of the radionuclide uptake mechanisms, EXAFS measurements were performed (see section 4.5).

This work has been presented at the International Migration Conference in Munich, 2007.

4.5 Surface analysis (EXAFS) investigations

EXAFS measurements were carried out with Am(III) instead of Eu(III) in order to avoid the interference of the structural Fe (K edge at 7112 eV) with the Eu L_{III} edge at 6977 eV.

Am(III) loaded Na-SWy-1 samples, prepared both in the absence and presence of inorganic carbonate and with different Am(III) occupancies, were measured at the L_{III} edge of Am(III) (18510 eV) in fluorescence mode.

Fig. 4.5 shows the Fourier transform and EXAFS spectra of Am loaded Na-montmorillonite (~ 970 ppm) at pH 8 in the absence of carbonate.

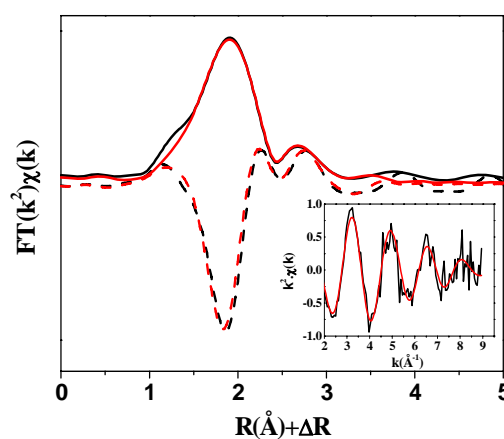


Fig. 4.5: Fourier transforms and k^3 -weighted EXAFS spectra of Am loaded Na-montmorillonite. Black line: experimental data, green line: modelled data, broken lines: imaginary part.

The EXAFS parameters obtained by fitting the spectra of this carbonate free sample are summarized in Table 4.3. The bond distances obtained are consistent with bond lengths from Am-O and Am-Si/Al backscattering pairs. The identification of Am-Al/Si distances is a clear indication that Am(III) forms inner sphere complexes at the SWy-1 surface.

Table 4.3: Structural information derived from the EXAFS analysis of Am(III) on Na-montmorillonite loaded in the absence of carbonate at pH 8.

Shell	CN	Distance R (Å)	σ^2 (Å ²)
Am-O	8.90 ± 1.7	2.47 ± 0.02	0.013 ± 0.003
Am-Si/Al	1.39 ± 0.3	3.13 ± 0.01	0.005 ± 0.001
Am-Si/Al	2.67 ± 0.53	3.74 ± 0.01	0.014 ± 0.004

For the samples prepared in the presence of carbonate, less good EXAFS spectra were obtained. The poor signal to noise ratio did not allow a reliable EXAFS data analysis of second shells to be performed. No oscillation or FT peak which could be attributed to an Am-C distance could be distinguished. This might be due to the weak backscatter amplitude of C ($z=6$) compared to Si ($z=14$). Thus, these preliminary spectroscopic measurements did not allow the formation of the ternary Am-carbonate/hydroxy-carbonate complexes at the montmorillonite surface to be verified. Better spectroscopic data are needed (better signal to noise ratio, higher k-range) in order to obtain reliable structural parameters for the actinide-carbonate-clay system. EXAFS measurements at low temperature (15 K) are planned in order to minimize the thermal disorder. Beamtime for these measurements at the INE beamline (ANKA, FZK) has recently been allocated for February 2008.

4.6 Np(V) investigations on clay

Within the framework of an ACTINET joint research project with the Johannes Gutenberg-University Mainz, Forschungszentrum Dresden and PSI the sorption of Np(V) on SWy-1 under air-equilibrated conditions is being investigated. Sorption edge and isotherm measurements have been carried out by a PhD student (S. Dierking) at the University of Mainz. For the Np(V)/montmorillonite system, several samples were prepared as wet pastes for an Np L_{III}-edge. An EXAFS spectroscopy measurement campaign took place at the Rossendorf Beamline (ROBL) at the ESRF place in the Spring of 2007. The data analysis of spectra with low Np(V) loading (a few hundred ppm) is currently underway. Similar previous investigations with kaolinite showed that the absence or the presence of CO₃²⁻/HCO₃⁻ dictates the nature of the surface complex formed. At least one more EXAFS measurement campaign in connection with this work is foreseen for 2008 at the ROBL beamline. The final goal of the Np-montmorillonite investigations is to perform surface complexation modelling with surface species which are consistent with the findings of the EXAFS investigations and the macroscopic sorption data.

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5 CEMENT SYSTEMS

E. Wieland, J. Tits, B. Fontana, D. Kunz, N. Macé, P. Mandaliev

5.1 Overview

In the proposed Swiss concept for the safe disposal of long-lived intermediate-level (ILW) and low-level and short-lived intermediate-level (L/ILW) radioactive waste it is foreseen that cement, already used to condition (solidify and stabilize) the waste materials, will also be used for the construction of the cavern (lining, backfill material) of the deep geological repositories. Therefore, cement is an important component of the engineered barrier system, and the interaction of radionuclides with cement and cement phases may control their retention in the repository near field in the long term. As a consequence, in PA studies it is considered that the source term for radionuclide migration into the host rock is determined by a combination of solubility and adsorption constraints in the cementitious near field.

The long-term aim of the sub-programme *Cement Systems* is to develop mechanistic models for the interaction of cementitious materials with safety relevant radionuclides and improve current knowledge on the chemical processes in the near field of the planned Swiss ILW and L/ILW repositories. The research programme is directed towards better source term descriptions and to strengthening the credibility of the sorption values used in PA studies. The hydrated cement material used in the experimental studies was prepared using the sulphate-resisting Portland cement CEM I 52.5 N HTS (Lafarge, France), which is currently used for the conditioning of L/ILW and ILW radioactive waste in Switzerland. Hardened cement paste (HCP) is a heterogeneous mixture consisting mainly of calcium (aluminium) silicate hydrates (C-(A)-S-H), portlandite and calcium aluminates (AFt- and AFm-type phases). In the ongoing research programme, wet chemistry and spectroscopic techniques are combined with the aim of gaining a detailed understanding of the radionuclide uptake by cementitious materials at the molecular level.

In the following, brief summaries of the main lines of investigation in 2007 are presented:

In 2007 a short-term study was carried out in conjunction with Nagra's contribution to a joint Nagra-NUMO-SKB-Posiva project. The aim of this international collaboration is to investigate the long-term safety aspects of superplasticizers and other organic cement admixtures. LES's contribution to this research project focussed on the determination of the concentration of selected concrete admixtures

(Rheobuild 1000, Glenium 51, Sigunit® L53 AF) in the porewater of intact HCP and on investigations of the influence of the concrete admixtures on the sorption behaviour of Ni(II), Eu(III) and Th(IV) onto cement. The former study was carried out in co-operation with the Laboratory for Concrete and Construction Chemistry, Empa, Dübendorf (Switzerland). The project was completed at the end of 2007.

LES is contributing to the Mont Terri field experiment on cement-Opalinus Clay interaction (CI project) through a laboratory programme carried out in collaboration with the above mentioned research group at Empa. In 2007 the hydration processes of the cements used in the field experiment were investigated.

Investigations on the interaction of dose-determining radionuclides, such as ^{79}Se , ^{129}I , ^{36}Cl and ^{14}C , with cement will be a main area of research in the future. In 2007 a first series of experimental studies on the uptake of ^{129}I and ^{36}Cl by HCP were carried out using the HTS cement currently being sold. The sorption values will be compared to those obtained from earlier studies with the "older HTS cement".

In 2007 the experimental programme on the interaction of actinides with cementitious materials was continued. The aim of these investigations is to corroborate the high sorption values of tri- and tetravalent actinides recommended for use in the cement SDB and to increase our understanding of the uptake processes of actinides. The work on the interaction of Eu(III) and Nd(III) is carried out in the framework of a PhD project in co-operation with the Institut für Nukleare Entsorgung (INE), Karlsruhe Institute of Technology (KIT), Germany. In the second project the speciation of U(VI) in cementitious matrices is addressed. In 2007 substantial improvements in the use of time resolved laser fluorescence spectroscopy (TRLFS) for U(VI) speciation studies in highly alkaline cementitious systems were achieved. The latter measurements were conducted in co-operation with the Institut für Radiochemie (IfR) at the Forschungszentrum Dresden-Rossendorf (FZD).

The uptake of redox sensitive actinides under the reducing conditions expected in a cementitious near field is poorly characterised. Th(IV) is commonly used as a chemical analogue for tetravalent actinides. To corroborate this assumption, a study on the uptake of Np(IV) and Np(V) by cement and C-S-H phases

under reducing conditions was started. Measurements under reducing conditions in alkaline media require the development of procedures to determine the chemical speciation of Np and to establish stable and known redox conditions in the experiments.

The properties of cementitious materials under the reducing conditions in a repository near field are poorly known mainly due to a lack of knowledge of the speciation of iron in the cement matrices. A research proposal on Fe speciation in cementitious systems, prepared in co-operation with Empa, was approved by the Swiss National Science Foundation (SNF) for funding. The PhD project will start in 2008.

On September 10 an international workshop on "Cement research at large-scale facilities" was held at PSI. The workshop was organized by LES on behalf of CEMNET, a network of Swiss researchers in the field of cement chemistry, and in co-operation with PSI's Swiss Light Source (SLS) and Spallation Neutron Source (SINQ).

The technician B. Fontana left the Cement System sub-programme in November 2007. The vacancy has been advertised and the search for a replacement has started.

5.2 Concrete admixtures

The workability of concretes can be significantly influenced by using superplasticizers (SPs), and therefore it is highly likely that SPs will be used in the construction of concrete-based components of the engineered barrier system in a repository. In particular, there is a growing interest in using polycarboxylate-based SPs such as Glenium 51. In 2007 a short-term study was carried out with the aim of determining the concentration of selected concrete admixtures (Rheobuild 1000, Glenium 51, Sigunit® L53 AF) in the porewaters of intact HCP, and to check their influence on the sorption behaviour of Ni(II), Eu(III) and Th(IV). Rheobuild 1000 is a commonly used sodium naphthalene sulphonate-based SP which was already employed in the study of GLAUS & VAN LOON (2003). Sigunit is a formiate-containing Al-salt solution used as accelerator for ESDRED shotcrete.

Three different cements were used in this study, ordinary Portland cement (OPC), the low-alkali cement (LAC) used in the CI project, and ESDRED shotcrete. OPC (CEM I 42.5 R HS) and LAC (CEM III/B 42.5 L cement, Nanosilica (Aerosil 200)) were each mixed with water and 1 or 2.6 wt % of Glenium or Rheobuild, respectively, added. ESDRED shotcrete (CEM I 42.5 N cement, SikaFume-HR/TU) contained in addition about 5 wt% Sigunit. The water-to-cement (w/c) ratios of the different mixes were adjusted to

optimise the workability (OPC: w/c = 0.8, LAC: w/c = 1.1, ESDRED: w/c = 0.5).

The content of organic carbon (NPOC = non purgable organic carbon) in the porewater of the above cement mixes after hydration times of 1 hour, 28 and 360 days was determined using a Shimadzu TOC-WP® analyser.

In Table 5.1 the initial concentrations of the SPs and those after 28 days of hydration are listed in terms of NPOC concentration (estimated error $\pm 15\%$). The results show a decrease in concentration of Rheobuild 1000, Glenium 51 and Sigunit during the hydration time. The concentrations of Glenium and Rheobuild in the different cement mixes only differ by a factor of about 2, indicating that the cement composition only weakly affects the partitioning of the SPs. Furthermore, the concentrations of Rheobuild in the porewater of hydrated OPC obtained in this study ($27 \text{ mmol} \cdot \text{L}^{-1}$) are comparable to those reported earlier ($14 \text{ mmol} \cdot \text{L}^{-1}$ NPOC in intact samples w/c = 0.7) by GLAUS & VAN LOON (2003). The concentrations determined in the two studies agree within a factor of 2, which is acceptable in view of the different experimental set-ups.

Table 5.1 further shows that, in the long run, the main contributor to the organic carbon concentration in the porewater of ESDRED cement is formiate from Sigunit. Formic acid is added in this cement to enhance the stability of the Al-salt solution (Al complexation).

Table 5.1: Concentration of the concrete admixtures in the porewater of the different cement mixes: Initially and after 28 days of hydration.

	Initial NPOC [mmol · L ⁻¹]	28 days NPOC [mmol · L ⁻¹]
<i>OPC</i>		
Glenium	207	42
Rheobuild	458	27
<i>LAC</i>		
Glenium	370	43
Rheobuild	1269	52
<i>ESDRED</i>		
Glenium	575	77
Rheobuild	1057	21
Sigunit	140	59

A series of sorption studies were carried with the aim of determining the influence of Glenium, Rheobuild and Sigunit on Ni, Eu and Th binding by cement. The above elements are considered to be representatives of important classes of radionuclides, e.g. Ni(II) represents the transition metal radionuclides, Eu(III) is considered to be a chemical analogue for the trivalent actinides, and Th(IV) is the corresponding chemical analogue for tetravalent actinides. The concentrations of the concrete admixtures in the sorption experiments were chosen so as to represent “real” conditions in the near field i.e. the concentrations were the same as those determined in the hydrated cement paste porewaters. In addition, concentrations were selected to assess the maximum effects on radionuclide retention (“worst-case conditions”) as reported in GLAUS & VAN LOON (2003). To simulate “real” conditions in the near field, the S/L ratio and the concentrations of the concrete admixtures were adjusted in the sorption experiment. The S/L ratio had to be reduced to $2.5 \cdot 10^{-4} \text{ kg} \cdot \text{L}^{-1}$ in the sorption experiments with ^{152}Eu and ^{228}Th in order to achieve count rates in the supernatant solutions well above the background. For the sorption experiments with ^{63}Ni , the S/L ratio was $2.5 \cdot 10^{-2} \text{ kg} \cdot \text{L}^{-1}$. Note that the S/L ratio in intact cement paste is significantly higher. The concentrations of the admixtures in the sorption experiments were reduced in proportion to the S/L ratios in the experiment and in the solid paste in order to achieve the same ratio of solid phase (cement) and dissolved admixtures as in the paste samples.

Fig. 5.1 shows the effect of Glenium, Rheobuild and Sigunit on ^{228}Th uptake by HCP. Uptake was found to be very high ($R_d > 100 \text{ m}^3 \cdot \text{kg}^{-1}$), which is consistent with in-house measurements on cement and calcium silicate hydrates (C-S-H) (WIELAND et al., 1998; WIELAND et al., 2002; WIELAND et al., 2004; TITS et al., 2007). No significant influence of the SPs and Sigunit on ^{228}Th uptake was observed in the concentration range relevant to the near field. At very high concentrations of Rheobuild and Sigunit, however, ^{228}Th uptake seemed to be enhanced compared to a system free of concrete admixtures. The formation of ternary complexes in the case of Rheobuild, or modification of the cement particles by precipitation of Al phases in the case of Sigunit, may give rise to enhanced sorption. The findings were similar in the cases of ^{63}Ni and ^{152}Eu . From the above study it is inferred that Glenium 51, Rheobuild 1000 and Sigunit® L53 AF have no significant influence on the mobilisation of ^{63}Ni , ^{152}Eu and ^{228}Th compared to admixture-free cementitious systems.

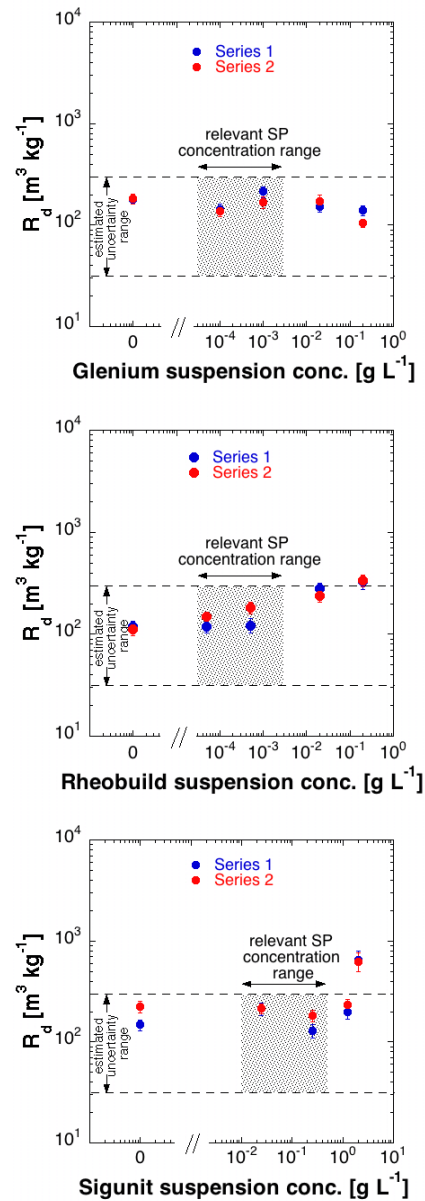


Fig.5.1: Influence of Rheobuild, Glenium and Sigunit on the uptake of ^{228}Th by HCP. The uncertainty range given in the figures is consistent with the estimated uncertainty range used in the cement sorption data base (WIELAND & VAN LOON, 2002). The shaded areas highlight the concentration range of the SPs and Sigunit as determined in the porewater of intact cement samples.

5.3 CI project

The hydration processes in the three cements OPC, LAC, ESDRED shotcrete are currently being investigated in the framework of the CI project in cooperation with Empa. Sample preparation, and sampling of the porewater using the steel die method, were carried out at Empa with LES support. pH measurements were carried out immediately after collecting the porewater. ICP-OES measurements were carried out at PSI to determine the

concentrations of the main elements, i.e., Ca, Si, Na, K, Al, S. Preliminary data from these experiments show that the evolution of the composition of the pore water in OPC (CEM I 42.5 R HS) is similar to that observed for the OPC CEM I 52.5 N HTS (LOTHENBACH & WIELAND 2006). The chemical compositions of the pore waters of ESDRED cement and LAC, however, show significant differences to that of OPC due to the addition of siliceous materials (silica fume or nanosilica, respectively). For LAC, a blended slag cement, CEM III/B 42.5 L was used and therefore reduced sulphur species were detected in the LAC pore water in addition to sulphate. This project will be continued in 2008.

5.4 Uptake of dose-determining radionuclides

Investigations into the interaction of the dose-determining radionuclides ^{129}I , ^{36}Cl and ^{79}Se with cementitious materials aim at i) resolving apparent inconsistencies observed between the sorption values determined in dispersed and intact cementitious systems (up-scaling), and ii) identifying the cement mineral(s) responsible for the long-term immobilization of these radionuclides in the cementitious near field. Point i) is particularly relevant to ^{129}I and regarding point ii) Ca aluminates i.e., AFm- and AFt-type phases, and hydrotalcite are considered to be the most important cement phases. In 2007 a series of sorption experiments with ^{125}I and ^{36}Cl were carried out using the “modified HTS cement”. Note that the “modified HTS cement” contains roughly 4% calcite (LOTHENBACH & WIELAND 2006). In contrast, the “older HTS cement”, which was manufactured about 20 years ago and used in the earlier in-house sorption studies with ^{129}I (BONHOURE et al., 2002) contains no calcite.

In the present study the uptake of ^{125}I and ^{36}Cl was studied on the same samples in dual labelling experiments. ^{125}I is a gamma/beta emitter, while ^{36}Cl is a pure beta emitter. Fig. 5.2 shows the uptake kinetics of ^{125}I and ^{36}Cl by the “modified HTS cement” in a Na/K rich artificial cement pore water (ACW) at pH = 13.3. Equilibrium was attained within about 7 days after tracer addition, indicating a relatively slow uptake process. Furthermore, ^{125}I binds significantly stronger to “modified HTS cement” than ^{36}Cl .

Differences in the extent of interaction of the two radionuclides with cement had already been observed in earlier studies with the “older HTS cement” (Table 5.2).

The R_d value for ^{36}Cl is about a factor of 7 lower than the value for ^{125}I , revealing that chloride binds much weaker to cement than iodide. The difference is even more pronounced in the case of the “modified HTS

cement” (factor of about 17). The latter finding is predominantly due to much stronger uptake of ^{125}I by the “modified HTS cement”, since the interaction of ^{36}Cl with the “modified HTS cement” is only slightly enhanced. At present, the reasons for the observed differences in the sorption behaviour of iodide and chloride are unclear.

The speciation of ^{14}C in the near field, and the interaction of ^{14}C containing organic compounds with cement, are largely unknown. In 2007 a research project on the interaction of ^{14}C labelled organic compounds (acetic acid) with cementitious materials was started. In the first phase radio assay methodologies for the measurement of ^{14}C under highly alkaline conditions are being developed. Complementary to the experimental programme a literature survey of the state-of-knowledge on the speciation of carbon released from carbon steel during anaerobic corrosion and the behaviour of the ^{14}C labelled compounds in the cementitious near field has been started in co-operation with the Geochemical Modelling Group.

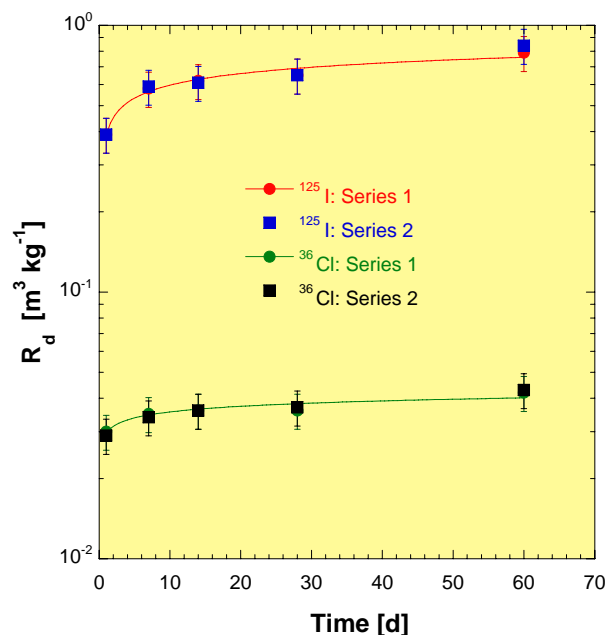


Fig. 5.2: Uptake kinetics of ^{125}I and ^{36}Cl by “modified HTS cement” (CEM I 52.5 N HTS).

Table 5.2: Sorption values for iodide and chloride on “older” and “modified” HTS cements. Experimental conditions: S/L ratio: $25 \text{ g} \cdot \text{L}^{-1}$; equilibration time: 28 days. Tracer concentration: $10^{-8} - 10^{-5} \text{ mol} \cdot \text{L}^{-1}$.

	R_d value on “older HTS cement” [$\text{m}^3 \cdot \text{kg}^{-1}$]	R_d value on “modified HTS cement” [$\text{m}^3 \cdot \text{kg}^{-1}$]
^{36}Cl	0.023	0.036
^{125}I	0.16	0.65

5.5 Redox chemistry in cementitious systems

5.5.1 Neptunium(IV/V) sorption experiments

Sorption experiments with Np(V) carried out in previous years (PROGRESS REPORT, 2004/2005) showed an unexpectedly strong sorption of this radionuclide on C-S-H phases and HCP. It was speculated that Np(V) was reduced to Np(IV) in the experiments, giving rise to the strong uptake measured. In 2007 a chemical separation method used to distinguish Np(IV)/Np(V) redox states, which is based upon extraction of Np(IV) with the help of Thenoyltrifluoroacetone (TTA) in xylene, was checked to assess the possibility of Np(V) reduction. Extractions carried out with a Np(IV) solution as a function of time showed that 1 hour after preparation of the dilute Np(IV) solution, about 60% of the Np was already detected in the aqueous phase, indicating that 60% of the Np(IV) had been oxidized to Np(V). After 1 day, the Np fraction observed in the aqueous phase corresponding to Np(V) increased to 95%. This clearly showed that Np(IV) can be readily oxidized to Np(V) even in the controlled N₂ atmosphere of a glove box. The above finding implies that i) the very strong uptake of Np(V) by C-S-H phases as previously reported ($10 \text{ m}^3 \cdot \text{kg}^{-1} < R_d < 1000 \text{ m}^3 \cdot \text{kg}^{-1}$) was most probably true since Np(IV) is not stable under the given experimental conditions, and ii) uptake studies with Np(IV) on cementitious materials require careful control of the redox potential in the C-S-H and cement suspensions. Several options are currently being tested; control of the redox potential with the help of electrochemical methods or by the addition of a reducing agent such as Na-dithionite (Na₂S₂O₄) or hydroxylamine.

Sorption under reducing conditions is one of the main subjects in the 7th EU Framework Programme Integrated Project ReCosy (**Redox** phenomena **controlling** systems). Thus, future investigations on the interaction of Np(IV/V) with cementitious materials using a combination of wet chemistry and synchrotron-based micro-spectroscopic techniques will be carried out in the framework of this collaborative project.

5.5.2 Iron speciation in cement

The strongly reducing conditions prevailing in repository systems may have an influence on the long term sorption properties of cementitious materials. The mineral composition and stability of the cement matrix under these conditions is poorly known, mainly due to a lack of knowledge concerning the speciation of iron in cement matrices. Fe(II)/Fe(III) is the most important potential redox couple in the cement matrix (total Fe is ~2 wt%). In 2007 a PhD proposal was

prepared jointly with Empa with the aim of addressing this gap in our knowledge. The proposal was submitted to the Swiss National Science Foundation (SNF) for funding and was accepted. The PhD project is planned to start in the first quarter of 2008.

5.6 Uptake of lanthanides and actinides by cementitious materials

5.6.1 Eu(III)/Nd(III) binding

A study on the uptake of Nd(III) and Eu(III) by cementitious materials is being carried out in the framework of a PhD project. It was started with the aim of substantiating the high sorption values determined earlier by WIELAND et al. (1998), TITS et al. (2003) and WIELAND et al. (2004). The project focuses on the development of a molecular-level understanding of the uptake process of lanthanides with a view to assessing chemical analogy between lanthanides and trivalent actinides in cementitious systems. The 1.13 nm tobermorite and xonotlite used in this study are crystalline C-S-H phases which are considered to be appropriate model compounds for the development of a mechanistic understanding of lanthanide and actinide binding to C-S-H phases. The basic structural element of both solids is the layer of Ca-polyhedra bound together by silicate chains (HEJNY & ARMBRUSTER, 2001; MERLINO et al., 2001; RICHARDSON, 2004). Nevertheless, there is structural dissimilarity: tobermorite has an interlayer of Ca atoms and water molecules, while xonotlite has no interlayer. Note that both structural features, i.e., the Ca-Si framework and the presence of interlayer, are also found in amorphous C-S-H phases which is the main constituent of hydrated cement.

In 2007 X-ray diffraction (XRD) studies coupled with Rietveld refinement were carried out with the aim of determining the crystallographic position of Nd(III) bound in the structures of 1.13 nm tobermorite and xonotlite. The measurements were conducted on beamline 10.3.2 at the Advanced Light Source (ALS), Berkeley, USA, and with a conventional diffractometer using Nd(III) doped samples (350 µmol Nd/g C-S-H). Fig. 5.3 shows the characteristic XRD patterns of 1.13 nm tobermorite and xonotlite which do not show any evidence for the presence of impurities such as portlandite or calcite.

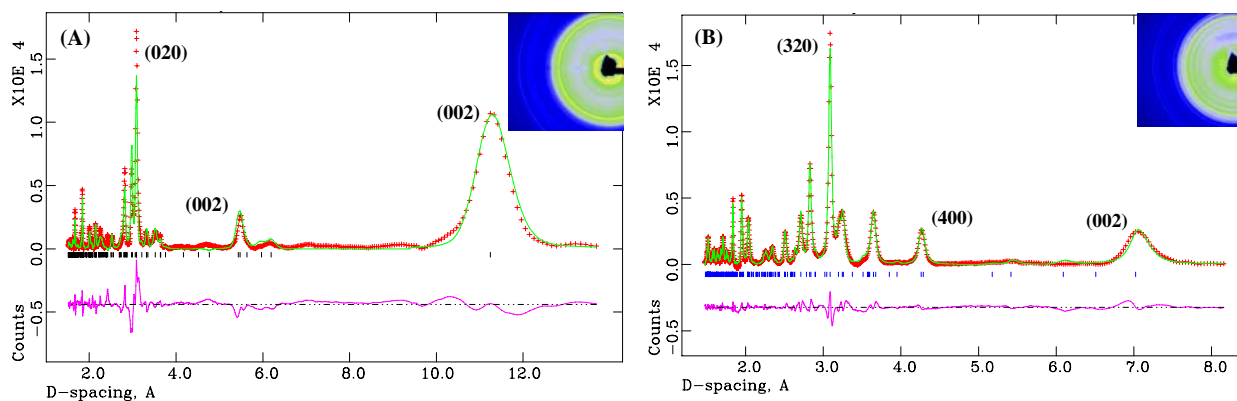


Fig. 5.3: Observed (green line) and calculated (red crosses) X-ray diffraction patterns of Nd(III) doped (A) 1.13 nm tobermorite and (B) xonotlite after 90 days reaction time. The difference between the observed and calculated patterns is plotted below (pink). The vertical bars mark all possible Bragg reflection (blue). Inset: Corresponding Debye rings as collected at a photon energy of 14 keV.

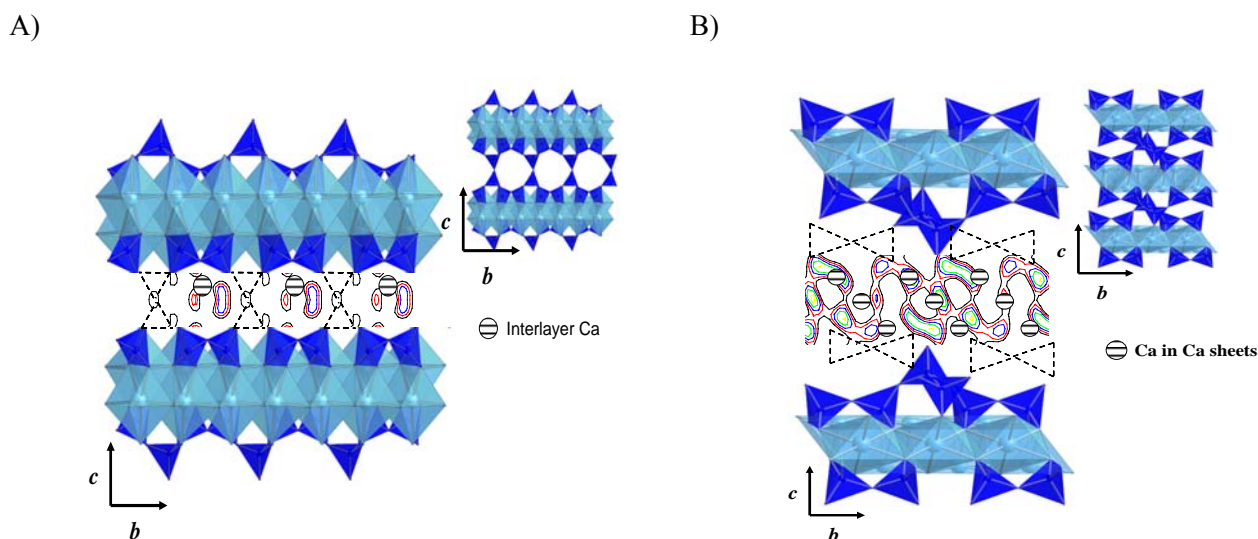


Fig. 5.4: Difference-Fourier maps at $y = \frac{1}{2}$, superimposed onto projection of A) the tobermorite structure looking down the “a” axis ($\alpha = 90^\circ$), and B) the xonotlite structure looking down the “a” axis ($\alpha = 89.75^\circ$). The contour map indicates areas of additional electron density. The contour interval is $0.30 e^- / \text{\AA}^3$. Maxima in the contour maps indicate potential crystallographic positions of Nd(III), e.g., greenish shaded regions in Fig. 5.4 A and B.

The Difference-Fourier maps (Fig. 5.4), calculated on the basis of the observed Bragg intensities (see for example McCUSKER et al., 1999), show the additional electron density in the interlayer of tobermorite and the Ca sheet of xonotlite arising from the structural differences between undoped and Nd(III) doped C-S-H phases. The maps show maxima in the electron density (green regions in Fig. 5.4 A/B), which correspond to potential crystallographic regions for Nd(III) binding. The data reveal that Nd(III) can be incorporated in the Ca sheets and in the interlayer of 1.13 nm tobermorite as well as in the Ca sheets of xonotlite. The exact positions of Nd(III) in the interlayer and the Ca sheet were determined from Rietveld refinement. Agreement of modelled and

calculated diffractograms indicated that the structural parameters obtained from Rietveld refinement allow excellent modelling of the XRD pattern.

The Nd-Nd distances in the interlayer of 1.13 nm tobermorite were determined to be 5.67 Å and 5.89 Å, while the Nd-Nd distance in the Ca sheet of xonotlite was found to range from 3.90 Å to 3.95 Å. Note that the long and short Nd distances are similar to the Ca-Ca distance between Ca in the interlayer and in the neighbouring Ca sheet in 1.13 nm tobermorite (5.5-5.6 Å) and the Ca-Ca distance in the Ca sheets of xonotlite and tobermorite (3.8 Å), respectively.

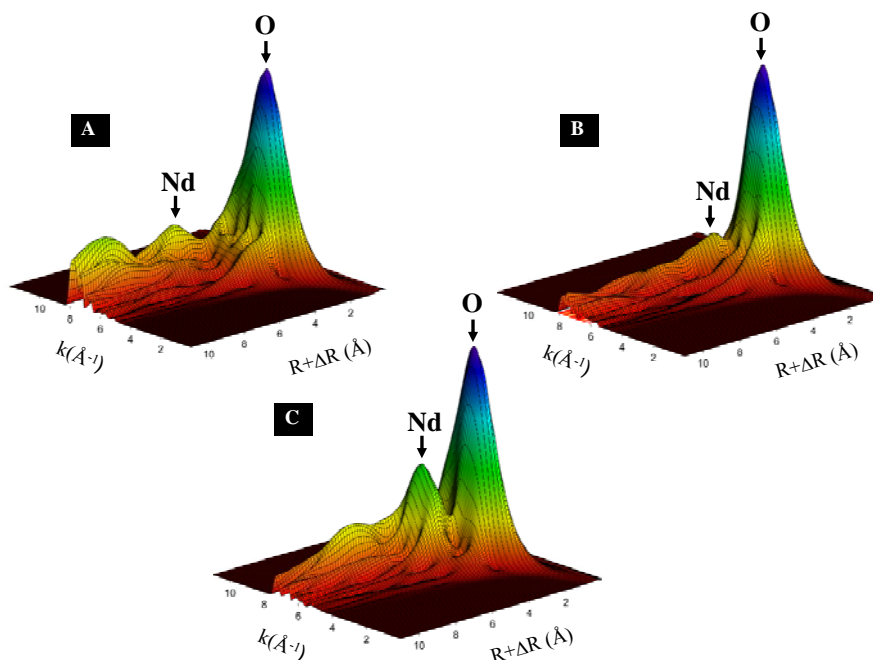


Fig. 5.5: Wavelet analysis of (A) Nd(III) doped 1.13 nm tobermorite, (B) Nd(III) doped xonotlite, (C) Nd(OH)₃.

Complementary X-ray Absorption Fine Structure (XAFS) studies were carried out to determine the coordination environment of Nd(III) in xonotlite and tobermorite at lower Nd(III) loading (35 μmol Nd/g C-S-H). XAFS measurements were carried out on beamline BM26A (DUBBLE) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, and the XAS beamline of the Angstromquelle Karlsruhe (ANKA). Fig. 5.5 shows Wavelet analysis of the XAFS data of Nd(OH)₃, Nd(III) doped tobermorite and xonotlite reacted for 270 days using the Morlet parameters $\eta = 7$, $\sigma = 1$, and a signal weighting of k^3 . Wavelet analysis of the measured XAFS spectra was applied to resolve the k dependence of the absorption signal, which allows the heavier and lighter backscattering atoms to be distinguished from each other, even if they are at the same or similar distance from the central atom (FUNKE et al., 2005). Fig. 5.5 shows maxima at $R + \Delta R \sim 5.6 \text{ \AA}$ and $k \sim 7.8 \text{ \AA}^{-1}$ in tobermorite, and $R + \Delta R \sim 3.8 \text{ \AA}$ and $k \sim 7.8 \text{ \AA}^{-1}$ in xonotlite. Note that the Nd-Nd backscattering contributions in Nd(OH)₃ appear in the same k range ($k \sim 7.8 \text{ \AA}^{-1}$). Based on this comparison it is concluded that the peak maxima located in the Nd(III) doped tobermorite and xonotlite samples at $k \sim 7.8 \text{ \AA}^{-1}$ and $R + \Delta R \sim 5.6 \text{ \AA}$ and $R + \Delta R \sim 3.8 \text{ \AA}$, respectively, correspond to Nd-Nd neighbouring pairs.

The XRD and XAFS investigations show that Nd(III) is bound in the structure of crystalline C-S-H phases. This finding further implies that the strong uptake of lanthanides by C-S-H phases, as observed in the

earlier wet chemistry experiments, is due to immobilization in the structure of the C-S-H phases.

5.6.2 U(VI) time-resolved laser fluorescence spectroscopy (TRLFS) studies

TRLFS was found to be a powerful tool for investigating U(VI) speciation under strongly alkaline conditions. Fig. 5.6 shows that U(VI) luminescence spectra collected at a temperature of 150 K are characterized by six emission bands resulting from the de-excitation of excited electrons to different energy levels of the ground state, which are related to the totally symmetric stretching frequencies of the linear O=U=O ion.

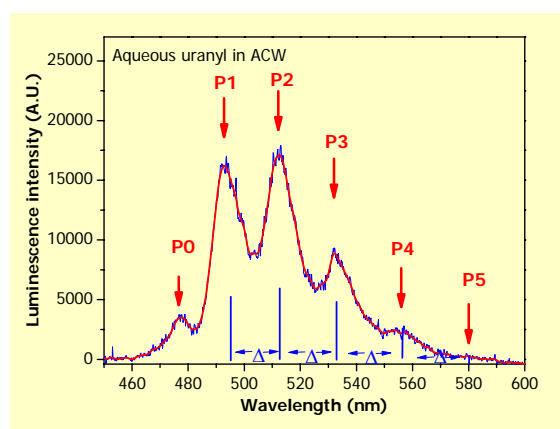


Fig. 5.6: Typical uranyl luminescence spectrum characterized by its band position (P_i), band spacing (Δ) and the relative intensities of the emission bands (P_i/P_{i+1}).

The position of the emission bands (\downarrow), the band spacing (Δ), and the relative intensities of the emission bands (P_i/P_{i+1}), are sensitive to the uranyl structure and the chemical environment. The symmetrical vibrational frequency (ν in cm^{-1}) of the uranyl ion, which is obtained from the band spacing (Δ) of the luminescence emission, allows the U-O axial bond length to be estimated as reported in by BARTLETT & COONEY (1989). Furthermore, the number of luminescing uranyl species present in the system can be deduced from the luminescence decay behaviour.

In 2007 TRLFS measurements were carried out on U(VI) doped C-S-H suspensions with the aim of evaluating the effect of U(VI) loading, pH and C-S-H composition on U(VI) speciation. The spectral characteristics of U(VI) sorbed on C-S-H phases varied with the calcium-to-silica (C:S) ratio and pH. The factor analysis programme developed by ROSSBERG et al. (2003) was applied, which allows the spectra of the pure sorbed U(VI) species to be identified by de-convolution in samples containing multiple U(VI) species. In Fig. 5.7, the spectra of the pure U(VI) sorbed species found in C-S-H systems with varying C:S ratios using varying U(VI) loadings under alkali-free conditions and in ACW are presented. At least three species with different spectral characteristics can be identified: Species A was found in all U(VI) - C-S-H systems. Species B was found at high U(VI) loadings under ACW conditions and closely resembles the spectrum of U(VI) precipitated in ACW. Species C was found on C-S-H phases with

a C:S ratio of 0.75. Species B dominates at high loadings, suggesting that it could correspond to a U(VI) precipitate formed on C-S-H. For the C-S-H phase with a C:S ratio of 1.6, the factor analysis programme identified two different species. Their spectra have identical peak maxima but different relative intensities in the emission bands. Note that at present it has not been fully resolved as to whether the two spectra actually represent two different species.

This project will be continued in the framework of a postdoctoral project (MISUC), which is fully financed through the Euratom Research & Training Programme in the framework of a Marie-Curie fellowship. Furthermore, this project is embedded in the EU 6th Framework integrated programme ACTINET.

5.7 Other activities

On September 10, 2007, a one-day workshop on "Cement research at large-scale facilities" was held at PSI. The workshop was organized by LES on behalf of CEMNET, a network of Swiss researchers active in the field of cement chemistry, and in co-operation with the PSI Swiss Light Source (SLS) and Spallation Neutron Source (SINQ). The workshop was attended by nearly 70 participants from various European countries, and focused on the application of modern synchrotron-based spectro-microscopic techniques and neutron scattering and imaging for molecular-scale and structural investigations of cementitious materials.

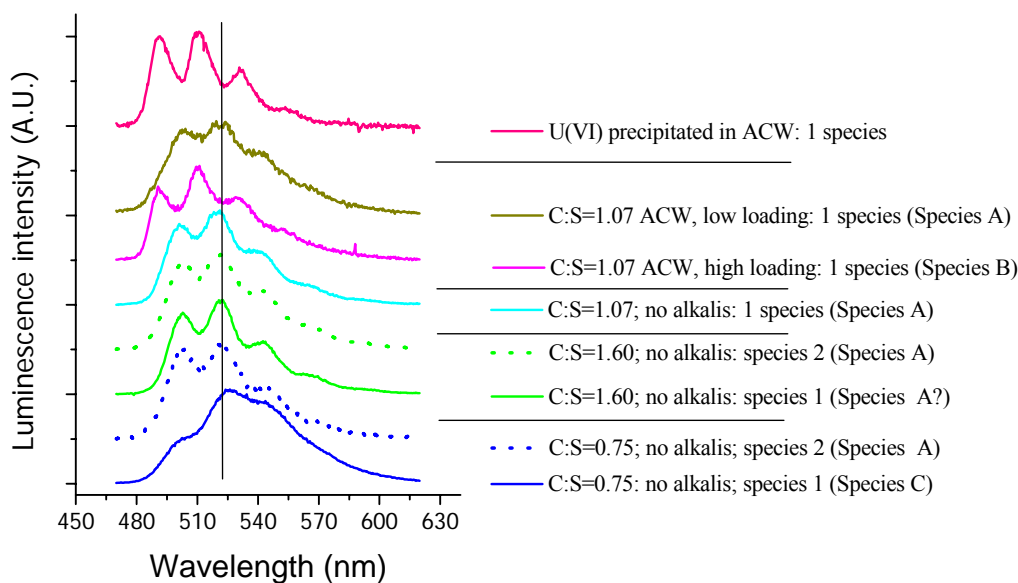


Fig. 5.7: Time-resolved laser fluorescence spectra of U(VI) precipitates and U(VI) sorbed on C-S-H phases under alkaline conditions in the absence of alkalis (in Water) and in ACW. Species A, B and C have clearly different fluorescence spectra.

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6 COLLOID CHEMISTRY

C. Degueldre, K. Bessho, S. Frick, S. Garcia-Garcia, R. Rossé

6.1 Introduction

The colloid sub-programme aims to understand the role of colloids in the migration of radionuclides in the geosphere. The colloid properties studied are their concentration, size distribution and nature under safety relevant conditions. This report summarises our activities during the last year in the frame of the Grimsel colloid project: “Colloid Formation and Migration” (CFM). The focus remains on colloid generation using single particle counting (SPC) techniques, and on colloid characterisation using electron energy loss spectroscopy (EELS) coupled to a transmission electron microscope (TEM).

6.2 Activities in the CFM project

The Colloid and Radionuclide Retardation (CRR) experiment was discontinued in 2005 and the new project “Colloid Formation and Migration” (CFM) started. We have been participating in the CFM project since 2005. The main aim of this project is to understand the generation of colloids at a bentonite block/groundwater flow interface with quasi-stagnant water. Experiments are performed, amongst others, to investigate colloid generation rates and mechanisms at the engineered barrier system – host rock boundary under *in-situ* conditions

This project involves 12 laboratories including:

INE/FZK, CIEMAT, ANDRA, JAEA, AIST, CRIEPI, LANL, NAGRA/Solexpert, KTH/SKB and PSI...

In the CFM project bentonite colloids are considered as part of the EBS (engineered barrier system). We are currently studying the generation of montmorillonite colloids in the quasi-stagnant water in contact with a compacted pellet. Tests are performed at the laboratory level in support of the field studies. Fig. 6.1 presents the cell design for both colloid re-suspension (generation) and sedimentation (elimination) experiments. FEBEX clay colloids, generated from pellets in contact with solutions and during sedimentation from concentrated solutions, were measured by SPC. The tests were carried out in cylindrical batch systems. The colloid size distributions in the suspensions studied were measured to be in the range 50–5000 nm as a function of generation and sedimentation time. It was striking to observe that the colloid size distributions determined in the generation and sedimentation batches tended towards a similar specific size distribution. This suggests a pseudo-equilibrium of the colloid population corresponding to generation-

sedimentation coupling. A first series of apparent distribution data corresponding to this pseudo-equilibrium were derived from these tests. The concentration values decrease by orders of magnitude for sizes going from 50 to 2000 nm suggesting the elimination of colloids by sedimentation for 2000 nm, while the 200 nm colloids may remain in suspension. The particle size distribution of the FEBEX material was determined at the beginning of the sedimentation tests, see Fig. 6.2.

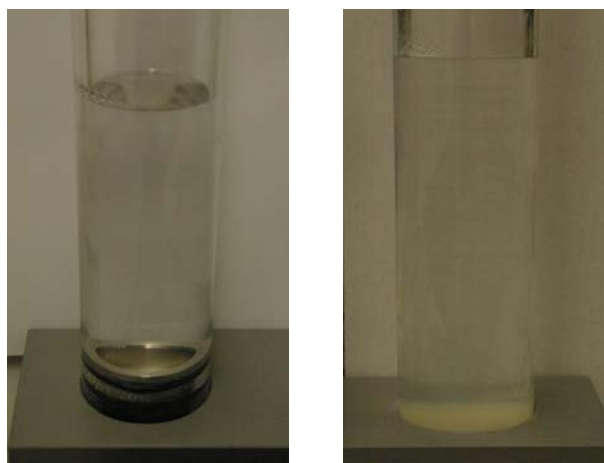


Fig. 6.1: New cells for the colloid generation and sedimentation tests. Note, in the generation test the pellet in the steel mold swells after contact with water and develops a colloid bed and a thick suspension; in the sedimentation tests the suspension yields a colloid bed. When the pseudo-equilibrium is reached, both systems are similar.

A mathematical model describing the changes of colloidal suspension properties over a colloid bed in a batch tests was developed and tested with experimentally obtained data. The model is based on population balance equations and takes into account the particle fluxes due to diffusion, aggregation and sedimentation. These processes were combined with two novel processes of colloid creation. These are realised by adding terms related to spontaneous diffusion from the colloid bed as well as a term reflecting colloid generation by the impact of settling particles on the colloid bed. The modelling of both generation and elimination mechanisms was performed until a pseudo-equilibrium is reached.

The sedimentation and generation results are shown together in Fig. 6.2. In the sedimentation tests, starting with a concentrated suspension, the larger particles settle first. For the generation tests, the concentration of small sized colloids increases rapidly through spontaneous diffusion from the pellet. After several

hundred hours, both systems reach a pseudo-equilibrium. The model was applied to clay suspensions in batch experiments in columns of height “h” with a sampling point at elevation “z” carried out in a generation or a sedimentation mode in the groundwater system. In laboratory “hydrogeological” systems (colloid concentration gradient q , surface tension σ , water viscosity η at temperature T), the colloid size normalised concentration reached values of the order of $10^{-6} \text{ ml}^{-1} \cdot \text{nm}^{-1}$ for attachment coefficient (α) values of 10^{-5} and for colloid sizes of 50 nm, 10 cm above the colloid bed. The small colloids (~ 10 nm) are generated more rapidly than the large ones (~ 1000 nm) which are eliminated faster. Fig. 6.2 shows the Febex colloid results for generation and sedimentation tested for 3 values of the attachment coefficient, α , and for contact times, t , ranging from 20,000 to 100,000 h.

It is foreseen to compare the behaviour of Febex clay with the behaviour of Kunigel and Wyoming clays in contact with 10^{-3} and 10^{-2} M NaCl solutions.

6.3 Other colloid activities

The association of Th onto colloids has been studied earlier with emphasis on Th polymers. This work has now been published. The study will be completed by EELS investigations in order to observe whether polymerisation takes place or not. The work will now be focused on colloid generation from a bentonite block source as well as on the characterisation of CFM colloids utilising EELS.

Granitic groundwater sampling and characterisation studies (KFM11A, KLX17A and KLX15A) were carried out in the framework of our co-operation with Scandinavian groups. A publication has been submitted. This study completes our former activities on granitic groundwater colloids.

Single particle analysis has been performed using inductively coupled plasma - mass spectrometry (ICP-MS) over the past few years. The ICP-MS results were compared with those from SPC and SEM. Comparing the analytical potential of the techniques used for colloid analysis it can be stated that SEM allows chemical analysis (>500 nm / EDS) and morphological analysis (>50 nm) of colloids in approximately 20 hours. SPC allows particles (>30 nm) to be counted in only 20 minutes. ICP-MS allows colloid analysis (isotope for isotope) in 20 seconds

(>50 -100 nm with a classical torch). This clearly indicates the potential of this technique.

6.4 Future work

For the CFM project the generation of colloids at a bentonite block/groundwater flow interface with quasi-stagnant water is being studied from a mechanistic point of view. Colloid size distributions from the bentonite source will be compared with those from the groundwater system sampled during the experiment, as well as those obtained by contacting FEBEX bentonite in the Grimsel Test Site.

Next year, we will celebrate the 20th anniversary of the Grimsel Colloid Exercise. A meeting is foreseen in September 2008 in which the aim is not only to summarise the lessons learned but also to discuss how to proceed in order to increase the understanding of the mechanisms which drive colloid facilitated transport.

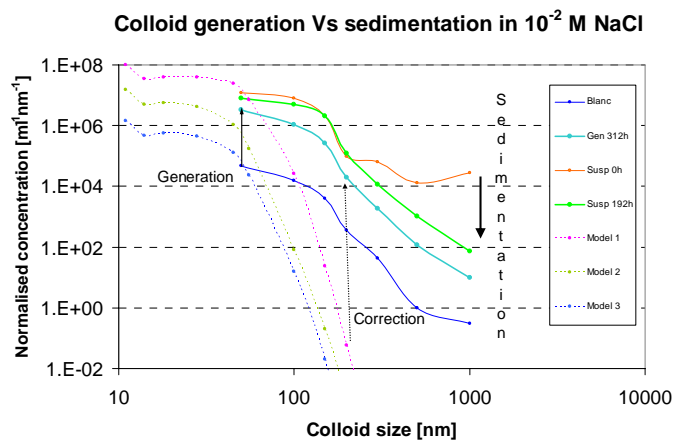


Fig. 6.2: Comparison of normalised size distributions for pseudo-equilibria calculated and observed for clay colloid population in the batch conditions.

Conditions: The experimental SPC data from generation and sedimentation tests at room temperature were obtained for Febex bentonite colloids in 10^{-2} M NaCl solution at pH 8 and $h \approx 20$ and $z \approx 10$ cm. The calculations are for: $T = 300$ K, $\rho_w = 1.0 \text{ g} \cdot \text{cm}^{-3}$, $\eta = 0.015$ P; clay: $\rho_{col} = 1.8 \text{ g} \cdot \text{cm}^{-3}$, clay in water: $N_i(t=0) = 10^7 \text{ cm}^{-3}$, gravity $g = 981 \text{ cm} \cdot \text{s}^{-2}$; clay and water: $q = 10^9 \text{ cm}^{-4}$, $\sigma_{col-w} = 63.4 \cdot \text{mJ} \cdot \text{m}^{-2}$, for $h = 20$ and $z = 10$ cm. **Model 1:** $t = 100'000$ h and $\alpha = 10^{-6}$, **model 2:** $t = 30'000$ h and $\alpha = 10^{-5}$, and **model 3:** $t = 20'000$ h and $\alpha = 10^{-4}$. Note, the model calculation values need to be corrected by those obtained for the blank values from high purity water.

7 DIFFUSION PROCESSES

L.R. Van Loon, M.A. Glaus, F. González, W. Müller, R. Rossé, J. Mibus, S. Frick

7.1 Introduction

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

The work on pure clay minerals (TRAPHICCS) was continued. A good set of diffusion data with $^{85}\text{Sr}^{2+}$, $^{22}\text{Na}^+$, $^{134}\text{Cs}^+$, $^{36}\text{Cl}^-$ and $^{35}\text{SO}_4^{2-}$ in Na-montmorillonite, Na-illite and kaolinite under different chemical conditions is now available and brings us a step forward to understanding diffusion in clays.

The work for the EU Integrated Project NF-PRO focused mainly on the sorption/diffusion of $^{134}\text{Cs}^+$ in bentonite at different bulk dry densities, and on the diffusion of $^{35}\text{SO}_4^{2-}$. It was found that the sorption of $^{134}\text{Cs}^+$ depends strongly on the degree of compaction. An increase in compaction results in an increase of the sorption which has been interpreted in terms of an increase in the Cs-Na ion exchange selectivity caused by a reduced amount of water in the interlayer. $^{35}\text{SO}_4^{2-}$ shows a similar diffusion behaviour to $^{36}\text{Cl}^-$. However, the rock capacity factor was higher, indicating that $^{35}\text{SO}_4^{2-}$ sorbs on the bentonite. Within the framework of the EU Integrated Project FUNMIG, the diffusion studies of ^{152}Eu in intact Opalinus Clay samples were continued. In addition, laboratory diffusion studies in support of the long-term diffusion experiments in Mont Terri (DR) were started.

The DINAPOR project (Diffusion of Nanoparticles in Argillaceous Media: Assessment of the Pore Structure; Euratom Research and Training Programme on Nuclear Energy Fellowship) started in November 2006. In a first phase, dendrimers of different molecular sizes were radio labelled with ^{14}C and their stability checked. Within the framework of this project, a student from the Dresden University of Applied Sciences (S. Brockmann) carried out her diploma work at PSI. The thesis defence took place on November 12th 2007 in Dresden.

F. González finished her PhD thesis: “Water diffusion through compacted clays analyzed by neutron scattering and tracer experiments” on schedule. The thesis defence took place on November 22nd 2007 in Bern.

The work on the reactivity of α -isosaccharinic acid under alkaline conditions (NIREX-SKB-NAGRA-PSI joint project) was summarised in a peer reviewed PSI report (GLAUS & VAN LOON, 2007).

A new PhD proposal: “Quantitative Analysis of Micro Heterogeneous Systems: A joint employment of complementary microbeam techniques“ was prepared in co-operation with D. Grolimund, μ -XAS beamline, and submitted to the Swiss National Science Foundation. The proposal deals with the application of micro beam techniques for studying the diffusive behaviour of strongly sorbing tracers in heterogeneous systems.

7.2 Diffusion in Opalinus Clay

The in-diffusion experiments of ^{152}Eu in Opalinus Clay were repeated. In order to avoid the problems associated with sorption on equipment, the tracer was directly applied on the surface of the rock. The profiles will be measured in 2008.

In the framework of the long-term diffusion/retention experiment (DR) in Mont Terri, a new set of 5 samples was prepared for radial diffusion experiments (VAN LOON et al., 2004). The diffusion of HTO showed very good agreement with previously measured values on samples obtained from another location at Mont Terri (DI site). Diffusion of I^- , Br^- , $^{36}\text{Cl}^-$, $^{22}\text{Na}^+$, D_2O and H_2^{18}O are ongoing and will be finished in early 2008.

The first experiments on the diffusion of $^{14}\text{CH}_3\text{COO}^-$ (OAc) in Opalinus Clay from Mont Terri were performed (Fig. 7.1). It was shown that $^{14}\text{CH}_3\text{COO}^-$ diffused through Opalinus Clay without retardation. The diffusion accessible porosity ($\varepsilon_{\text{Oac}} = 0.073 \pm 0.005$) was lower than that of HTO ($\varepsilon_{\text{HTO}} = 0.15 \pm 0.01$) but similar to that of $^{36}\text{Cl}^-$ ($\varepsilon_{\text{Cl}} = 0.0075 \pm 0.006$). The diffusion coefficient ($D_{e,\text{Oac}} = (1.4 \pm 0.1) \cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$) was lower than that of $^{36}\text{Cl}^-$ ($D_{e,\text{Cl}} = (4.1 \pm 0.3) \cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$).

The experiments on Opalinus Clay samples from Benken, in which the diffusion of $^{125}\text{I}^-$ and $^{125}\text{IO}_3^-$ were separately studied and in which the iodine speciation was monitored by high performance anion exchange chromatography, were finalised in 2007. The results for $^{125}\text{I}^-$ diffusion, $D_e = (4.5 \pm 0.5) \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$; $\alpha = 0.04 \pm 0.01$, showed that no sorption of $^{125}\text{I}^-$ takes place on Opalinus Clay since non-sorbing chloride exhibited the same rock capacity factor. In

the case of $^{125}\text{IO}_3^-$, no break-through was observed. Instead, a flux of $^{125}\text{I}^-$ into the collection reservoir was measured. This observation, together with the speciation analysis in the feed reservoir, showed that $^{125}\text{IO}_3^-$ was rapidly converted to $^{125}\text{I}^-$ upon contact with Opalinus Clay. Unknown catalytic sites in the clay must mediate a reductive transformation because no such reduction is observed in homogeneous aqueous solutions.

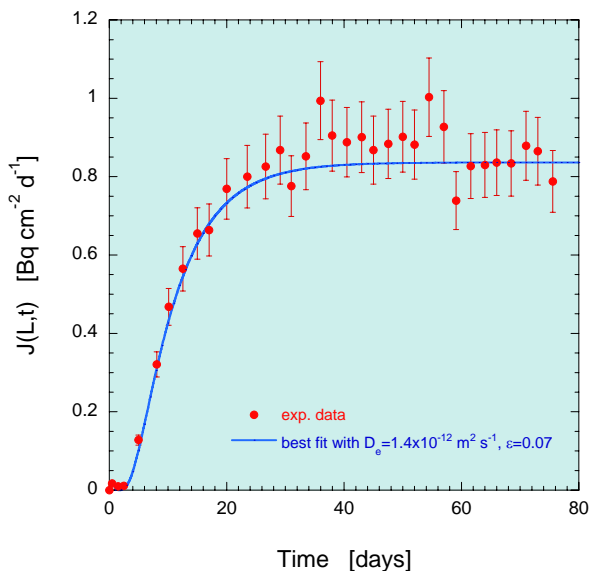


Fig. 7.1: Flux vs. time curve for the diffusion of $^{14}\text{CH}_3\text{COO}^-$ through Opalinus Clay from Mont Terri.

7.3 Diffusion in compacted bentonite

In order to obtain information on the effect of charge on the diffusion behaviour of anions, the diffusion of the bivalent $^{35}\text{SO}_4^{2-}$ anion was studied as a function of the dry density of the bentonite. The effective diffusion coefficient was found to depend strongly on the degree of compaction and was lower than that of $^{36}\text{Cl}^-$. The rock capacity factor of $^{35}\text{SO}_4^{2-}$ was larger than for $^{36}\text{Cl}^-$. This implies that $^{35}\text{SO}_4^{2-}$ sorbs on bentonite. One possibility is that the sorption arises from isotopic exchange with stable SO_4^{2-} in the celestite (SrSO_4) present in the bentonite.

Sorption studies with $^{134}\text{Cs}^+$ on compacted bentonite indicated that compaction strongly affects the sorption behaviour of Cs^+ . For bulk dry densities $\rho > 1300 \text{ kg} \cdot \text{m}^{-3}$, the sorption of $^{134}\text{Cs}^+$ was found to increase. This stronger sorption has been interpreted in terms of an increase in the Cs-Na ion exchange selectivity (Table 7.1) which is thought to be a consequence of a reduction in the interlayer space - caused by the compaction of the bentonite - leading to a lower availability of interlayer water for cation hydration. Cations with a low hydration tendency, such as cesium, can accumulate in the interlayer space whereas highly hydrated cations such as sodium, tend

to preferentially remain in the bulk water where water is easily available for hydration. (In order to enter the interlayer space the number of coordinated water molecules has to decrease.) The reduction of the interlayer space upon compaction was nicely demonstrated by basal space X-ray diffraction measurements performed by KOZAKI et al. (1998) on compacted Na-montmorillonite, and indirectly by $^{36}\text{Cl}^-$ diffusion measurements in bentonite (VAN LOON et al., 2007).

Table 7.1: Sorption distribution coefficients (R_d), selectivity coefficients (K_e) and free exchange energies (ΔG_{ex}) for the sorption of $^{134}\text{Cs}^+$ on Na-bentonite as a function of the degree of compaction (ρ).

ρ [kg m^{-3}]	1300	1600	1900
$[\text{Na}^+]$ [M]	0.183	0.207	0.254
R_d [$\text{dm}^3 \cdot \text{kg}^{-1}$]	69.0 ± 2.0	109 ± 4	620 ± 4
K_e	21.6	38.6	269
ΔG_{ex} [$\text{kJ} \cdot \text{mol}^{-1}$]	- 7.6	- 9.1	- 13.9

7.4 Transport phenomena in compacted clay systems (TRAPHICCS)

The through-diffusion of HTO, $^{22}\text{Na}^+$ and $^{36}\text{Cl}^-$ in kaolinite, Na-illite and Na-montmorillonite was measured as a function of the salt concentration in the 'external solution', i.e. in the solution in contact with the clay sample. The clays were chosen for this study because of their differences in the number and nature of sites for ion exchange. Na-montmorillonite has the highest cation exchange capacity, whereas kaolinite has almost none. Na-illite lies between these two extremes. Hence, Na-montmorillonite contains a large fraction of so-called interlayer water, where the presence of anions is excluded owing to the influence of the electrostatic field caused by the fixed negative charges. Cation exchange in the interlayers of Na-illite is almost completely impeded owing to the strong interaction of the fixed negative charges with K^+ . Further, the binding of K^+ leads to a situation in which there is no water present in the interlayers. Interparticle water is the only region where anions may be partially excluded in Na-illite. It can be expected that these structural differences lead to differences in the diffusive behaviour of cations and anions. The diffusion of cations in compacted clays with high fractions of interlayer or interparticle water has been shown to be driven by the concentration gradient of sorbed tracer cations (GLAUS et al., 2007), whereas the diffusion of anions is largely controlled by anion exclusion effects (VAN LOON et al., 2007).

The data in Fig. 7.2 show that there is a salt effect on the diffusion coefficients of charged species, decreasing in the order Na-montmorillonite to Na-illite to kaolinite. For uncharged HTO there is no such dependence. For the diffusion of $^{22}\text{Na}^+$ in Na-montmorillonite and Na-illite, the salt effect can be understood by realising that the sorption of $^{22}\text{Na}^+$ onto the clays is strongest at the lowest salt concentration and, consequently, the tracer concentration gradient in the interlayer or interparticle water is highest under these conditions. For anion diffusion an inverse dependence of the effective diffusion coefficients on the salinity in the external solution would be expected. This is because the effective volume for Cl^- diffusion in the chloride accessible porosity is influenced by the ionic strength through the extent of the diffuse double layer. For kaolinite almost no salt effects are expected because this clay contains essentially no fixed charges. Experiments such as those shown in Fig. 7.2 are thus in agreement with the expectations based on the structural differences of the clays and contribute to a better understanding of diffusion of charged and neutral species in argillaceous materials.

7.5 Dynamics of water in compacted clay systems

Because porewater is the medium through which radionuclides are transported in compacted clay, it is important to know its structure and properties. The main question is whether or not the waters in compacted systems have different (or similar) properties to bulk water. Pure clay minerals (montmorillonite, illite, kaolinite, and pyrophyllite) were chosen as model systems for studying water in compacted clays. A PhD thesis devoted to this topic was finished in 2007. Fátima González defended her thesis at the University of Bern on November 22nd. The supervisor of the thesis was Prof. L. Diamond.

The study clearly showed that in the case of charged clays (montmorillonite, illite) confined water is different from bulk water whereas for uncharged clays (kaolinite, pyrophyllite) confined water is similar to bulk water (GONZÁLEZ, 2007).

7.6 DINAPOR

The aim of the DINAPOR project is to develop an alternative method for determining the pore size distribution in compacted argillaceous materials. The basic idea is to extract this information from the diffusive behaviour of (macro-) molecules of different sizes. PAMAM (polyamidoamine) dendrimers were chosen for this work because of their well-defined structure, narrow polydispersity, well-defined nanoscale size and the ease of modification of the end groups (Fig. 7.3). In a first phase, PAMAM-OH dendrimers were radiolabelled with ^{14}C via a methylation of interior tertiary amine groups, resulting in internally quaternised PAMAM molecules (LEE et al., 2003). However, it turned out that the radiolabelling of the PAMAM dendrimers with ^{14}C was not stable, probably because too many tertiary amine groups were methylated, resulting in an unfavourable tertiary amine/quaternary amine ratio that destabilizes the PAMAM molecules. Steps to improve the labelling, i.e. to increase the tertiary amine/quaternary amine ratio by reducing the level of methylation, are ongoing.

A student (Sina Brockmann) from the Dresden University of Applied Sciences carried out work at PSI for her diploma on the diffusion of PAMAM dendrimers in free water and in model porous materials such as Vycor glas. The information on the diffusion behaviour in free water is important to understand the diffusion behaviour in porous media.

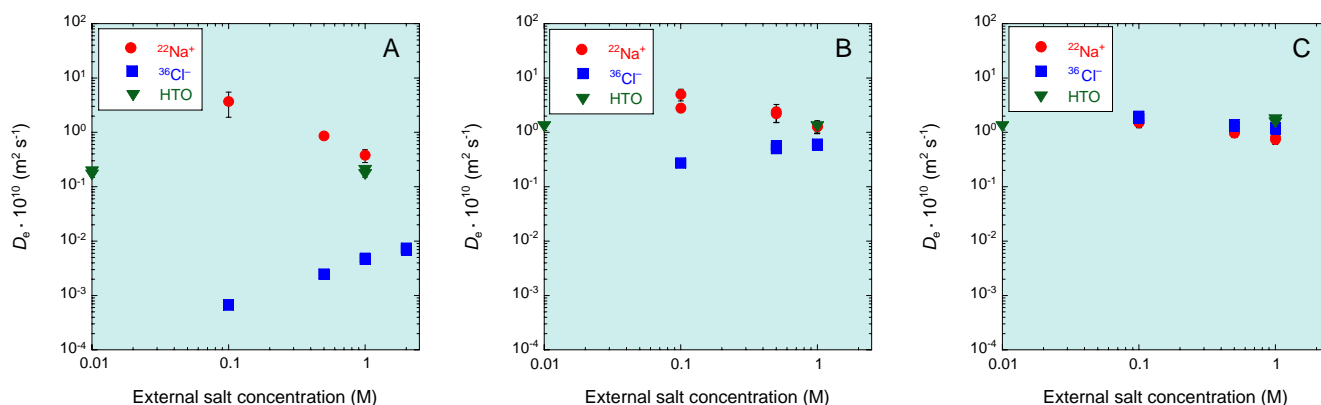


Fig. 7.2: Dependence of the effective diffusion coefficients (D_e) on the external salt concentration for Na-montmorillonite (A), Na-illite (B) and kaolinite (C) compacted to a bulk dry density of $1900 \text{ kg} \cdot \text{m}^{-3}$.

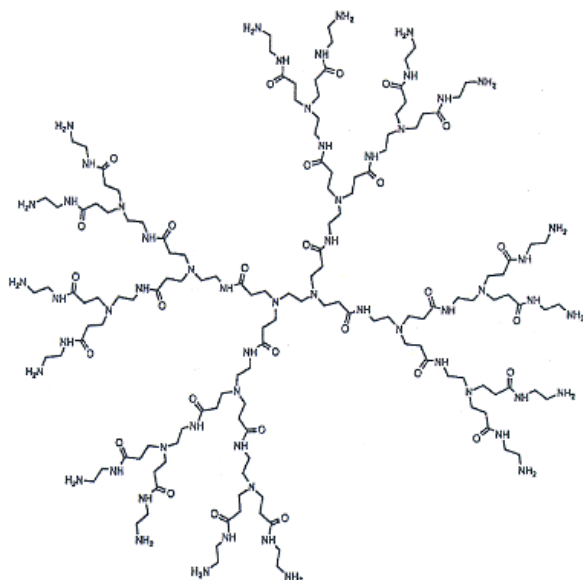


Fig. 7.3: Structure of a PAMAM (G2) dendrimer.

An important outcome of the diploma thesis was that the diffusion of PAMAM dendrimers in free water was almost independent of their molecular weight and deviated from the expression of HAYDUK & LAUDIE (1974) describing the relationship between the diffusion coefficient in water and the molar volume of the diffusing molecule:

$$D_w = \frac{13.26 \cdot 10^{-5}}{\eta^{1.4} \cdot V^{0.589}}$$

where D_w is the diffusion coefficient in water ($\text{m}^2 \cdot \text{s}^{-1}$), η is the viscosity of water (cP) and V is the molar volume of the solute ($\text{cm}^3 \cdot \text{mol}^{-1}$). This shows that the diffusive behaviour of such large molecules depends not only on the radius, but also on the shape of the molecule (Fig. 7.4). It could also be shown that none of the used dendrimers diffused through the Vycor glass, although the pore size of the glass was larger than the diameter of the dendrimers. This result has been explained in terms of a coagulation of the dendrimers in the narrow glass pores (BROCKMANN, 2007).

The thesis defence took place on November 12th at the Dresden University of Applied Sciences. Supervisor of the thesis was Prof. Dr. J. Schmelzer.

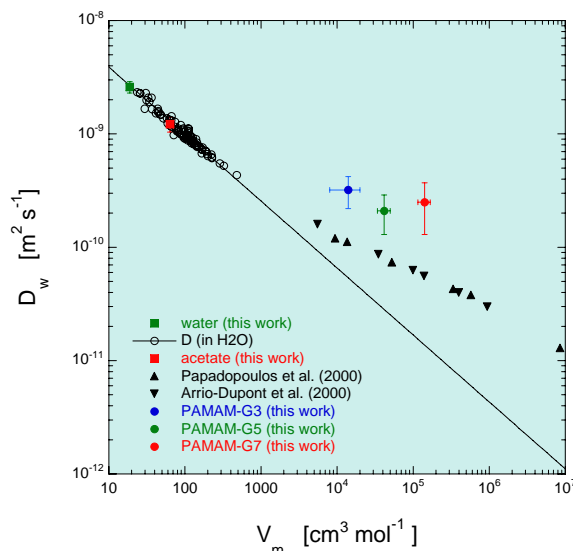


Fig. 7.4 : The relationship between the molar volume of a molecule and its diffusion coefficient in free water (after BROCKMANN, 2007). The large molecules ($V > 10^4 \text{ cm}^3 \cdot \text{mol}^{-1}$) do not follow the empirical relationship of HAYDUK & LAUDIE (1974). Open circles: Data for diffusion of small organic molecules (HAYDUK & LAUDIE, 1974). Triangles: Diffusion of globular proteins (PAPADOPOULOS *et al.*, 2000; ARRIO-DUPONT *et al.*, 2000).

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8 THE MICROXAS BEAMLINE PROJECT: STATUS AND MICROXAS RESULTS

D. Grolimund, C.N. Borca, B. Meyer, M. Willmann

8.1 General

Based on the initiative and under the direction of the Laboratory for Waste Management (LES), a high resolution hard X-ray microprobe station was built at the Swiss Light Source: the microXAS beamline. This analytical facility allows the investigation of materials and matter by means of high intensity X-ray beams with a spatial resolution of approximately $1 \mu\text{m}^2$ (GROLIMUND et al., 2002). Without doubt, the capability to determine element-specific chemical properties such as local co-ordination environments or oxidation states by means of X-ray absorption spectroscopy is of fundamental importance. Using micro-focused X-ray beams, chemical speciation can be determined within single micro-domains simultaneously with local structural analysis.

Two features make the microXAS beamline an exclusive X-ray microprobe facility. First, the microXAS beamline permits the investigation of radioactive materials. At present, hardly any X-ray microprobe facility around the globe accepts 'beaming in' on radioactive samples. Second, the microXAS beamline is the optical part of the FEMTO project. Within this project X-ray pulses of ~ 100 femto-seconds duration are produced allowing ultrafast X-ray science.

LES is in charge of the future beamline development and maintenance as well as the daily operation of the microXAS user facility. The period covered by the present annual report corresponds to the first full year of user operation. Within the following we will present selected research highlights of this first year of user operation. The different highlights have been chosen to provide a representative overview of the beamline's capabilities and the related scientific activities.

8.2 High resolution X-ray absorption spectroscopy

Chemical speciation describes the electronic state and the local environment of an atom. This information provides key knowledge concerning chemical reactivity, toxicity, bioavailability as well as the structure of X-ray amorphous materials. X-ray absorption spectroscopy provides detailed chemical and structural information such as number, chemical identity and distance of neighboring atoms and oxidation state. X-ray absorption spectroscopy can be applied to (non-) crystalline solids, species in solution

or in the gaseous phase, as well as to interfacial species.

A precise structural determination of the co-ordination environment requires high precision EXAFS data (large k -range covered). An example is shown in Fig. 8.1. The goal of the experiment was to obtain structural information on size-selected gold nano-clusters. These clusters consist of 10 to 40 gold atoms and are passivated by thiol ligands. Such monolayer protected metal nano-clusters are of considerable interest due to their potential application for bio-sensing, catalysis, electronics and nanotechnology. The structural information obtained is used to validate the ringlike structural shapes recently proposed based on density functional theory calculations.

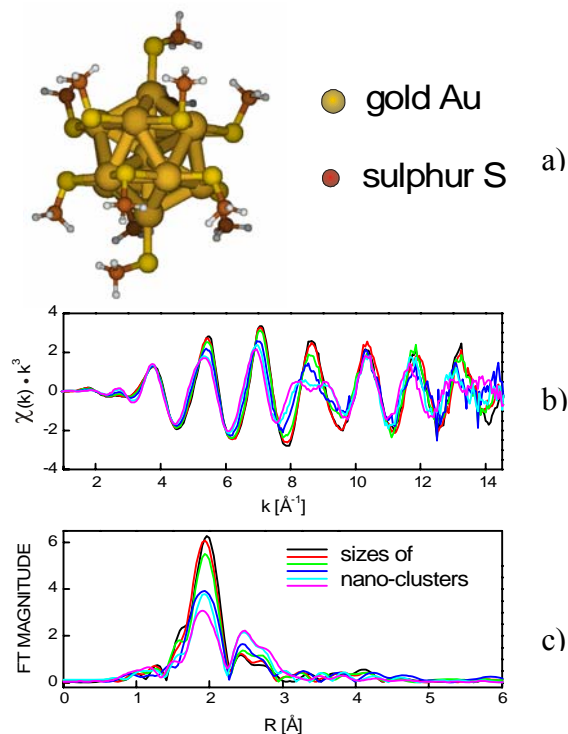


Fig. 8.1: Structure determination of different size-classes of gold nano-clusters by EXAFS spectroscopy. a) Illustration of a stabilized gold nano-cluster, b) EXAFS c) Fourier transform revealing the structural and compositional changes as a function of cluster size.

8.3 X-ray micro absorption spectroscopy

By combining the analytical capabilities of synchrotron-based X-ray absorption spectroscopy with microfocused X-ray beams, chemical speciation can be determined with high spatial resolution allowing the imaging of chemical state variations or

probing the chemical properties of micron-sized objects in complex matrices.

An illustrative example is represented in Fig. 8.2. The oxidation state of platinum in a Pt-based catalyst along a fixed-bed reactor during partial oxidation of methane was investigated by microXANES and microEXAFS (a study by J.-D. Grundwaldt et al.). A strong gradient in the oxidation state and structure of Pt was observed; the structure of the noble metal particles was clearly changing under the reaction conditions. Structure-activity relationships gained by such in-situ studies of catalytic materials are considered as the key to the further development of advanced heterogeneous catalysts.

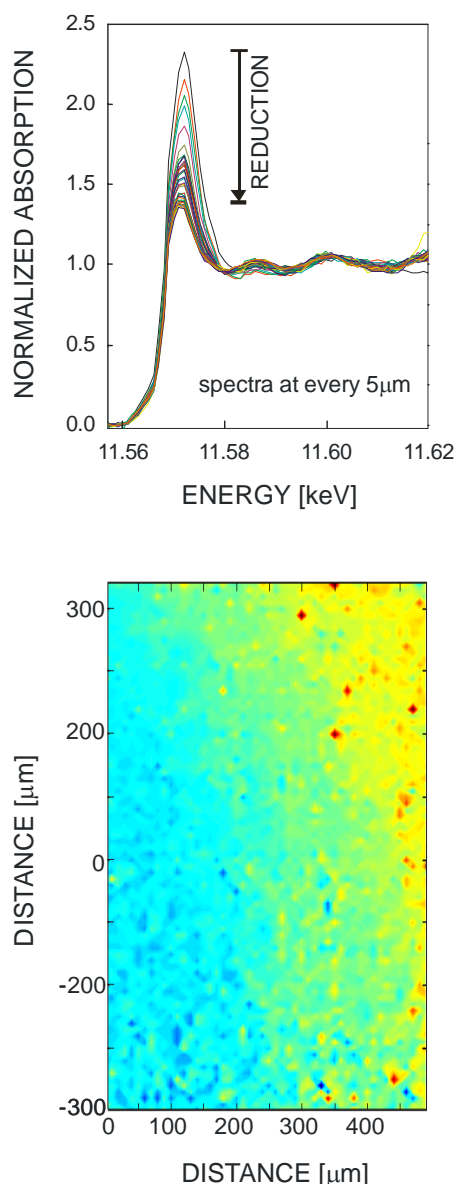


Fig. 8.2: Spatially resolved Pt speciation in a capillary micro-catalyst. Top: Pt XANES spectra taken every 5 μm across the reactive redox front within the micro-catalyst. Bottom: Two-dimensional spectroscopic imaging providing oxidation state maps.

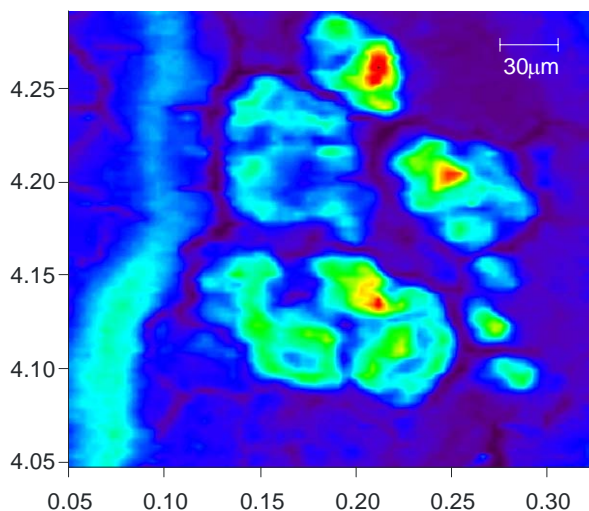
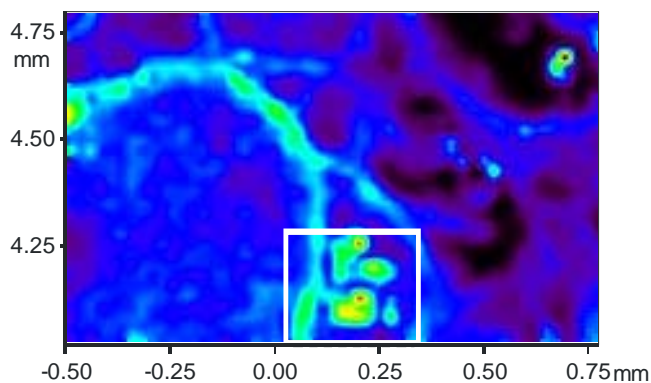
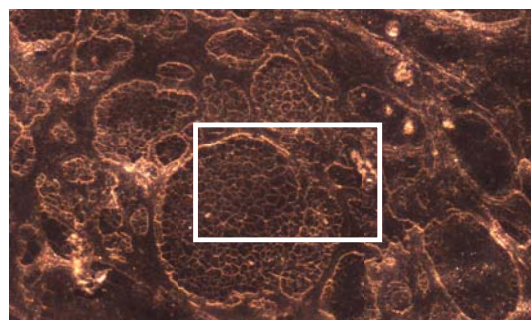


Fig. 8.3: Structural and chemical investigations of prostate cancer tissue. Top: Visible microscope image. Middle and Bottom: Corresponding Zn distributions obtained by micro-focused X-ray fluorescence measurements.

8.4 Micro X-ray fluorescence imaging

The spatial distribution patterns of chemical elements relate directly to the physical structure and chemical reactivity of materials. X-ray micro-fluorescence imaging is based on recording element specific fluorescence radiation emitted during relaxation processes following excitation by incident X-ray photons. The synchrotron-specific tunability of the excitation energy allows for exploring deliberately the

large changes in excitation efficiency (absorption cross sections) near the element specific absorption edges. As a result, synchrotron-based XRF allows element specific imaging with superior selectivity, sensitivity, and low detection limits.

Micron-scale imaging (combined with micro-spectroscopy) has become an important tool in cancer research, complementing classical histology. Biological tissues have very complex structures which are often composed of non-homogenous types of cells (among cancerous cells there are non-cancerous ones). Further, many transition metals are considered to be directly involved in carcinogenic processes. Accordingly, knowledge related to trace element concentrations in tissues as well as their spatial distribution and chemical speciation, in particular their oxidation states, is of fundamental importance. Fig. 8.3 shows the distribution of zinc within prostate cancer tissue. Investigating the elemental Zn distribution relative to other elements (in the present case particularly sulphur), complemented by XANES/EXAFS spectral information, can provide basic information about possible zinc binding proteins present in prostate cancer tissues and cells.

8.5 Nano-imaging

The unique information obtainable today at the micrometer scale by X-ray microprobes provided the incentive for the nano-scale investigations. Currently, at many synchrotron sources, a significant effort is being put into the development of the reliable, efficient focusing of hard X-rays (photon energies above 8 keV) to submicron dimensions. One of the most promising devices for nano-focusing of X-rays is the Fresnel zone plate (FZP). FZPs have proven to give focal spots with excellent spatial resolution combined with a low background. However, in contrast to *soft* X-rays, the efficient focusing of *hard* X-rays by FZPs is more difficult. In order to achieve acceptable diffraction efficiencies, the zone plate structures have to be made from heavy materials, and, most challenging of all for the FZP nano structures, their height should exceed their width by a factor of approximately 10-20, preferably even more. New FZP concepts and innovative fabrication processes correspond to a major research focus of the Laboratory for Micro- and Nanotechnology (LMN) at PSI (DAVID et al., 2004). Fig. 8.4 shows preliminary results on the focusing of 15 keV X-rays at the microXAS beamline by JESIMOVIS et al., (2007). For the investigated test pattern, structures as small as 200nm can be resolved.

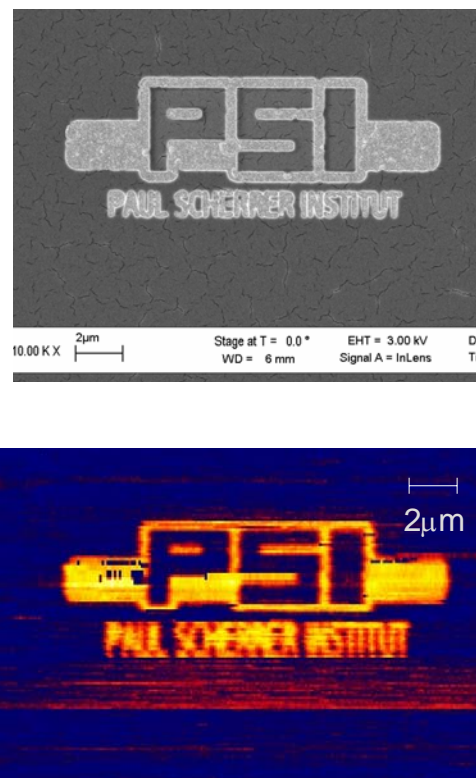


Fig. 8.4: Top: Scanning electron microscopy image of a nano-patterned test object. Bottom: Corresponding image obtained by nano-focused X-ray transmission measurements.

8.6 X-ray micro diffraction

Knowledge of the structure of materials in terms of their atomistic positions is fundamental to understanding the mesoscopic properties. X-ray diffraction is capable of probing the long-range order of crystalline phases. X-ray microdiffraction allows the mapping of crystal structure, texture, and strain within micro domains. The microXAS beamline project allows for different types of microdiffraction studies. As a speciality, in addition to the tunable monochromatic radiation, white light (polychromatic radiation) can be used to conduct X-ray diffraction experiments either in various Laue or reflection geometries.

Length-scale dependencies of physical properties have received much attention in recent years. Experimental results clearly contradict conventional theories which do not explicitly incorporate geometric length scale size effects. In some pioneering studies at the microXAS beamline, MAASS et al. (2006, 2007), polychromatic Laue microdiffraction investigations were performed elucidating the in-situ deformation of micron-sized objects (Fig. 8.5).

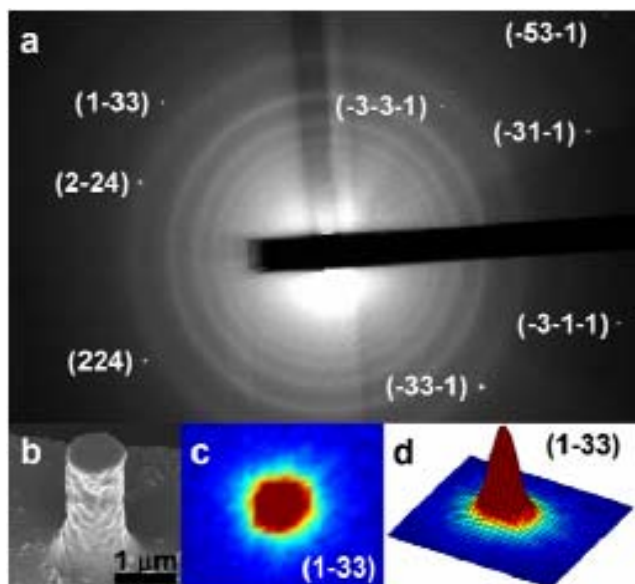


Fig. 8.5: Microdiffraction of micron-sized object. a) 'white' light Laue pattern, b) SEM picture, c) truncated contour plot (c) and d) 2D intensity distribution. Image courtesy of R.. Maass (MAASS et al., 2006).

8.7 Ultrafast, time-resolved X-ray science

The investigation of ultrafast structural dynamics is of predominant importance and interest in fundamental physical and chemical research. Of particular interest are atomic motions as well as atomic rearrangements occurring during phase transitions in solids, chemical reactions or fast biological processes.

A tunable undulator source for femtosecond X-rays in the range 4–12 keV is now in operation in the SLS storage ring (INGOLD et al., 2006, 2007). The source combines accelerator and laser technology relevant for the next generation of light sources. It provides inherently synchronized femtosecond laser "pump" and X-ray "probe" enabling time-resolved absorption and diffraction experiments to be performed.

Initial experiments have demonstrated the excellent spatial and temporal stability of the source, thus allowing direct quantitative measurement of ultrafast molecular or lattice dynamics as well as phase transitions (BEAUD et al., 2007), (Fig. 8.6).

8.8 X-ray microprobe analysis of radioactive materials

Radioactive or activated materials are part of crucial activities of modern societies such as energy production, medicine, or basic research. Specialized analytical facilities are required to investigate materials emitting ionizing radiation.

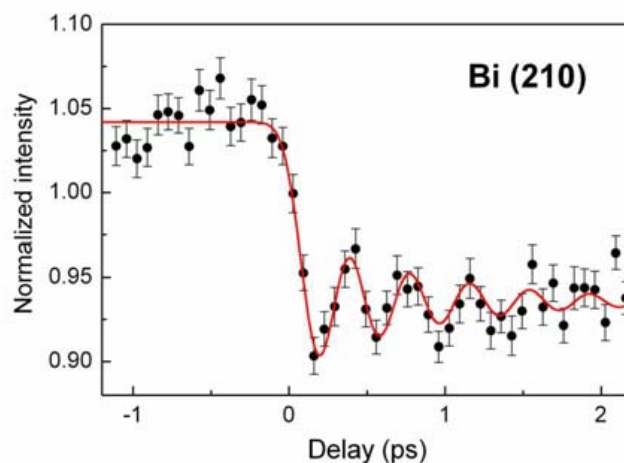


Fig. 8.6: Integrated diffracted intensity from the bulk Bi (210) reflection as a function of time after excitation with a fs laser pump pulse. Image courtesy of S.L. Johnson (BEAUD et al., 2007).

The microXAS beamline was designed as a hard X-ray microprobe facility dedicated to XAS and XRF with the option of (rudimentary) XRD. However, in addition – and going beyond any existing X-ray microprobe instrumentation – the measurement of closed radioactive samples with micro-scale resolution was already foreseen in the original beamline concept. At present, several X-ray techniques such as XRF, XAS, and XRD can be applied to active sample specimen with micron resolution.

Over the past year, several investigations on radioactive samples were successfully carried out at the microXAS beamline. Samples included solidified radioactive waste, irradiated alloys, activated corrosion products (crud), and analogues of the next generation of fuel materials. In most cases, elemental distribution maps were recorded by collecting two-dimensional microXRF data. Following such structural investigations, chemical information was gained by collecting the microXAS spectra at specific locations within the radioactive specimen.

Fig. 8.7 shows some preliminary results of the investigation of an active crud sample. The crud was scraped from a steel surface and consisted of particles and/or splinters. MicroXRF provided information about the elemental composition of each particle. A broad variability in the types of particles could be identified indicating segregation phenomena during the crud formation process. Micro-spectroscopic analysis of individual particles contributes to identifying the chemical identity of the different crud formation products.

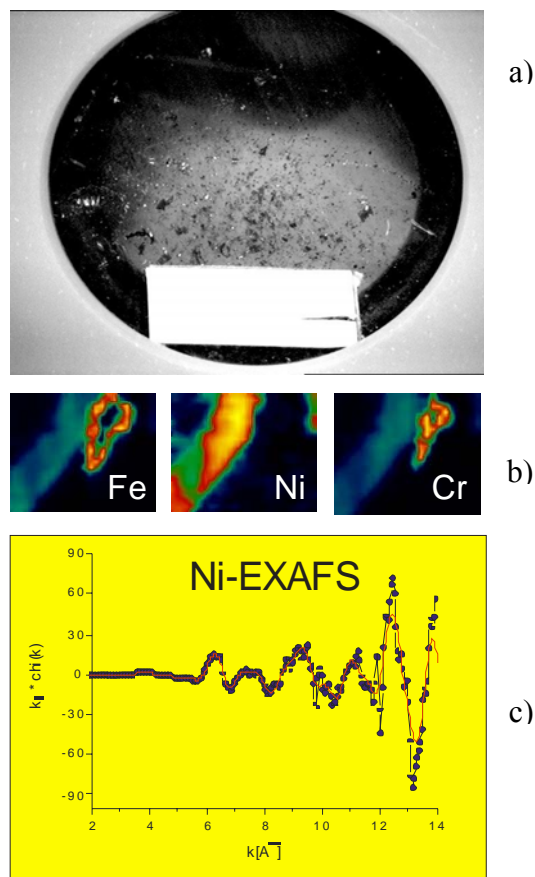


Fig. 8.7: Investigation of radioactive samples. a) Crud particles immobilized in the specialized microXAS samples holder, b) elemental distribution maps of individual crud particles, c) EXAFS spectrum revealing the chemical speciation dominant within a single particle.

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MAASS R., VAN PETEGEM S., GROLIMUND D., VAN SWYGENHOVEN H., UCHIC M.D.¹

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¹ Air Force Research Laboratory, Wright-Patterson, USA

MIBUS J., SACHS S.¹, PFINGSTEN W., NEBELUNG C.¹, BERNHARD G.¹

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¹ FZD, Dresden, Deutschland

PHAM V.-T.¹, GAWELDA W.¹, ZAUSHITSYN Y.¹, KAISER M.¹, GROLIMUND D., JOHNSON S.L., ABELA R., BRESSLER CH.¹, CHERGUI M.¹

Observation of the solvent shell reorganization around photoexcited atomic solutes by picosecond X-ray absorption spectroscopy. *J. Am. Chem. Soc.* 129(6), 1530-1531 (2007).

¹ EPFL, Lausanne, Switzerland

TITS J., IJIMA K.¹, WIELAND E., KAMEI G.¹

Radium binding by calcium silicate hydrates and hardened cement paste. *Radiochim. Acta* 94, 637-643 (2006).

¹ JAEA, Tokai, Japan

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Anion exclusion effects in compacted bentonites: towards a better understanding of anion diffusion. *Appl. Geochem.* 22, 2536-2552 (2007).

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Micro-scale investigations of Ni uptake by cement using a combination of scanning electron microscopy and synchrotron-based techniques. *Environ. Sci. Technol.* 40, 7702-7709 (2006).

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The influence of hydration time on Ni uptake by cement. *Czech J. Physics* 56, D599-D607 (2006).

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YAROSHCHUK A.E., GLAUS M.A., VAN LOON L.R.

Studies of electrochemical properties of compacted clays by the concentration potential method. *J. Colloid Interface Sci.* 309, 262-271 (2007).

9.2 Conference Proceedings

MCDERMOTT C.I.¹, XIE M.¹, KOSAKOWSKI G., METTIER R., MOOG H.², KOLDITZ O.¹

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¹ University of Tübingen, Tübingen, Germany

² GRS, Braunschweig, Germany

PFINGSTEN W., KULIK D.A.

Two alternative geochemical modules used within a reactive transport code - coupling and computing performance investigated for a multi mineral front system. In: P. Gourbesville, J. Cunge, V. Guinot and S.-Y. Liong (eds), 7th International Conference on Hydroinformatics 2006. Research Publishing Services, Singapore, Nice, France, 457-464.

9.3 Conferences/Workshops/Presentations

BORCA C.N., BAC S., FLANK A.-M., LAGARDE P., MEYER B., SCHEIDEGGER A.M., VANTELON D., WETTER R., GROLMUND D., HARFOUCHE M., WILLIMANN M., JANOUSCH M.

LUCIA & microXAS: Enlightening Environmental Problems. SLS Symposium Series, Paul Scherrer Institute, Villigen PSI, Switzerland, 6 February 2007.

BORCA C.N., CANULESCU S., LOVIAT F., LIPPERT T., GROLMUND D., DÖBELI M., WAMBACH J., WOKAUN A.

Analysis of the electronic configuration of the pulsed laser deposited La_{0.7}Ca_{0.3}MnO₃ thin films. European Materials Research Society – EMRS, Strasbourg, France, 27 May - 1 June 2007.

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Electronic configuration of the pulsed laser deposited La_{0.7}Ca_{0.3}Mn_{0.8}Fe_{0.2}O₃ thin films. 6th Summer School on Correlated Electron Materials, Zuoz, Switzerland, 18-25 August 2007.

CUI D.¹, PURANEN A.², SCHEIDEGGER A.M., WIELAND E., SPAHIU K.³

Se-Tc immobilization on the iron canister material under near field conditions. 11th International Conference on “Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere” Migration 2007, Munich, Germany, 26-31 August 2007.

¹ Studsvik Nuclear, Studsvik, Sweden

² KTH, Stockholm, Sweden

³ SKB, Stockholm, Sweden

DÄHN R., BAEYENS B., BRADBURY M.H.

EXAFS study of U(VI) uptake onto illite. DFG-GRK Symposium “Speciation of Radionuclides in the Environment”, University of Mainz, Institute of Nuclear Chemistry, Mainz, Germany, 21 September 2006.

DÄHN R., VESPA M., SHUH D.K.¹, TYLISZCZAK T.¹, WIELAND E.

Soft X-ray-scanning transmission spectroscopy of cementitious materials. Goldschmidt Conference 2007, Cologne, Germany, 19-24 August 2007.

¹ LBNL, Berkeley, USA

DEGUELDRE C.

Colloids studies by single particle analysis and single site modelling. Seminar, University McGill, Montreal, CA, 20 June 2007.

DEGUELDRE C.

Analysis of colloids by ICP-MS in a single particle mode: results on Al₂O₃, gold, and UO₂ colloids, Seminar, University of Berkeley, Berkeley, USA, 3 October 2007.

DEGUELDRE C.

Modelling and testing the colloid generation/elimination dynamic processes toward a pseudo-equilibrium. Colloid Meeting KTH, Stockholm, 15-16 November 2007.

GIMMI T.

DR experiment Mont Terri: Model comparisons and comparisons with first data. ANDRA Haute Marne Underground Research Laboratory, Bure, France, 11-13 June 2007.

GLAUS M.A., MÜLLER W., VAN LOON L.R.

Diffusion of iodide and iodate through Opalinus Clay: Monitoring of the redox state using an anion chromatographic technique. International Workshop on “Mobile Fission and Activation Products in Nuclear Waste (MOFAP)”, La Baule, France, 16-19 January 2007.

GLAUS M.A., VAN LOON L.R., SCHWYN B.¹, VINES S.², WILLIAMS S.J.², LARSSON P.³, PUIGDOMÈNECH I.³

Long-term predictions of the concentration of α- isosaccharinic acid in cement pore water. 31th International Symposium on the Scientific Basis for Nuclear Waste Management MRS 2007, Sheffield, UK, 16-21 September 2007.

¹ Nagra, Wettingen, Switzerland

² NDA, Harwell, UK

³ SKB, Stockholm, Sweden

GLAUS M.A., ROSSÉ R., VAN LOON L.R.

Diffusive properties of stainless steel filter discs before and after use in diffusion experiments with compacted clays. 3rd International Meeting “Clays in Natural & Engineered Barriers for Radioactive Waste Confinement”, Lille, France, 17-20 September 2007.

GONZÁLEZ F., JURÁNYI F., GIMMI T., VAN LOON L.R., UNRUH T.¹

Translational diffusion of water in charged and uncharged clays. 4th European Conference on Neutron Scattering, Lund, Sweden, 25-29 June 2007.

¹ Forschungsneutronenquelle Heinz Maier-Leibnitz, Garching, Germany

GROLIMUND D., VAN LOON L., BORCA C.N., GÜNTHER D., BARMETTLER K.¹, WERSIN P², HEALD S.M.³ (2007)

Contaminant transport in complex heterogeneous geological media: retardation – new insights through micro-imaging and micro-spectroscopy. International Meeting on Mont Terri DI-A, DR field scale experiments, ANDRA Haute Marne Underground Research Laboratory, Bure, France, 11-13 June 2007

¹ ETH, Zürich, Switzerland

² Nagra, Wettingen, Switzerland

³ PNC-CAT, Chicago, USA

HUMMEL W.

Organics & Strategy of TDB update. Meeting of the TDB III ad-hoc group for the preparation of a new phase of NEA TDB. International Workshop on “Mobile Fission and Activation Products in Nuclear Waste (MOFAP)”, La Baule, France, 16-19 January 2007

HUMMEL W.

Tschernobyl und die Folgen aus umweltchemischer Sicht. Habilitationsvortrag, ETH Zürich, 26 January 2007.

KOSAKOWSKI G.

Stirbt das Tote Meer? Habilitationsvortrag, Universität Tübingen, Deutschland, 20. Juni 2007.

KOSAKOWSKI G., GONZÁLEZ F., JURANYI F., GIMMI T.

Water diffusion in clays: Modelling quasi elastic neutron scattering spectra (QENS). 11th International Conference on “Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere” Migration 2007, Munich, Germany, 26-31 August 2007.

KOSAKOWSKI G., GONZÁLEZ F., JURANYI F., GIMMI T.

Molecular modelling of water diffusion in clays: Comparison of simulated and measured quasi-elastic neutron scattering (QENS) spectra. 11th International Conference on “Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere” Migration 2007, Munich, Germany, 26-31 August 2007.

KULIK D., TITS J., WIELAND E.

Aqueous-solid solution model of strontium uptake in C-S-H phases. Goldschmidt Conference 2007, Cologne, Germany, 19-24 August 2007.

KULIK D., TITS J., WIELAND E.

Extension of the C-S-H aqueous – solid solution model for GEM calculations on strontium retention in cementitious media. 11th International Conference on “Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere” Migration 2007, Munich, Germany, 26-31 August 2007.

MANDALIEV P., WIELAND E., DÄHN R., TITS J., CHURAKOV S.V.

Investigation of lanthanide binding mechanisms in 1.13 nm tobermorite and xonotlite. 5th ANKA Users Meeting, Karlsruhe, Germany, 9-10 October 2006.

MANDALIEV P., WIELAND E., DÄHN R., TITS J., CHURAKOV S.V.

Investigation of lanthanide binding mechanisms in crystalline C-S-H phases. Workshop on X-ray absorption spectroscopy and theory of XAS, Villigen PSI, Switzerland, 28 February - 1 March 2007.

MANDALIEV P., WIELAND E., TITS J., DÄHN R., CHURAKOV S.V.

Application of theoretical approaches, XRD and XAFS spectroscopy to identify lanthanide binding mechanisms in C-S-H phases. 12th International Congress on the Chemistry of Cement (ICCCO7), Montreal, Canada, 8-13 July 2007.

MANDALIEV P., WIELAND E., TITS J., DÄHN R., CHURAKOV S.V.

Determination of the uptake mechanisms of Nd(III) on crystalline calcium silicate hydrates (C-S-H). 11th International Conference on “Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere” Migration 2007, Munich, Germany, 26-31 August 2007.

MANDALIEV P., WIELAND E., DÄHN R., TITS J., CHURAKOV S.V.

Nd(III) interaction with cementitious materials. 6th ANKA Users Meeting, Karlsruhe, Germany, 1 October 2007.

MANDALIEV P., WIELAND E., DÄHN R., TITS J., CHURAKOV S.V.

Macroscopic and microscopic investigations of the Nd(III) binding mechanism in calcium silicate hydrates (C-S-H). CEMNET Workshop “Cement Research at Large-Scale Facilities”, Paul Scherrer Institut, Villigen, Switzerland, 10 September 2007.

MARQUES FERNANDES M., BAEYENS B., BRADBURY M.H.

The influence of carbonate complexation on actinide/lanthanide sorption on montmorillonite: surface complexation modeling. 11th International Conference on "Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere" Migration 2007, Munich, Germany, 26-31 August 2007.

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

A time resolved laser fluorescence and x-ray absorption spectroscopy study of lanthanide/actinide sorption on clay minerals: Influence of carbonate complexation. 3rd International Meeting "Clays in Natural & Engineered Barriers for Radioactive Waste Confinement", Lille, France, 17-20 September 2007.

¹ FZK, Karlsruhe, Germany

MAZUREK M.¹, ALT-EPPING P.¹, GIMMI T.,
WABER H.N.¹, BATH A.², BUSCHAERT S.³,
GAUTSCHI A.⁴

Tracer profiles across argillaceous formations: A tool to constrain transport processes. 12th International Symposium on Water-Rock Interaction, Kunming, 31 July-5 August 2007.

¹ University of Bern, Bern, Switzerland

² IntelliSci, Loughborough, United Kingdom

³ Andra, Bure, France

⁴ Nagra, Wettingen, Switzerland

MIBUS J., SACHS S.

Influence of Humic colloids on the Migration of U(VI) in compacted clay. 3rd International Meeting "Clays in Natural & Engineered Barriers for Radioactive Waste Confinement", Lille, France, 17-20 September 2007.

MIBUS J., GLAUS M.A., VAN LOON L.R.

Diffusion of pamam dendrimers in Opalinus Clay. 11th International Conference on "Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere" Migration 2007, Munich, Germany, 26-31 August 2007.

PFINGSTEN W.

The influence of the experimental set-up and the model approach on the determination of diffusion coefficients for radionuclides in laboratory column experiments. 6th Int. Conference on Calibration and Reliability in Groundwater Modelling, Copenhagen, 9-13 September 2007.

PFINGSTEN W., BAEYENS B., JAKOB A., BRADBURY M.H.

Mechanistic sorption models included in reactive transport calculations - new insights with respect to Kd-sorption modelling and competitive sorption effects. 11th International Conference on "Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere" Migration 2007, Munich, Germany, 26-31 August 2007.

THOENEN T.

Uncertainty analysis in geochemical modeling. Progress Meeting Geochemical Analysis of Geochemical Data (GD), BRGM, Orléans, France, 3-4 May 2007.

THOENEN T.

Monte Carlo sensitivity analysis of modelled Opalinus Clay porewaters from the Mont Terri Rock Laboratory. 3rd International Meeting "Clays in Natural & Engineered Barriers for Radioactive Waste Confinement", Lille, France, 17-20 September 2007.

THOENEN T.

Uncertainty analysis in geochemical modeling of clay porewaters using Monte Carlo methods. Workshop "From Experimental Evidences to Reactive Transport Modelling: 10 Years of Geochemical Investigations at Mont Terri", Bure, France, 7-8 November 2007.

TITS J., GEIPEL G.¹, EILZER M.¹, KUNZ D., WIELAND E.

Wet chemistry and time-resolved laser fluorescence spectroscopy investigations of uranyl retention by cementitious materials. 11th International Conference on "Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere" Migration 2007, Munich, Germany, 26-31 August 2007.

¹ FZD, Dresden, Germany

TITS J., FUJITA T.¹, TSUKAMOTO M.¹, WIELAND E.

Uranium(VI) uptake by synthetic calcium silicate hydrates. 31th International Symposium on the Scientific Basis for Nuclear Waste Management MRS 2007, Sheffield, UK, 16-21 September 2007.

¹ CRIEPI, Tokyo, Japan

VAN LOON L.R., JAKOB A., MÜLLER W.

Laboratory diffusion studies at PSI. Annual Meeting on the Mont Terri Diffusion and Retention Project (DR), Bure, France, 11-13 June 2007.

VAN LOON L.R., GLAUS M.A.

Understanding diffusion of radionuclides in argillaceous materials: beyond applying Fick's law. 11th International Conference on "Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere" Migration 2007, Munich, Germany, 26-31 August 2007.

VAN LOON L.R., GLAUS M.A., MIBUS J., BROCKMANN S.¹

The effect of compaction on the retention of sodium, strontium and caesium in compacted Na-bentonite. 11th International Conference on "Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere" Migration 2007, Munich, Germany, 26-31 August 2007.

¹FZD, Dresden, Germany

VAN LOON L.R., GLAUS M.A.

Anion exclusion effects in compacted bentonites: towards a better understanding of anion diffusion. 3rd International Meeting "Clays in Natural & Engineered Barriers for Radioactive Waste Confinement", Lille, France, 17-20 September 2007.

WABER H.N.¹, GIMMI T., SMELLIE J.A.T.²

Large-scale matrix diffusion in crystalline rocks revealed by natural Cl, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ tracers in pore water. Goldschmidt Conference 2007, Cologne, Germany, 19-24 August 2007.

¹ University of Bern, Bern, Switzerland

² Conterra AB, Stockholm, Sweden

WERSIN P.¹, GIMMI T., VAN LOON L., SOLER J.M.², DEWONCK S.³, EIKENBERG J., BAEYENS B., HERNÁN P.⁴

Diffusion of HTO, Br⁻, I⁻, Cs⁺, $^{85}\text{Sr}^{2+}$, $^{60}\text{Co}^{2+}$ and Eu³⁺ in a clay formation: First results from an in-situ experiment in Opalinus Clay. 11th International Conference on "Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere" Migration 2007, Munich, Germany, 26-31 August 2007.

¹ Nagra, Wettingen, Switzerland

² CSIC-IJA, Barcelona, Spain

³ Andra, Bure, France

⁴ Enresa, E-28043 Madrid, Spain

WERSIN P.¹, SOLER J.², VAN LOON L., DEWONCK S.³, EIKENBERG J., BAEYENS B., GROLIMUND D., GIMMI T.

In-situ diffusion test in Opalinus Clay with tritium, anionic and cationic tracers: Comparison with laboratory experiments and modelling. 3rd International Meeting "Clays in Natural & Engineered Barriers for Radioactive Waste Confinement", Lille, France, 17-20 September 2007.

¹ Nagra, Wettingen, Switzerland

² CSIC-IJA, Barcelona, Spain

³ Andra, Bure, France

WERSIN P.¹, GIMMI T., SOLER J.M.², DEWONCK S.³, SAVOYE S.⁴, VAN LOON L.R., EIKENBERG J., BAEYENS B., YANG Q.⁵, SAMPER J.⁵

Diffusion and retention of radionuclides in Opalinus Clay: Results from a long-term migration in-situ test. 11th International Conference on "Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere" Migration 2007, Munich, Germany, 26-31 August 2007.

¹ Nagra, Wettingen, Switzerland

² CSIC-IJA, Barcelona, Spain

³ Andra, Bure, France

⁴ IRSN, Fontenay-aux-Roses, France

⁵ University of La Coruña, La Coruña, Spain

WIELAND E., VESPA M., DÄHN R., GROLIMUND D., SCHEIDEGGER A.M.

The use of X-ray absorption spectroscopy for speciation studies in cementitious systems. 12th International Congress on the Chemistry of Cement (ICCCO7), Montreal, Canada, 8-13 July 2007.

WIELAND E., TITS J., JOHNSON C.A.¹, SCHEIDEGGER A.M.

Uptake of selenite and selenate by cementitious materials. International Workshop on "Mobile Fission and Activation Products in Nuclear Waste (MOFAP)", La Baule, France, 16-19 January 2007.

¹ EAWAG, Dübendorf, Switzerland

9.4 Invited talks

BAEYENS B., BRADBURY M.H.

A quasi-mechanistic modelling approach to trace metal sorption on clay minerals. Interdisziplinäres GraduiertenKolleG GRK 826: "Spurenanalytik von Elementspezies: Methodenentwicklung und Anwendungen" Johannes Gutenberg-University Mainz, Institute of Nuclear Chemistry, Mainz, Germany, 25 April 2007.

BRADBURY M.H., BAEYENS B.

Correspondence between sorption measured on compacted and dispersed systems and sorption model predictions. 3rd International Meeting "Clays in Natural & Engineered Barriers for Radioactive Waste Confinement", Lille, France, 17-20 September 2007.

BRADBURY M.H.

Some aspects of the long term safety of a HLW/SF radioactive waste repository. Vertiefungskurs "Management radioaktiver Rückstände" Nuklear Forum Zürich, Switzerland. 22/23 November 2007.

CHURAKOV S.V. (2007)

Ab initio modelling of cement phases. EMPA, Dübendorf, Switzerland, 22 May 2007.

DÄHN R.

Investigations of the cement heterogeneity using scanning X-ray microscopy (STXM). CEMNET Workshop "Cement Research at Large-Scale Facilities", Paul Scherrer Institut, Villigen, Switzerland, 10 September 2007.

DÄHN R.

Investigations of the cement heterogeneity by scanning transmission X-ray microscopy. CEMNET Meeting, University of Bern, Institute of Geological Sciences, Bern, Switzerland, 14 March 2007.

GROLIMUND D.

Synchrotron based 2D imaging using X-ray fluorescence and absorption. European training school on the analysis of ancient artefacts using synchrotron radiation, SOLEIL Synchrotron Source, Paris, France, 12-16 March 2007.

GROLIMUND D., JANOUSCH M., NACHTEGAAL M. (2007)

The XAS beamlines at the Swiss Light Source (SLS). 2nd Int. Workshop on X-ray spectroscopic and microscopic methods, Paul Scherrer Institut, Villigen PSI, Switzerland, 28 February-1 March 2007.

HUMMEL W.

Geochemische Aspekte in der Sicherheitsanalyse des Schweizer Projekts Opalinuston. Workshop des Verbundprojektes "Wechselwirkung und Transport von Actiniden im natürlichen Tongestein unter Berücksichtigung von Huminstoffen und Tonorganika". 3. Actinidenverbund-Projekttagung, Saarbrücken, Germany, 11-12 October 2007.

KOSAKOWSKI G., GONZÁLEZ F.

Water diffusion in clays: Modelling quasi elastic neutron scattering spectra (QENS). 5. Dezember 2006, LES Palaver, Villigen Switzerland.

KULIK D.A., TITS J, WIELAND E.

Aqueous-solid solution model of strontium uptake in C-S-H phases. Geoch. Cosmoch. Acta 71 (15-S1), Goldschmidt Conference 2007, Cologne, Germany, 19-24 August 2007.

KULIK D.A.

GEM-Selektor code package: History and perspective in GEM chemical thermodynamic modeling. Nanocem Workshop on Chemical Thermodynamic Modelling, EMPA, Dübendorf, Switzerland, 19-20 November 2007.

VAN LOON L.R.

Diffusion of radionuclides in Opalinus Clay: from laboratory to field scale. 3. Actinidenverbund-Projekttagung, Saarbrücken, Germany, 11-12 October 2007.

9.5 Internal reports

AEBERHARD PH., DEGUELDRE C.

Modelling of colloid generation/elimination dynamic processes: toward a pseudo-equilibrium, Technical Report, TM 44-07-01.

9.6 Internal presentations

BAEYENS B.

Geplante Messungen (Sorption/TRLFS/XAS) von Actiniden im Rahmen des INCA-projektes.

CURTIE E.

X-ray spectroscopic studies of corroded Swiss reference glasses.

GLAUS M.

Diffusion von Iodid/Iodat im Opalinuston.

HUMMEL W.

Tschernobyl und die Folgen aus umweltchemischer Sicht.

JAKOB A.

Die Problematik der numerischen Auswertung von Diffusionsexperimenten.

KULIK D.

SSAS Modellierung der Aufnahme von Sr, K, Na durch C-S-H.

MANDALIEV P.

XRD Messungen an Nd dotierten kristallinen C-S-H.

MANDALIEV P.

Nd and Eu immobilisation in crystalline CSH phases.

9.7 Teachings

ALT-EPPING P.¹, GIMMI T.

Geochemical Modelling II: Reactive Transport. Lecture and computer lab (2.25 ECTS, 2h/week), Master Course in Environmental and Resource Geochemistry, University of Bern. Summer Semester 07

¹ University of Bern, Bern, Switzerland

CURTIE E.

Near field processes. Two hours lecture given at the University of Bern in the framework of the Masters programme lecture "Disposal of radioactive waste", SS 2007.

GIMMI T., MAZUREK M.¹, MERCOLLI I.¹, PETTKE T.¹
Fluids in the Crust. Lecture (2.25 ECTS, 2h/week),
Master Course in Environmental and Resource
Geochemistry, University of Bern. Winter Semester
06/07.

¹ University of Bern, Bern, Switzerland

JOHNSON A., HUMMEL W., PLÖTZE L.M.
Landfilling, nuclear repositories and contaminated
sites. Course for Major in Biogeochemistry and
Pollutant Dynamics (Master of Environmental
Sciences) and for Major in Ecological Systems Design
and Waste Management (Master of Environmental
Engineering), ETH Zurich, Autumn Semester 2007.

KOSAKOWSKI G.
Geostatistics I. Lecture series for the course “Masters
in Applied Environmental Geoscience”, University of
Tübingen, Germany, SS 2007.

KOSAKOWSKI G.
Geostatistics II. Lecture series for the course “Masters
in Applied Environmental Geoscience”, University of
Tübingen, Germany, WS 2006/2007.

KULIK D.A.
Participation (invited) in Discussion Meeting on EIL
phenomena and Surface Complexation (discussion
meeting aimed at finding new conventions in surface
chemistry and thermodynamic modelling of
adsorption on oxides), Opatija, Croatia, 7-13 October
2007.

NILSSON A.CH.¹, HEDQVIST I.², DEGUELDRE C.
Granitic groundwater colloids sampling and
characterisation: a strategy for artefact elimination.
Euro Analysis XIV Antwerpen. 9-14 September 2007.

¹ Geosigma, Uppsala, Sweden

² Studsvik, Nyköping, Sweden

9.5 PhD and Diploma Theses

BROCKMANN S.

“Diffusion behaviour of dendrimers: Influence of
molecular size and confinement”. Diplomarbeit
Hochschule für Technik und Wirtschaft Dresden,
Studiengang Chemieingenieurwesen 69 (2007)

GONZÁLEZ F.

“Water diffusion through compacted clays analyzed
by neutron scattering and tracer experiments”. PhD
Thesis, University of Bern, pp. 150 (2007)

HUMMEL W.

Nukleare Umweltchemie: Wissenschaft im Schatten
von Tschernobyl? Antrittsvorlesung, ETH Zürich, 17
October 2007.

HUMMEL W.

Radioactive contaminants in the subsurface: The
influence of complexing ligands on trace metal
speciation. Habilitation Thesis submitted to the ETH
Zurich, Switzerland.

KOSAKOWSKI G.

Transport in fractured media: Concepts, models and
applications. Habilitation Thesis submitted to
Geowissenschaftliche Fakultät, Universität Tübingen,
Tübingen, Germany.

KOSAKOWSKI G.

Modellierung des Radionuklidtransports: Von der
Nanometer zur Kilometerskala., Antrittsvorlesung,
Universität Tübingen, Deutschland, 21. November
2007.

PAUL SCHERRER INSTITUT



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