

Progress Report 2011

Laboratory for Waste Management
Nuclear Energy and Safety Research Department

Cover photo

Main figure: Extended Archie's relation (solid line) describing the relationship between the diffusion accessible porosity and the effective diffusion coefficient including experimental data for several potential Swiss host rocks for a radioactive waste repository (Opalinus Clay, "Brauner Dogger", Effingen Member and Marl of Helveticum).

Other figures: Diffusion set-up used at PSI for measuring diffusion properties of argillaceous rocks.

PAUL SCHERRER INSTITUT



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Preface

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

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

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

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

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1 OVERVIEW

M.H. Bradbury

1.1 Introduction

The progress made in the Laboratory for Waste Management (LES) over the period from January 1, 2011 to December 31, 2011 is summarised in the first part of the report. The activities carried out in the individual groups are described in chapters 2 to 7 and are either predominantly “experimental” or predominantly “modelling” in their nature. However, there are strong interactions between groups and between experimentalists and modellers.

1.2 General

Since October 2008 Nagra and their partners have focused their technical and scientific work on the preparations for Stage 2 of the Sachplan Geologische Tiefenlagerung, SGT (“Sectoral Plan”) in which at least 2 sites each for high-level (HLW) and low- and intermediate-level L/ILW radioactive waste repositories will be chosen from the proposed 6 geological siting regions. An important requirement set by the Swiss Nuclear Safety Inspectorate (ENSI) is that the information available on all of the sites must be sufficient to allow safety analyses to be carried out which adequately represent the conditions at the sites and take into account the existing uncertainties. In response to this requirement, Nagra produced a report evaluating the information for the Provisional Safety Analyses in Stage 2 of the Sectoral Plan. In the meantime ENSI has examined this report in detail and concluded that the necessary geological knowledge can be obtained with the ongoing and planned investigations by Nagra i.e. it will not be necessary in Stage 2 to drill additional boreholes.

The Lab is fully integrated in the geochemical and radionuclide transport activities related to Stage 2 of the Sectoral Plan.

The visitor center at the Mont Terri Underground Laboratory in St. Ursanne (JU) was inaugurated on the 5th September 2011. Planning and construction lasted nearly 2 years and cost 1.7 MSFr. The exhibition serves as a platform for discussions on research in the field of radioactive waste management. The center is jointly managed by three Swiss organizations: swisstopo, ENSI and Nagra.

The Lab is involved in four projects in the 7th EU Framework Programme: “Redox Phenomena Controlling Systems”, ReCosy (finishing date March, 2012), “Processes of Cation Diffusion in Clay Rocks”,

CatClay (finishing date May, 2014), ACTINET I3 (finishing date September, 2012), and “Slow Processes in Close-to-Equilibrium Conditions for Radionuclides in Water/Solid Systems of Relevance to Nuclear Waste Management”, SKIN (finishing date December, 2014), and in a joint programme of work with the Health and Environmental Physics Department, (KFKI Atomic Energy Research Institute) in connection with the Schweizer Erweiterungsbeitrag DEZA/SECO agreement (finishing date October, 2013).

The main multi- and bi-lateral co-operations with external institutions and universities 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 7 th FP (ACTINET-I3, ReCosy, CatClay, SKIN) OECD/NEA (sorption III project) Mont Terri Project (<u>D</u> iffusion <u>R</u> etardation, <u>C</u> ement <u>I</u> nteraction experiments) Grimsel Test Site (<u>C</u> olloid <u>F</u> ormation <u>M</u> igration)
Universities Bern, Switzerland (mineralogy, petrography, water chemistry) Surrey, United Kingdom; EPFL, Switzerland (cement systems, molecular modelling) UC London, United Kingdom (molecular modelling) Mainz, Germany (cement, montmorillonite) Strasbourg, France (glass) Tübingen, Germany (geosphere transport) ETHZ, Switzerland (GEMS)
Research Centres CEA*, France (near and far field) CIEMAT, Spain (colloids) EAWAG, Switzerland (cement) EMPA*, Switzerland (cement) IFR, HZDR*, Germany (XAS, TRLFS) INE, KIT*, Germany (near and far field; TRLFS) KFKI, AEKI, Hungary (argillaceous rocks) SCK/CEN, Belgium (clays) UFZ*, Germany (reactive transport) *formal co-operation agreements

Current PhD and postdoc projects being carried out in LES are listed below:

L. Aimoz (PhD): “Uptake of iodine (I) and selenium (SeO_3^{2-}) onto pyrite and LDHs.” Started September 2008. (Funding: Virtual Institute (INE) / PSI.)

M. Bestel (PhD): “Water dynamics in compacted clay systems.” Started September 2009. (Funding: SNF.) LES participation.

B. Dilnesa (PhD): “The fate of iron during the hydration of cement”. Started February 2008, (Funding: SNF). LES participation.

F. Hingerl (PhD): “Simulation of geochemical processes in Enhanced Geothermal Systems (EGS).” Co-operation between LES and the Institut für Isotopengeologie und Mineralische Rohstoffe, ETHZ. Started: October 2008. (Funding: Competence Center for Environment and Sustainability.)

D. Soltermann (PhD): “The influence of Fe(II) on clay properties, the sorption of Fe(II) on clays and competitive sorption investigations: a combined macroscopic and microscopic study.” Started: August 2010. (Funding: SNF.)

H. Wang (PhD): “A novel *Micro Beam Analysis Alliance* (MBA²) strategy for micro-heterogeneous systems.” Started: September 2009. (Funding: SNF.) LES participation.

Dr. M. Tyagi (postdoc): “Up-scaling modeling molecular diffusion coefficients using mesoscopic transport models. Multi-scale modeling of diffusion in clays – From molecular simulations to the continuum scale.” Started: July 2010. (Funding: PSI FoKo FK.)

Dr. B. Thien (postdoc): “Development of new theoretical approaches to geochemical modelling of slow, kinetically controlled radionuclide uptake by (re)crystallizing host minerals.” Started: 1 February 2011. (Funding: 7th EU Framework Programme, SKIN project.)

Dr. L. Pegado (postdoc): “Stable phase composition in cementitious systems: C-A-S-H.” Started: November 2010. (Funding: SNF-Sinergia project.)

Dr. P. Schaub (postdoc): “Application and development of a micro diffraction synchrotron-based approach for the characterization of complex materials in radioactive waste management.” Started: 1 September 2011. (Funding: NES.)

1 PhD and 1 postdoc supervised by Dr. Faux (Physics Dep., Uni. Surrey, UK) and S. Churakov (LES) within a joint international project on “Water transport in cements: A bottom – up approach based on NMR relaxation and imaging analysis and numerical

modelling”. Lead taken by Prof. P. McDonald from Uni. Surrey, UK.

Candidates for the following three PhD projects, partially funded by Nagra, are currently being sought:

“Porosity and structural changes at clay-cement interfaces and their relations to transport properties.” (This project was accepted as a “PSI Cross proposal” in collaboration with the Neutron Activation and Imaging Group (NUM).)

“Retardation of low molecular weight organic compounds in clays (ROLOC).”

“Experimental benchmarks for verification and validation of reactive transport codes.”

It is worthwhile noting that the majority of the fundings for postdocs and PhDs comes from additional (non Nagra) external sources.

Dr. T. Ishidera, (Guest Scientist) returned to JAEA, Japan, in March 2011.

Dr. N. Diaz (postdoc) and Dr. M. Hayek (postdoc) completed their projects in March 2011 and November 2011, respectively. Dr. Hayek has since taken up a position with AF Consulting, Baden, Switzerland.

LES took part for the first time in a NES internal competitive activity for funding from Swissnuclear. A joint proposal with the Hot Laboratory entitled: “Investigations on the chemical speciation of C-14 released from activated steel: Development of the analytical methods for speciation studies and the set-up for long-term corrosion experiments” was submitted and accepted. The funding is initially for 2 years for a project which is planned to last for 6 years.

During 2011 members of LES continued to participate in international technical review groups: (i) “SARG (SFR extension, Application Review Group)”, SKB, Sweden (ii) “Expert Panel on Radionuclide Migration in Plastic Clay”, Ondraf/Niras and SCK-CEN, Belgium (iii) “Near surface disposal of Category A waste at Dessel”, Ondraf/Niras, Belgium and (iv) Expert elicitation group, “the selection of solubility and sorption data”, Posiva, Finland.

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

The Waste Management Program Committee did not meet in 2011. Instead, LES underwent a Scientific Evaluation on 2/3 March 2011 at the request of the ETHZ Council. (Eventually, such evaluations of all the larger Labs within PSI will take place.) In addition to Programme Committee Members, the Evaluation Committee consisted of Professor S. Clark, Washington State University (chair) and Professor L. Diamond, University of Bern. The aim was to evaluate LES in terms of its overall scientific performance during the past 5 years and its scientific strategy and plans for the coming 5 years. In particular, the committee was asked to assess the scientific independence of the research carried out by the Lab. The findings of the committee were formally communicated to the PSI Director and the ETH Council in a written report.

The assessment of the Lab's performance over the past 5 years, and the prospects for the next 5 years, were judged very positively. The committee members and Profs. Clark and Diamond are thanked for their participation in the evaluation and the recommendations contained in their report.

1.3 Sachplan Geologische Tiefenlager, SGT ("Sectoral Plan")

For Stage 2 of the Sectoral Plan a whole series of provisional safety analyses are foreseen for the rock types under consideration. Detailed, host-rock specific information and data bases will be required. The Lab has already completed, or is in the process of completing, scientific reports in support of the safety analyses. Some of the most important topics treated in these reports are listed below:

- Documentation of the Nagra/PSI TDB update 2009.
- State-of-the-art report on diffusion in argillaceous rocks.
- Sorption (incl. diffusion) in a cementitious near field.
- Solubility limits in a cementitious near field.
- Sorption (incl. diffusion) in bentonite.
- Solubility limits in a SF/HLW near field (bentonite).
- Sorption (incl. diffusion) in the geosphere: OPA, Effingen Member, "Brauner Dogger" and Marl of Helveticum.
- Review of the chemistry of safety-relevant nuclides (L/ILW repository).

- Colloid behaviour in the geosphere: Opalinus Clay, Effingen Member, "Brauner Dogger", Marl of Helveticum.

Porewater chemistry calculations for MX-80 bentonite and Opalinus Clay using the GEMS code were carried out in which the masses and chemical properties of the clay minerals in each system were taken into account. The driving force for this approach was that coupling chemistry and transport models calls for chemical systems to be defined as realistically as possible concerning masses and volumes. The results from this new approach were compared with those using more conventional approaches to estimate uncertainty ranges in the calculated porewater chemistries.

SDBs are being produced using the new procedures developed during Stage 1 of the Sectoral Plan, and in order to check the values derived. An extensive sorption programme on the various potential host rock types was started in 2011. A report on the experiments, and the results of the comparisons, will be completed in the latter half of 2012. In addition, an assessment on the influence of competitive sorption effects on the magnitude of sorption values in the SDBs is in preparation and will be completed in spring 2012.

Two major reports on the chemical evolution of the cementitious L/ILW near field (caverns, surrounding host rock, backfilled access tunnels), and the chemical evolution of the HLW near field (tunnels, bentonite backfill, surrounding host rock) were completed in 2011.

Additional diffusion measurements on Effingen Member, Marl of Helveticum and "Brauner Dogger" confirmed the validity of the extended Archie's relation and provided increased confidence in its use in safety analysis for estimating diffusion coefficients.

An assessment was made of the interaction of waste materials with cement and the sorption reduction effects resulting from the presence of complexing ligands such as isosaccarinic acid.

As in the past few years, the majority of the efforts in LES in 2011 were directed towards work related to the Sectoral Plan. This trend is expected to continue in the medium term.

1.4 Foundations of repository chemistry

Extensive speciation calculations were carried out as part of the development work for SDBs for the potential host rocks Opalinus Clay, “Brauner Dogger”, Effingen Member, Marl of Helveticum, and cementitious systems. In the latter case, speciation calculations were made for cement porewaters with various salinities (ionic strength up to 1.3 mol kg^{-1}) in order to assess the potential influence of high salinity ground waters on the sorption in cementitious systems.

Thermodynamic data were compiled for Ag, Co, Cd, Pb, Sb, Hf, Sm, Ho, Pa, Mo, Be and Bi, which are not currently contained in the PSI/Nagra Chemical Thermodynamic Database. A literature survey on Polonium-210 yielded only sparse data which were nevertheless sufficient to indicate that Po(IV) is the most stable redox state in aqueous solutions and that Th is the closest chemical analogue.

After 12 years leaching at 90°C , micro-XRF maps showed that the cerium in the MW simulated nuclear waste glass remained as Ce(IV) in the unaltered glass, but was present as Ce(III) at corroded grain boundaries associated with secondary Mg-clay formed as the main glass alteration product. The reduction of Ce(IV) was probably mediated by Fe(0) from the steel reaction vessel. These results, in conjunction with a comparison between the Eh–pH diagrams for Ce and Pu, revealed that the reduction of Pu(IV) to Pu(III) would require considerably stronger reducing conditions than Ce(IV) to Ce(III) and therefore it was concluded that Ce is not a good chemical analogue for Pu.

The potential uptake of long-lived anionic radionuclides such as ^{129}I , ^{79}Se , and ^{99}Tc by “positively charged” minerals such as AFm or AFt phases in a cement-based repository is an important issue. Radiotracer experiments, powder X-ray diffraction, and extended X-ray absorption fine structure spectroscopy were used to obtain a molecular-level understanding of the uptake mechanisms of iodide by such cement minerals. The results indicate the formation of a stable solid solution between AFm- I_2 and AFm- SO_4 and explain the preferential uptake of iodide at trace-level by AFm- SO_4 , and the lack of uptake by AFm- Cl_2 and AFm- CO_3 which do not form solid solutions with AFm- I_2 .

Irreversible trace element uptake in minerals is a potentially important retention mechanism in waste repository geochemical systems. It cannot be

predicted using simple aqueous solid-solution models, and kinetic processes need to be considered. In this context, three kinetic models of trace element uptake in minerals were compared in preparation for inclusion into the geochemical code GEMS.

Spectroscopic studies and atomistic simulations of (hydr)oxide surfaces have corroborated the use of multi-dentate surface species in aquatic surface complexation models. The work on thermodynamic sorption modelling and the development of theoretical conversions of intrinsic adsorption constants between different site densities, ‘denticities’, and concentration scales has continued.

1.5 Repository near field

1.5.1 Clay systems

The influence of competitive sorption on radionuclide uptake in the near- and far-fields of a radioactive waste repository have, as yet, not been properly assessed. Experimental work has been carried out on montmorillonite and illite to characterise the effects of competitive sorption. The understanding gained will be used to bound its influence on the sorption values in SDBs.

In connection with the above, and because “iron” is present everywhere in the repository system, a study, centred on a PhD project, is investigating the sorption of Fe(II) on montmorillonites from various sources under controlled redox conditions.

The nature of the surface complexes of Am(III) on montmorillonite, formed in the absence and presence of inorganic carbon, were investigated further. P-EXAFS measurements performed on $^{243}\text{Am(III)}$ loaded self-supporting film samples confirmed the previous interpretation from batch sorption experiments and modeling that ternary Am-carbonate complexes are formed at the surface of montmorillonite.

A concept has been previously described that allowed up-scaling of local pore scale diffusion coefficients for a given pore space model. In order to make this concept generally applicable to different clay types, an operational algorithm has been developed which allows the generation of clay pore structural maps based on a knowledge of the mineralogical components and macroscopic properties such as porosity, mean grain size, and grain and pore size distributions.

In order to investigate further the diffusion mechanisms in compacted clay systems some very interesting diffusion experiments have been carried out with a salt gradient across a compacted montmorillonite sample. After equilibration with 0.1 M NaClO₄ on one side, and 0.5 M NaClO₄ on the other side, of the diffusion cell, ²²Na⁺ was added to both reservoirs to give equal activities in the two compartments. The result was that the concentration of ²²Na⁺ in the 0.5 M NaClO₄ compartment gradually increased, while that in the 0.1 M NaClO₄ decreased, which is opposite to what would be intuitively expected. An explanation has been proposed based on the main diffusion path way being the interlayer space where the “driving force” is the sorbed ²²Na⁺ (“sorption enhanced diffusion”). Experiments and modelling are continuing.

The long term effects of the interaction of near-field components with one another and with the host rock, have become, and will remain, an important activity in LES. Modelling the interactions in systems such as cement/clay host rock, cement/sand-bentonite backfill, cement/bentonite backfill, etc. requires sophisticated reactive transport codes and thermodynamic models with a consistent setup for concretes, bentonite, Opalinus Clay and other potential host rocks. Gas and radionuclide transport are two important processes which can be significantly influenced by the “clogging” of pore spaces resulting from dissolution / precipitation effects arising from the contact between two chemically dissimilar assemblages e.g. bentonite and cement. An important piece of information missing is the relation between changes in diffusion/permeability as a function of porosity as the clogging reactions proceed. In order to try to fill this gap in our knowledge a new research project will be started in 2012 involving a co-operation between the Transport Mechanisms Group, the Diffusion Processes Group and the University of Bern. In addition, the work will be supported by two PhD projects.

1.5.2 Cement

In the sulfate-resisting Portland cement CEM I 52.5 N HTS, Lafarge, France (currently used for the conditioning of radioactive waste in Switzerland), calcium silicate hydrate (C-S-H) phases in hardened cement paste (HCP) are considered to control the immobilisation of metal cations, while the AFm (Al₂O₃-Fe₂O₃-mono) and AFt (Al₂O₃-Fe₂O₃-tri) phases control anion binding.

Since the planned L/ILW repository could be located in a geological formation with significant Cl⁻

concentrations in the groundwater, sorption studies with the dose determining isotopes of Cl⁻, I⁻ and Se(IV) on HCP, and other cement minerals, under saline conditions were carried out. (Note that HCP exposed to highly saline groundwater is subject to mineral transformations.) The measurements show that ³⁶Cl and ¹²⁵I are taken up selectively by just a few minerals, in particular Friedel’s salt (AFm-Cl₂) in the case of ³⁶Cl and calcium monosulfoaluminate (AFm-SO₄) in the case of ¹²⁵I. ⁷⁵Se is taken up by all phases, and even binds strongly to most of them. The negative influence of increasing Cl⁻ concentrations on ¹²⁵I uptake by fresh and degraded HCP is significant, while the effect on ³⁶Cl and ⁷⁵Se binding is much weaker.

The Np(IV,V,VI) uptake by HCP and C-S-H phases under oxidizing, anoxic and reducing conditions was investigated. The experiments were carried out using the short-lived ²³⁹Np isotope (t_{1/2} = 2.355 days), Na-dithionite as a reducing agent in the case of Np(IV) and Na-hypochlorite as an oxidizing agent in the case of Np(VI). No redox buffer was used in the experiments with Np(V). The sorption of Np(IV,V) was generally very high (10⁵ – 10⁶ L kg⁻¹) in the pH range 10 to 13. The sorption of Np(VI) was equally high in the pH range 10-11 and decreased thereafter to ~5 x 10⁴ L kg⁻¹ at pH ~ 12.5. The observations suggest that variations in the C:S ratio have little effect on the uptake processes and that the aqueous speciation is far more important. Also, an incorporation mechanism is considered to control the uptake of Np(V,VI) by C-S-H phases in a manner similar to that identified for Np(IV).

¹⁴C, possibly in the form of small organic molecules generated during steel corrosion, is a potential major contributor to the dose released from the L/ILW repository. A programme of work has begun focused on 1) the determination of the chemical nature of the ¹⁴C containing organic compounds released during steel corrosion under reducing conditions, and 2) an evaluation of the long-term chemical stability of these compounds under the alkaline conditions of a cementitious near field. In 2011 a high performance ion exclusion chromatography – mass spectrometer system was installed, which allows oxygenated low molecular weight (LMW) organic compounds to be identified. Analytical protocols for the detection of LMW carboxylic acid and aldehydes (C ≤ 5) using mass spectrometry and conductivity detection methods are also currently being developed and assessed. Gas tight autoclave cells have been evaluated and purchased for the long-term chemical stability studies.

The LES-hosted sub-project, “Thermodynamic equilibrium in C(-A)-S-H from molecular simulations”, within the three year program SNF-funded Sinergia project, is aimed at investigating the influence of aluminium substitution in C-S-H phases on alkali and alkaline ion sorption using *ab initio* calculations, classical atomistic molecular dynamics (MD) simulations, and Grand-Canonical Monte Carlo (GCMC) simulations of ion sorption.

1.6 Repository far field

Diffusion measurements with HTO, $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ on the potential host rocks Marl of Helveticum, “Brauner Dogger” and Effingen Member were used to confirm/check the validity of the extended Archie’s relation over a wide range of porosities for estimating effective diffusion coefficients to be used in performance assessment studies. The $^{36}\text{Cl}^-$ diffusion measurements on samples of Effingen Member showed that the anion accessible porosity was 50% of the total porosity, and not 25% as estimated from previous water activity measurements. Additional measurements on new samples of Effingen Member confirmed the result. The porosity value is a critical parameter in the derivation of porewater compositions.

The diffusion profiles of $^{60}\text{Co(II)}$ in OPA showed two regions. The reactive transport code MCOTAC was used to model several possible physical and chemical processes which could explain the observed Co concentration profiles e.g. competitive sorption between Co and the intrinsically present Fe(II), surface complexation kinetics and a mismatch between the clay pore water and the diffusion cell reservoir water with respect to concentration gradients for Fe and pH. None of these variations could explain the observed Co profiles. The modelling exercise did however indicate that the 40 days usually used to equilibrate the sample with the reservoir concentration was not long enough. Finally, a 2-D model setup assuming a heterogeneous distribution of sorption sites within the clay sample could be made to agree with the measured two stage Co concentration profile, but such an assumption would have to be justified experimentally. Alternatively, since two sorption mechanisms contribute to the uptake of Co on OPA, i.e. ion exchange and surface complexation, two different pathways could be involved in the diffusive transport, one involving diffusion in the external pore space and the other involving ‘sorption-enhanced diffusion’ in the interlayer space (see section 7.5). The modelling work is on going.

An experimental programme is in progress whose aim is to provide support for the SDBs produced for the Provisional Safety Analyses in Stage 2 of the Sectoral Plan. Sorption isotherms of selected radionuclides i.e. Cs(I), Ni(II), Co(II), Eu(III), Th(IV) and U(VI) are being measured on samples of the host rocks under consideration. The measurements on the Effingen Member have been completed. The measurements on “Brauner Dogger” and Marl of Helveticum are on going. Data sets already exist for MX-80 bentonite. As mentioned in section 1.3, the idea is to make a comparison between the predicted values contained in the SDBs and the corresponding measured values with the aim of increasing the confidence in the sorption values in the SDBs.

The predictive capabilities of the two site protolysis non electrostatic surface complexation and cation exchange model have been examined in a blind test exercise against sorption isotherms for Eu(III), Th(IV) and U(VI) measured on MX-80 bentonite and Opalinus Clay following the so called “bottom up” approach. The measurements cover over 4 orders of magnitude of aqueous metal equilibrium concentrations and the agreement between modelled and experimental data is good to very good, with the calculated values lying, in most cases, within the experimental error bars.

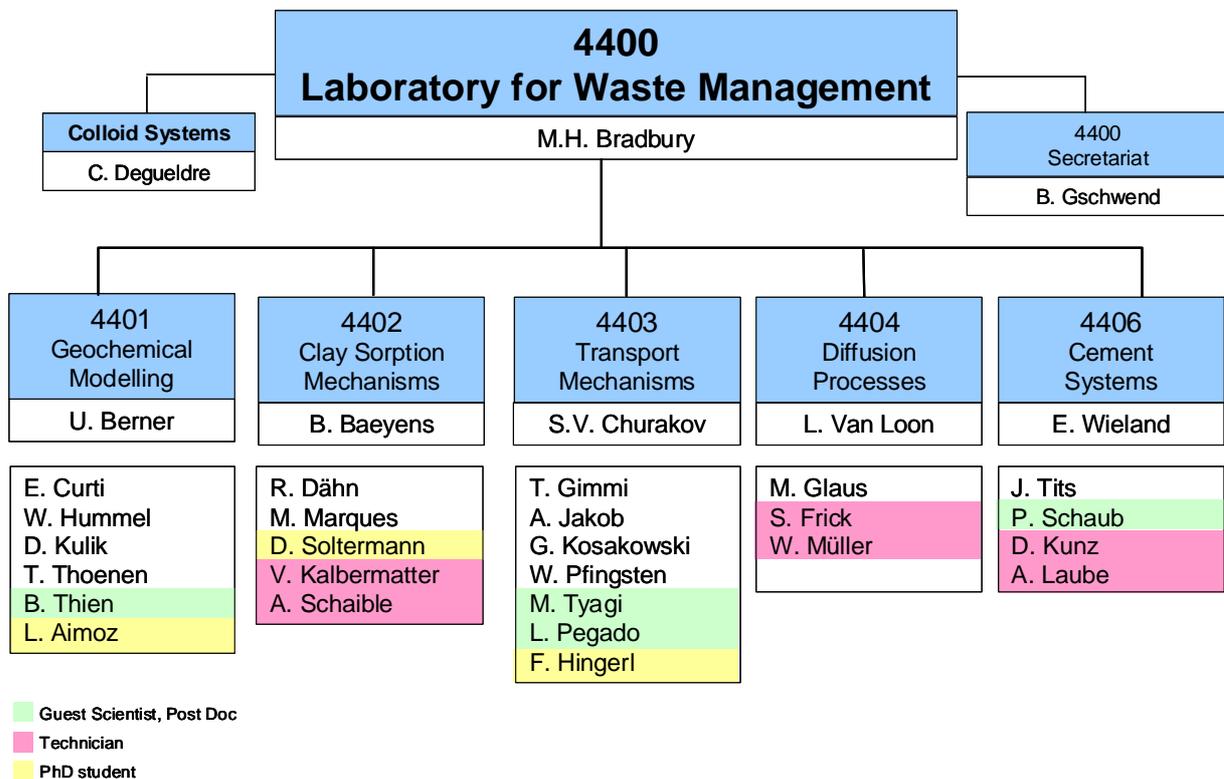
A fairly large modelling effort was devoted to the current and planned diffusion experiments at Mont Terri. Scoping calculations were performed for the DR-A experiment which started in November 2011. HTO, ^{85}Sr , ^{60}Co , Cs, Eu, I, and Br tracers have been added in an artificial pore water in a packered off section of the borehole. At some later stage it is planned to exchange the tracers pore water with a somewhat different artificial pore water, again tracers, to create a chemical disturbance. The ability of geochemical models to simulate the measured changes will be tested. To support the planning of a possible long-term diffusion experiment (DR-B), a series of scoping calculations was carried out using a conservative tracer and a time span of 20 years. For a borehole axis crossing the clay bedding plane at an angle of roughly 45 degrees, the full geometrical complexity in 3D was taken into account in the calculations.

The benchmarking of codes in use in LES is an on going process. Recently, clogging (i.e. the strong reduction of porosity) has received special attention in transport modelling of cement-bentonite interfaces. Numerous claims that reactive transport codes can solve the reaction transport problem with feedback on

porosity need to be validated against analytical solutions. Over the last two years a postdoc, Mohamed Hayek, has derived analytical solutions for multi-component transport coupled to a single precipitation/dissolution reaction in one, two and three dimensions. One of the proposed analytical solutions has been used to compare numerical solutions obtained from two conceptually different reactive transport codes: a commercial finite element code COMSOL-Multiphysics and open access finite elements code OpenGeoSys. The numerical results obtained agreed well with the analytical solutions for spatial and temporal evolution of concentrations and porosities.

Also, the LES in-house code, MCOTAC, and COMSOL Multiphysics, were benchmarked using the case of Cs through-diffusion in an Opalinus Clay sample, taking into account the non-linear sorption of Cs. Results from both codes for through-diffusion times, as well as Cs concentration values, agreed well for a wide range of initial Cs concentrations (10^{-3} – 10^{-7} mol/l) assumed to be constant at one boundary of the sample, even though COMSOL and MCOTAC use different spatial discretisation schemes, different strategies for solving the diffusion equation and different implementations of the non-linear sorption isotherm.

Table 1.2: LES Organigram, December 2011



2 GEOCHEMICAL MODELLING

W. Hummel, U. Berner, E. Curti, D. Kulik, T. Thoenen, B. Thien (postdoc), L. Aimoz (PhD)

2.1 Overview

A large part of the geochemical modelling group's work in 2011 was related to the Swiss Sectoral Plan (*Sachplan*) for deep geological disposal. This work comprised of model calculations and extensive literature reviews which contributed to two Nagra Technical Reports on the geochemical evolution of the near-field of planned geological repositories for spent fuel/high-level waste and intermediate-level waste. Further topics related to the Swiss Sectoral Plan explicitly mentioned here are:

- Thermodynamic data evaluation and speciation calculations related to the development of solubility and sorption databases.
- The LES definition of the Opalinus Clay pore water.
- Bentonite pore water calculations.
- Ce(III/IV) mobilization and co-precipitation during aqueous corrosion of simulated nuclear waste glass.

Progress in the field of trace element behaviour was made in the framework of a PhD and a postdoc project (L. Aimoz and B. Thien).

- A structural study on iodide uptake by AFm phases indicates the formation of a stable solid solution between AFm-I₂ and AFm-SO₄. The latter phase could act as a potential sink for ¹²⁹I in the cement-based engineered barrier of a nuclear waste repository.
- Kinetic models of trace element uptake in host minerals were compared.

Furthermore, advances in thermodynamic sorption modelling have been achieved with the development of theoretical conversions of intrinsic adsorption constants between different site densities, denticities, and concentration scales. Proposals are made how to define the conventional standard site density for multi-dentate surface species.

2.2 Work related to the Sectoral Plan

2.2.1 Thermodynamic data and speciation calculations

In support of the development of sorption databases to be used in Stage 2 of the Sectoral Plan, numerous speciation calculations covering all safety-relevant radionuclides were performed for Opalinus Clay, "Brown Dogger", Effingen Member, and Helvetic Marl porewaters.

In addition, speciation calculations were made for various cement porewaters with normal and high salinities (ionic strength of 1.3 mol kg⁻¹), as part of the assessment of the sorption properties of cementitious materials in contact with the high salinity variant of the Effingen Member porewater.

Since several of the safety-relevant radionuclides are not contained in the PSI/Nagra Chemical Thermodynamic Database, thermodynamic data were compiled (but not reviewed) for Ag, Co, Cd, Pb, Sb, Hf, Sm, Ho, Pa, Mo, Be, and Bi. Data files were prepared for use with PHREEQC and GEMS.

Polonium-210 is a radionuclide whose thermodynamic behaviour was thought to be unknown because of a total lack of data in thermodynamic databases. A literature review revealed sparse data on the solubility and hydrolysis of Po but which, unfortunately, were too inconsistent to derive equilibrium constants. However, the data were sufficient to conclude that Po(IV) is the most stable redox state in aqueous solutions and that Th would be the closest chemical analogue concerning solubility and sorption behaviour.

2.2.2 LES definition of the Opalinus Clay pore water

The Opalinus Clay pore water for use in the ongoing Sectoral Plan has been defined by MÄDER (2009) in accordance with, and from a conceptual point of view compatible with, earlier models from NAGRA (2002) and PEARSON (2002). In principle, the water composition relies on saturation of calcite, dolomite, quartz, celestite, siderite and pyrite in 160 mmol/kg_{H2O} of NaCl at log₁₀(pCO₂) = -2.2 and at [SO₄²⁻]/[Cl⁻] = 0.155. In this water, a key parameter in defining the pH (7.20) and the carbonate system is the arbitrarily set partial pressure of CO₂ (pCO₂). Note that this

arbitrarily set $p\text{CO}_2$ is consistent with the phase rule. MÄDER (2009) varied $\log_{10}(p\text{CO}_2)$ from -1.8 to -2.8 and calculated pH values ranging from 7.00 to 7.51 at constant ionic strength.

Coupling chemistry and transport models calls for chemical systems as realistic as possible concerning masses and volumes. Therefore, an alternative Opalinus Clay pore water model was set up including, in addition, the masses and chemical properties of the minerals illite, kaolinite and montmorillonite (and barite), which all together make up more than 50 % w/w of the measured Opalinus Clay phase assembly. Different from the model of MÄDER (2009), an ideal solid solution model consisting of seven montmorillonite end-members was used to represent cation exchange.

The resulting pore water, based on the same starting conditions (ionic strength and $\text{SO}_4^{2-}/\text{Cl}^-$ ratio) is nearly identical with the MÄDER (2009) water (see BERNER & KOSAKOWSKI, 2011 for details). In the LES set up it is no longer allowed to freely set $p\text{CO}_2$. The extended phase assembly constrains the arbitrary chemical parameters to $[\text{Cl}^-]$ and the $\text{SO}_4^{2-}/\text{Cl}^-$ ratio. The former free key parameter $p\text{CO}_2$ is now defined by the extended phase assembly, which again is consistent with the phase rule.

In this system $[\text{Cl}^-]$ was varied in the range 60 mmol/kg_{H₂O} (minimum content in Opalinus Clay pore water) to 580 mmol/kg_{H₂O} (high saline Mt. Russelin variant; MÄDER, 2009) and as a second dimension the $\text{SO}_4^{2-}/\text{Cl}^-$ ratio from 0.017 (celestite becomes unstable) to 1.04 (limited by gypsum precipitation). The thus modelled Opalinus Clay systems revealed a remarkable robustness, apart from the changing starting conditions. Amounts of phases and the cation exchange capacity did not vary. The $\log_{10}(p\text{CO}_2)$ varied in the very narrow range -2.3- -2.31, pH in the range 7.63-6.91 and ionic strength between 74 and 690 mmol/kg_{H₂O}. Both, $[\text{Ca}^{2+}]$ and $[\text{Mg}^{2+}]$ varied in the range 1-50 mmol/kg_{H₂O}.

How are differing $p\text{CO}_2$ values obtained, which are comparable to the ranges explored in MÄDER (2009), in this (obviously robust) chemical system when $\log_{10}(p\text{CO}_2)$ cannot be set as a parameter in the model calculation? Variations in $p\text{CO}_2$ are obtained with modified system mass balances. $\log_{10}(p\text{CO}_2) = -1.8$ was modelled when “adding” 175.5 mmol of CO_2 to 1000 cm³ (2535 g) of the Opalinus Clay reference system, and vice versa $\log_{10}(p\text{CO}_2) = -2.8$ when “removing” 142.5 mmol of CO_2 . The resulting pH range is now 7.82-7.29.

The unexpected result is an increase in pH when adding the acid “ CO_2 ”. The detailed analysis reveals that significant amounts (~40 %) of montmorillonite convert to kaolinite, quartz, dolomite, siderite, illite and additional pore solution (from water chemically combined with montmorillonite). Due to the absence of a second sodium carrying phase, the charge of the Na^+ released from the smectite needs to be compensated by significantly increased concentrations of CO_3^{2-} and SO_4^{2-} . This in turn forces some oxidation of pyrite to provide the necessary sulphate, and reduces the Eh by about 40 mV. The ionic strength increases from 0.23 to 0.30 mol/kg H₂O, and the anion accessible porosity increases by 40 % at constant total porosity. The cation exchange capacity decreases from 101 to 58 mmol/kg_{OPA}. Note that all reactions proceed in reversed order when removing CO_2 to obtain $\log_{10}(p\text{CO}_2) = -2.8$.

Based on this sensitivity analysis, the key importance of the solid phase selection on the pore water composition is evident. It is also recognized that the partial pressure of CO_2 is most likely not a freely “settable” parameter in these complex systems, but is determined by the solid phase assembly, provided that the system behaves according to the assumptions of thermodynamic equilibrium. However, the above phase assembly cannot yet be considered as the final conclusion. It is not a priori understandable why small amounts of added CO_2 (0.3 %) should induce the modelled substantial rearrangement in the phase assembly. It is suspected that a complementary sodium-controlling phase would be essential in order to increase the modelled system robustness against changes in the chemical input parameters. This will certainly be a topic for further developments.

2.2.3 Bentonite pore water calculations

In the framework of activities in Stage 2 of the Sectoral Plan, pore water compositions in equilibrium with compacted bentonite under repository conditions have been derived using a novel approach in which montmorillonite is treated as a multicomponent solid solution phase that may undergo dissolution/precipitation reactions, as described in the preceding section. For comparative purposes additional calculations have been performed by applying the model used in a previous safety assessment (“Opalinus Clay Project”, OCP), however using more realistic assumptions and thermodynamic data. Specifically, it was assumed that the reacting Opalinus Clay pore water penetrates into the anion accessible porosity (5 % of the total volume) only after the montmorillonite interlayer becomes saturated via vapour adsorption. In addition, attempts have been

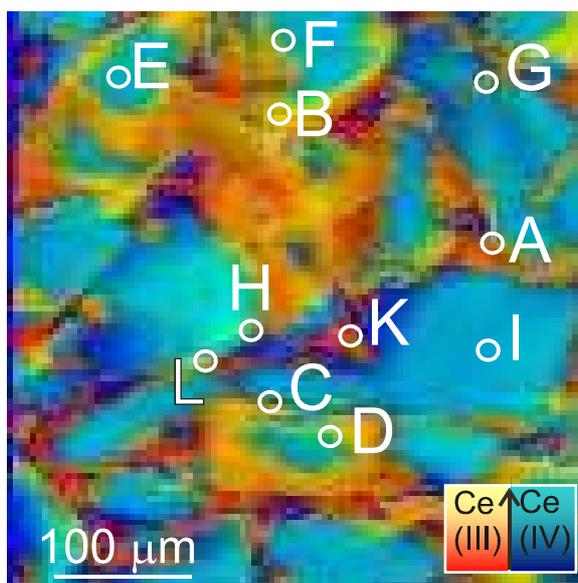
made to model uncharged pore water in conjunction with a diffuse double layer, using the model of BORKOVEC & WESTALL (1983).

The conventional (OCP) model differs from the novel approach in as much as it treats montmorillonite as a pure exchanger phase with a fixed number of surface sites without accounting for precipitation / dissolution reactions. Moreover, in the OCP model equilibrium between the aqueous solution-bentonite system and a fixed CO_2 partial pressure ($10^{-1.8} - 10^{-2.8}$ bar, from the original OPA porewater) is assumed, leading to significantly lower pHs (7.0 – 7.4 vs. 7.75).

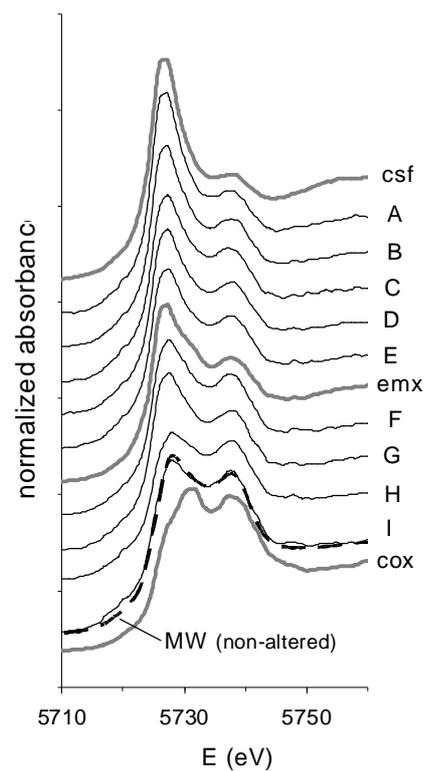
Calculated redox potentials also differ slightly (-0.178 V to -0.150 V vs. -0.198 V) by virtue of a different choice of Eh-buffering phases. The elemental compositions of the two types of water are nevertheless similar, and differences in concentrations of major species do not exceed one order of magnitude.

2.2.4 Ce(III/IV) mobilization and co-precipitation during aqueous corrosion of simulated nuclear waste glass

The microscopic distribution and oxidation state of Ce in the MW (Magnox Waste) simulated nuclear waste glass were studied using micro-XRF mapping techniques and micro-XANES after 12 years leaching at 90°C in initially pure water (CURTI et al., 2011). The micro-XRF maps revealed that Ce, initially present as oxidized species (Ce^{IV}) in the pristine glass, was partly reduced and re-immobilized as Ce^{III} during the aqueous corrosion process, preferentially at grain boundaries or in the interstitial spaces between the glass particles (Fig. 2.1a). The Ce^{III} abundance was found to spatially correlate with the distribution of secondary Mg-clay formed as the main glass alteration product during the aqueous corrosion. Micro-XANES spectra collected at locations representative of both altered and non-altered glass domains confirmed the findings obtained by the redox mapping (Fig. 2.1b).



(a)



(b)

Fig. 2.1: (a) Redox map showing Ce^{III} and Ce^{IV} prevalent regions in altered MW glass. (b) Micro-XANES spectra of locations shown in map (A-I) compared to those of reference compounds (csf = $\text{Ce}^{\text{III}}_2(\text{SO}_4)_3$, cox = $\text{Ce}^{\text{IV}}\text{O}_2$, emx = equimolar mixture of the two latter compounds). The spectrum of non-altered MW glass (thick broken line) is superposed to the XANES of spot I.

Because redox-sensitive elements in the pristine MW glass (Fe, Cr, Se) occur almost exclusively as oxidized species, reduction of Ce^{IV} was probably mediated by an external source of reductants, such as Fe(0) from the steel reaction vessel.

These results, in conjunction with an Eh–pH stability diagram of the $\text{Ce}^{\text{III/IV}}\text{–O–H–C}^{\text{IV}}\text{–P–S}^{\text{VI}}\text{–Na–Cl}$ system, indicate that the glass was leached at relatively low oxidation potentials ($\text{Eh} < 0.2 \text{ V}$). However, the comparison with an equivalent Eh–pH diagram for Pu revealed that the reduction of Pu^{IV} to Pu^{III} would require considerably stronger reducing conditions ($\text{Eh} < -0.3 \text{ V}$). It is, therefore, concluded that Ce is not a good chemical analogue of Pu, in spite of its wide use as a surrogate in simulated radioactive waste.

2.3 Trace element behaviour

2.3.1 Solid solutions: Structural study of iodide uptake by AFm phases

“Positively-charged” cement minerals may potentially reduce the mobility of long-lived anionic radionuclides such as ^{129}I , ^{79}Se , and ^{99}Tc in the near-field of a cement-based repository. In the context of an ongoing PhD project (L. Aimoz), radiotracer experiments, powder X-ray diffraction (XRD), and extended X-ray absorption fine structure (EXAFS) spectroscopy were used to obtain a molecular-level understanding of the uptake mechanisms of iodide (I⁻) by cement minerals bearing positively-charged sheets or channels (AFm or AFt phases, respectively).

First, the uptake of trace levels of iodide ($4 \times 10^{-11} \text{ M}$) by the most common “positively-charged” cement minerals was quantified by performing sorption experiments using ^{125}I . For the phases hydroxalite, ettringite, AFm- Cl_2 , AFm- CO_3 and AFm- SO_4 , the AFm- SO_4 phase was found to be the only one to take up iodide. Thanks to the selection of a high solid-to-liquid ratio ($\sim 10 \text{ kg kg}^{-1}$), an R_d value for iodide sorption onto AFm- SO_4 of $2.6 \pm 0.3 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ could be measured.

With the aim of understanding this preferential uptake, synthesis experiments were carried out to incorporate iodide together with chloride, carbonate or sulphate in AFm samples. Co-precipitation and substitution experiments were performed in a glove box to avoid carbonation. In the co-precipitation experiments, stoichiometric amounts of C_3A and calcium salt (using different molar ratios of CaI_2 and CaCl_2 , or CaCO_3 , or CaSO_4) were mixed and equilibrated over a period of 1 month. For substitution

experiments, varying amounts of potassium salts (KCl , K_2CO_3 or K_2SO_4) were added to a 1-month equilibrated suspension of AFm- I_2 and further equilibrated for at least 48 hours.

In order to characterize the synthetic samples, XRD measurements were performed on an X’Pert Pro Phillips diffractometer using a Cu- $\text{K}\alpha$ source and a scan rate of $0.02^\circ/\text{s}$. In addition, EXAFS studies at the iodine K-edge were carried out to determine the coordination environment of iodine in each sample. The structure models required for fitting the EXAFS spectra were obtained using ab-initio simulations in collaboration with the Transport Mechanisms Group. EXAFS measurements were performed in transmission at the Dutch-Belgian beamline of the European Synchrotron Radiation Facilities (ESRF, Grenoble, France), using a He cryostat at 15K to improve data quality.

The AFm- I_2 phase undergoes a phase transition at low temperatures. This transition was observed by X-ray diffraction measured at 100K at the Swiss-Norwegian beamline of the ESRF. Small displacements of the position of the 110 and 006 diffraction lines were observed (Fig. 2.2). This indicates that this phase transition induces only minor modifications of the high temperature lattice. Therefore, the modifications to the inter atomic distances induced at low temperature by the phase change are assumed to be within the uncertainties of the EXAFS technique.

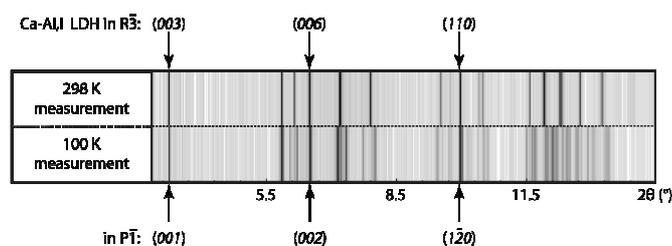


Fig. 2.2: Comparison of diffraction lines from the HT and LT Ca-Al,I LDH polymorph measured ($\lambda = 0.5020 \text{ \AA}$) between 2° and 21° .

A bi-anionic single AFm phase only formed between AFm- I_2 and AFm- SO_4 . In both co-precipitation and substitution experiments AFm- Cl_2 and AFm- I_2 segregated. Similarly, AFm- I_2 and AFm- CO_3 segregated in the substitution experiments (Fig. 2.3).

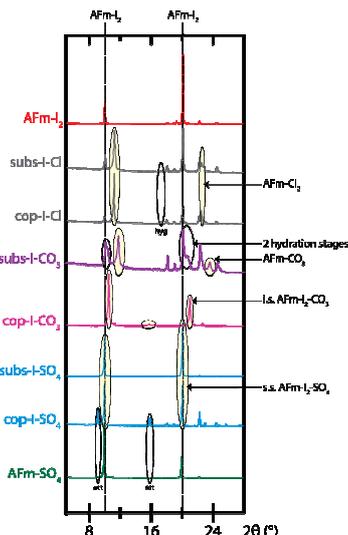


Fig. 2.3: X-ray diffraction patterns of AFm samples containing Cl⁻ or CO₃²⁻ or SO₄²⁻ together with an initial I content of 50% prepared by co-precipitation (cop) or by substitution (subs). Pure AFm-I₂ and AFm-SO₄ are plotted for comparison. Impurities of hydrogarnet (hyg) and ettringite (ett) are circled.

These re-crystallization processes emphasized the greater stability of AFm-Cl₂ and AFm-CO₃ compared to AFm-I₂. In addition, I K-edge EXAFS spectra fits of these mixtures resulted in two I-O backscattering pairs at R~3.6 Å and R~3.8 Å (Fig. 2.4), similar to pure AFm-I₂. These findings indicate that iodine in these mixtures of two phases has a similar coordination environment to that in pure AFm-I₂. Therefore, the presence of co-forming AFm-Cl₂ and AFm-CO₃ did not disturb the structure of AFm-I₂ even at short distances around iodine atoms.

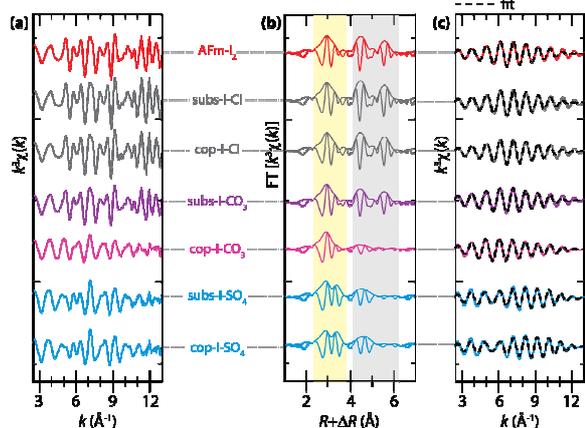


Fig. 2.4: Experimental EXAFS spectra and corresponding fit models at the I K-edge of AFm samples containing Cl⁻ or CO₃²⁻ or SO₄²⁻ together with an initial I content of 50% prepared by co-precipitation (cop) or by substitution (subs). (a) k³-weighted; (b) FT (modulus, imaginary part) (c) FT⁻¹.

In contrast, single 00l lines corresponding to single AFm phases are observed in the co-precipitated I-CO₃ and I-SO₄ and in the substituted I-SO₄ samples (Fig. 2.3). For co-precipitated I-CO₃, a regular stacking of interlayer spaces alternately filled with I and (OH-CO₃²⁻) is anticipated, giving rise to a supercell of d₀₀₁ = 17.03 Å (Fig. 2.3). This stacking results in a local disorder of iodine compared to pure AFm-I₂, as was previously observed for Zn-Al,I layered double hydroxides. Indeed, limited structural information was observed at large R+ΔR (Fig. 2.4). A single I-O pair alone could be fitted at R~3.6 Å in the FT⁻¹.

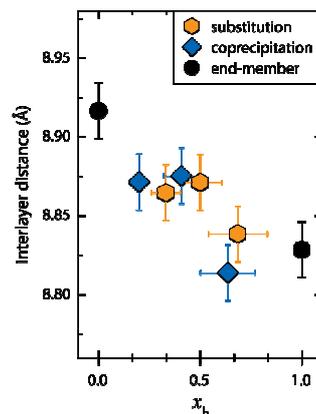


Fig. 2.5: Evolution of the unit cell parameter c based on the position of the 006 line against the I content in the AFm-I₂-SO₄ samples prepared by co-precipitation or by substitution, respectively.

For I-SO₄ samples, the interlayer distance decreased linearly with the iodide content, indicating mixing of iodide and sulphate within the same interlayers (Fig. 2.5). The splitting of the first shell found in the FT of the EXAFS spectra between two maxima at R+ΔR = 2.9 Å and 3.4 Å shows that iodine has a different coordination environment than in pure AFm-I₂. Results from the fit show that the first shell I-O distance in I-SO₄ samples (~3.5 Å) is smaller than in any other of the investigated samples (~3.6 Å). A different atomic configuration of oxygen atoms around iodine in the absence or in the presence of SO₄²⁻ is in good agreement with a short-range mixing of I and SO₄²⁻ within the same interlayers. Indeed, the coordination environment around iodine atoms includes oxygen atoms from hydroxide groups, from water molecules coordinated with Ca, and from space-filling water molecules linked to the presence of sulphate (Fig. 2.6).

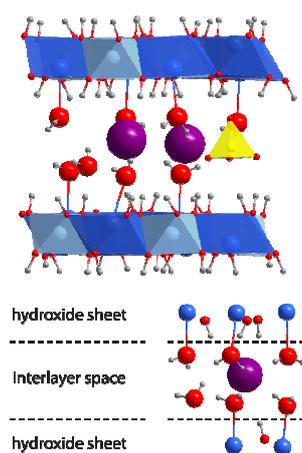


Fig. 2.6: Optimized structure of an $AFm-I-(SO_4)_{0.5}$ obtained from *ab-initio* simulations. Grey, red, light blue, dark blue, yellow, and violet colours are representative for H, O, Al, Ca, S, and I, respectively.

These results indicate the formation of a stable solid solution between $AFm-I_2$ and $AFm-SO_4$. This solid solution formation explains the preferential uptake of iodide at trace-level by $AFm-SO_4$. Hence, $AFm-SO_4$, in contrast to $AFm-Cl_2$ and $AFm-CO_3$, is a potential sink for ^{129}I in the cement-based engineered barrier of a nuclear waste repository. Future studies will include the evaluation of the thermodynamic stability of the $AFm-I_2 - AFm-SO_4$ solid solution.

2.3.2 Kinetics of trace element retention in minerals

Irreversible trace element uptake in growing minerals cannot be predicted using a simple aqueous solid-solution model since experimentally measured trace element concentrations deviate from equilibrium. Any suitable model must account for this deviation. To succeed in the prediction of trace element uptake in growing minerals, certain questions must be answered: Why does trace element uptake in a host mineral depend on the precipitation (re-crystallization) rate? What are the mechanisms? What is the equilibrium (uptake) distribution, as a reference for kinetic-dependent uptake?

Three existing models of trace element uptake in host minerals in the context of waste repository geochemical systems were studied and evaluated (B. Thien, postdoc).

The first one is the Surface Entrapment Model (WATSON, 2004). It is assumed that a growing crystal keeps the same concentration as the surface, unless the diffusion in the near-surface region is significant during growth. In other words, there is a competition

between growth rate and diffusivity. For elements which do not fit in the mineral structure, i.e. are enriched in the surface layer relative to the bulk mineral, the higher the growth rate compared to the diffusivity, the more efficient is the entrapment of the considered trace element, and vice versa. This model also works for elements which do fit into the mineral structure (depleted in the surface layer, relative to the bulk mineral). This model describes very well the growth rate dependency of such compatible and incompatible trace element distribution coefficients in calcite, but some parameters, such as the apparent surface layer diffusivity are poorly known and must be fitted. This model is described by a reactive-transport equation and has been improved to account for possible depletion effects in the solution.

The second model is the Surface Reaction Kinetics Model (DEPAOLO, 2011). It is based on precipitation-dissolution dynamics. There is competition between a gross forward precipitation rate and a gross backward dissolution rate for each “end-member” e.g. calcite and strontianite in the case of Sr uptake by calcite. At equilibrium these two rates are equal. The competition between the two rates determines the net precipitation rate of the mineral and its trace element distribution coefficient. This model describes experimental results very well and provides very similar results to the Watson model. However, the mechanisms are quite different, and obtaining a realistic value for the gross backward dissolution rate remains a challenge. The main advantage of this model is that the resulting equation is very easy to solve without a computer code.

The last model is the Adsorption Diffusion Desorption Model (BARROW & BOWDEN, 1987). Surface trace element concentrations greater than in the bulk mineral, triggers a diffusion flux into the bulk of the mineral. In contrast to the Watson model, diffusion from the surface back into the solution is not allowed. This model does not account for mineral growth and has not yet been tested.

The next step is to include these models into the geochemical code GEMS, in order to take the chemistry of the solution into account. The results from future experiments carried out within the EU SKIN project will help us to find the most physically realistic model.

2.3.3 Thermodynamic sorption modelling

Spectroscopic studies and atomistic simulations of (hydr)oxide surfaces have corroborated the use of multi-dentate surface species in aquatic surface

complexation models. Major advances in thermodynamic sorption modelling have been achieved with the development of theoretical conversions of intrinsic adsorption constants between different site densities, ‘denticities’, and concentration scales (in collaboration with J. Lützenkirchen (KIT) and T.E. Payne (ANSTO)). We have shown (KULIK et al., 2011) that denticity (d) effects are not present in intrinsic equilibrium constant K^{int} values for mono-dentate binding reactions, but the $K^{\text{int},d}$ conversion factors between different concentration scales can be as large as 18 \log_{10} units for 4-dentate surface species. This can result in huge artefacts if $K^{\text{int},d}$, fitted in one speciation code, is used in another code without proper conversion. The application of only two surface concentration scales, the relative surface concentration, θ , and the relative surface density, o , eliminates the dependence of intrinsic adsorption constants K_M^{int} on denticity, d , for reactions of the form $d \cdot \equiv + M \leftrightarrow \equiv_d M$ (\equiv stands for a surface site). This allows the conversion of any $K_M^{\text{int},d}$ to a standard-state constant K_M^o suitable for deriving an internally consistent set of thermodynamic properties of surface complexes valid at different temperatures.

Further elaboration and acceptance of a general convention on the denticity-invariant standard state needs an agreement on the standard value of site density Γ_{Co} (for θ scale) numerically equal to the standard value of surface density Γ_o (for o scale). Can such a value be arbitrarily chosen (e.g. $1 \text{ mol} \cdot \text{m}^{-2}$), or is there a range of values preferable on physicochemical grounds? Our analysis of temperature corrections for $K_M^{\text{int},d}$ of multi-dentate adsorption reactions leads to a dependency of the entropy term on the surface concentration scale and on the chosen standard (site) density. Again, this dependence is not present for mono-dentate reactions. A complete set of the correction terms involved in the ‘intrinsic’ entropy term of the adsorption reaction taken from $K_M^{\text{int},d}$ at different temperatures has been derived using the Van’t Hoff or similar equations. These correction terms can be used for the easy conversion of ‘apparent’ to standard-state entropy terms without re-fitting the experimental data.

On the other hand, entropy and volume effects of adsorption are largely defined by the release of H_2O molecules from aqueous adsorbate species and from the surface. These effects can be predicted using available thermodynamic data on ion hydration and recent calorimetric data on surface hydration, if the number of H_2O molecules liberated from both sides upon adsorption is known e.g. from spectroscopic data

or from atomistic simulations. It turns out that a rather narrow range of Γ_o (Γ_{Co}) values is consistent with the independently estimated entropy and volume effects. For (hydr)oxide surfaces this range is from $3.3 \cdot 10^{-6}$ to $1.2 \cdot 10^{-4} \text{ mol} \cdot \text{m}^{-2}$ (or 2 to 72 nm^{-2}), i.e. similar to the density of H_2O molecules in a planar surface monolayer (6 nm^{-2}). For this reason, it is proposed to define a standard (site) density for all d -dentate surface species on mineral-water interfaces in the range $1 \cdot 10^{-5}$ to $2 \cdot 10^{-5} \text{ mol} \cdot \text{m}^{-2}$, which leads to physico-chemically consistent entropy effects and temperature extrapolations of equilibrium adsorption constants.

These results have been reported in part at the Goldschmidt 2011 Conference. A manuscript for publication (D. Kulik and J. Lützenkirchen) is in preparation.

2.4 Teaching activities

The teaching duties of W. Hummel as Privatdozent (PD) for “Nuclear Environmental Chemistry” at ETH Zurich included lectures and exercises on nuclear waste management within the scope of the courses “Nuclear Energy Systems” (Spring Semester 2011) and “Landfilling, nuclear repositories and contaminated sites” (Autumn Semester 2011).

Between May 19th and May 31st 2011 E. Curti taught at Bern University in the framework of the block course entitled “Geological disposal of radioactive waste” (shared with PD Dr. Martin Mazurek), which is an integral part of the master curriculum in Geological Sciences. The contribution involved about 12 hours teaching and exercise plus the preparation and evaluation of a written examination.

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3 TRANSPORT MECHANISMS

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3.1 Overview

An important milestone reached in 2011 was the submission of the reports on the geochemical evolution of the near field of HLW and L/ILW repositories (3.2). These reports incorporate results obtained over the last two years and will provide scientific support for the site selection process in Stage 2 of the Sectoral Plan (Sachplan Geologische Tiefenlager). We further participated in the modelling of data from the DR-experiment, initiation of the DR-A experiment and performed scoping calculations for the planned DR-B project, all being carried out at Mont Terri (3.2). Field experiments provide input data for modelling and are used for the validation of conceptual transport models. Inverse modelling of conventional diffusion experiments provides the radionuclide transport parameters needed in performance assessment studies (3.3). To begin to address top priority questions in performance assessment such as clogging and repository re-saturation, two PhD proposals were made for projects focused on transport in partially saturated media and porosity changes at cement clay interfaces (3.6). These projects were successfully approved by the PSI Research Commission (Foko).

The simulations carried out for performance assessment studies span time frames of a million years or more and thus have to be conceptually simple and numerically robust. The appropriateness of such simplified models is tested against field experiments wherever possible and the assumptions made are corroborated through a mechanistic understanding of the radionuclide transport and sorption mechanisms at the pore scale using advanced simulation techniques (3.4). Such studies take advantage of the unique analytical infrastructure available at PSI's large scale facilities and access to state-of-the-art computing. Indicative for this is the joint PhD project with the laboratory of neutron imaging in the NUM department which has received partial financial support from the CROSS initiative launched by the PSI-Directorate. Numerical codes are benchmarked and modelling competences are extended to maintain state-of-the-art capabilities and the conceptual quality of the system description (3.5). Teaching, supervision of PhD students and postdocs, have become an integral part of the group's activities that contribute to the knowledge transfer and the visibility of the research.

3.2 Sectoral Plan

3.2.1 Reactive transport modelling for the geochemical evolution of L/ILW and HAA repository near fields

The projects on the long-term evolution of cement/clay host rock, cement/sand-bentonite backfill and cement/bentonite backfill interfaces which started two years ago in co-operation with the Geochemical Modelling Group have been completed. The thermodynamic model applied in the simulations uses a consistent setup for concretes, bentonite, Opalinus Clay and other potential host rocks. It reproduces measured properties of pore waters (composition, pH), takes into account cation exchange and the pH buffering properties of the clay components, and makes a clear distinction between inter-particle and interlayer porosities of the clays. The results of the modelling made important contributions to the two reports.

For the report on the geochemical evolution of the HLW near field, numerical simulations were used to estimate the influence of a cementitious liner on the near field. The report on the geochemical evolution of the L/ILW near field, prepared in cooperation with the Geochemical Modelling Group and the Cement Systems Group, relied heavily on the novel geochemical model and the reactive transport calculations.

For each type of interfaces three different transport scenarios were investigated: (1) fully coupled diffusive transport, (2) diffusive transport without feedback of precipitation/dissolution reactions on the porosity and transport parameters of the media and (3) advective transport of a host-rock pore-water through the concrete near field and then the infiltration of the altered pore water into the host rock. The calculations allowed a comparative study of the geochemical evolution of the repository near field for different hydraulic scenarios and combinations of materials. All calculations showed a small porosity increase in the concrete due to portlandite dissolution. Scenarios with advective transport showed a strong dependency of the concrete degradation on the water flow rate. For realistic water flow rates, transport across the interfaces was dominated by diffusion. The diffusive

scenarios suggested strong porosity decreases at the interface due to the precipitation of C-S-H phases and other cement minerals. All of the calculations indicated only a small extent of mineralogical changes in the clay rocks (Fig. 3.1). The simulation concept applied relied on an equilibrium chemistry approach and treated the aggregates in concrete as inert phases. Therefore, a complete degradation of the concrete compartment was not possible in this setup. Some scoping calculations with kinetically controlled dissolution of the alkali-silica aggregates suggested that the cement degradation stage determined by portlandite saturation could potentially last for a much shorter period than anticipated from reference degradation scenarios based on diffusive or advective transport of host rock pore waters assuming inert alkali-silica aggregates.

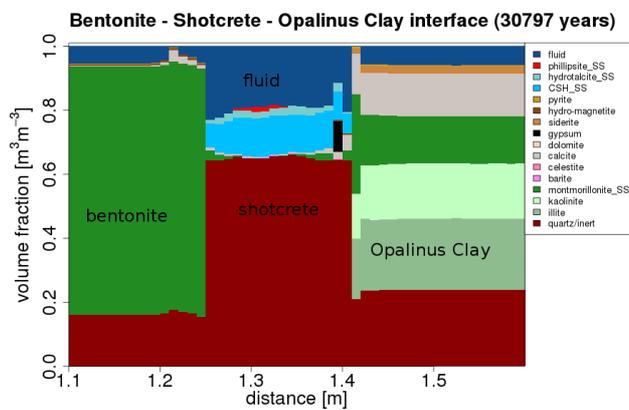


Fig. 3.1: Simulated mineralogical profile over bentonite, shotcrete and Opalinus Clay after 30'800 years. The solute diffusion across the material interfaces is hindered due to pore space clogging. The different material compartments are therefore isolated and are slowly re-equilibrating.

3.2.2 Scoping calculations for future long-term diffusion experiments in the Mont Terri underground rock laboratory (DR-B)

Experimental data obtained in field-scale long-term diffusion experiments form part of the scientific basis for performance assessment within the Sectoral Plan. To support the planning of a possible long-term diffusion experiments (DR-B) in the Mont Terri underground rock laboratory, a series of scoping calculations was carried out. The DR-B experiments could be conducted over many years and, consequently, a time-span of 20 years was considered in the calculations.

In field-diffusion experiments solute migration takes place under near in-situ conditions in three dimensions with preferential pathway parallel to the bedding of the argillaceous rock (Opalinus Clay). Since the borehole axis crosses the clay bedding plane at an angle of roughly 45 degrees, the full geometrical complexity in 3D has to be taken into account in the calculations. After a certain, pre-defined time span, the borehole can be overcored. By subsequent slicing or abrasive peeling of the core, the tracer distribution in the host rock can be determined. An additional source of information about tracer fluxes is the temporal evolution of the tracer concentrations in the borehole. A novel technique to be used for the monitoring of the temporal evolution of the tracer distribution in the rock will be based on X-ray fluorescence spectroscopy. With this technique the solute concentration in the injection reservoir will be measured in several complementary observation boreholes surrounding the source. Selected simulation results for 3D iodide tracer distribution in the core, and the evolution of the fluid composition in borehole, are illustrated in Fig. 3.2. The results of the modelling (JAKOB, 2011) will provide the scientific basis for deciding on the design of the planned field tracer experiments.

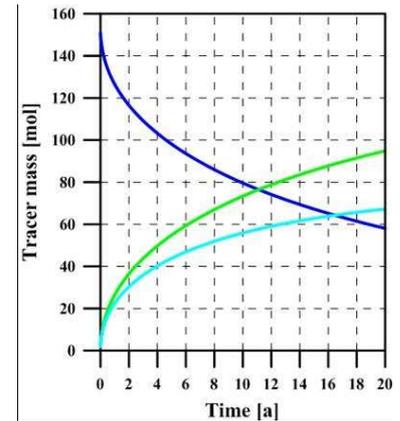
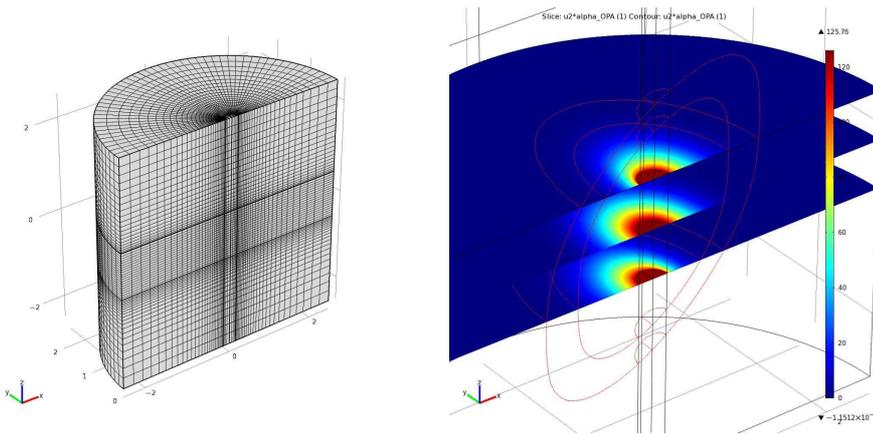


Fig. 3.2a: Half of the modelled domain and the grid used for the calculations. The inner vertical structure represents the borehole. The tracer is released in the middle section of the borehole over height of 1 m. Domain height and diameter are both 5 m.

Fig. 3.2b: Anisotropic tracer distribution in the Opalinus Clay after 20 years of diffusion. Red denotes high and blue low or even zero tracer concentration. The pink lines denote two different experimental detection limits for the iodide tracer at the intersecting vertical plane.

Fig. 3.2c: Amount of iodide tracer present in the Opalinus Clay as a function of time (green line). After 20 years some 40% of the initial 155.5 moles of tracer is still present in the source (blue line) and most of the migrated tracer remains in the middle section (light blue line).

3.2.3 DR experiment in the Mont Terri Rock Laboratory

The experimental work in the DR (Diffusion and Retention) experiment at the Mont Terri Rock Laboratory was finished in 2010. In this experiment, artificial pore water containing 13 different tracers was circulated in two short (15 cm) injection intervals in a borehole drilled perpendicular to the bedding of the Opalinus Clay (<http://www.mont-terri.ch/>). The decrease of tracers concentrations in the intervals was monitored over nearly 4 years. The injection intervals were then overcored and samples of variable size were taken at different vertical heights relative to the centre of the interval and at different radial distances from the borehole. Water contents and total tracer concentrations were determined in these samples so that the 2D distributions around the injection intervals could be displayed. For more strongly sorbing tracers (e.g. Cs, Co, Eu), only 1D radial profiles in the centre of the injection intervals were obtained.

Fig. 3.3 shows the measured 2D distribution of water in the core. The low water content measured at the external rim of the overcore, and also at the internal interface towards the injection interval, are artefacts caused by partial drying during the drilling with air. These values were ignored when determining the average water content for the simulations.

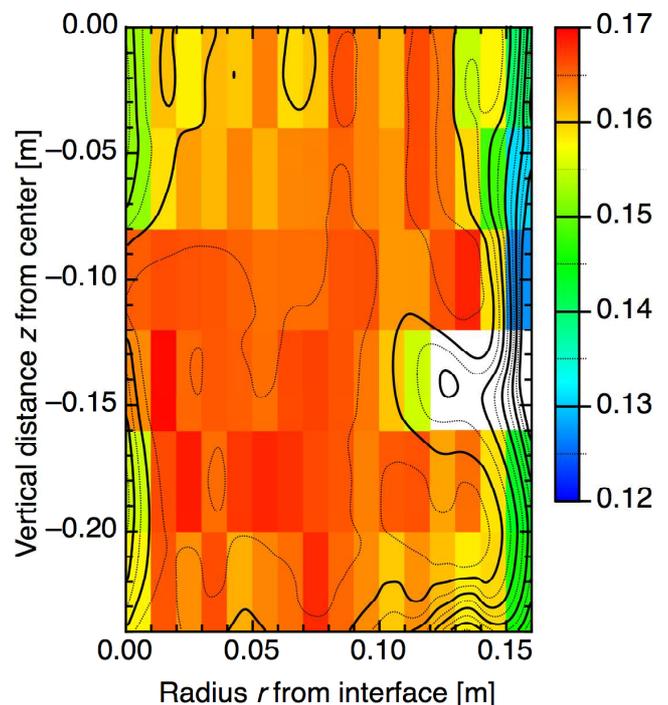


Fig. 3.3: Measured 2D water content distribution around the lower half of the lower injection interval (located at $r = 0$ m from $0 \leq z \leq -0.075$ m) in the DR experiment. The lower water contents at the right boundary, and partly at the left boundary, are artefacts caused by the sampling and the drilling with air during the overcoring.

Transport parameters for each tracer were obtained based on the two data sets (borehole, 2D or 1D profiles). The procedure first included the screening and checking of the different data sets. The modelling considered an axi-symmetric 2D domain that included the central injection interval, the filters, a small gap around the filters and the surrounding rock. It was shown that the decrease of the fluid volume in the reservoir tank during the experiment, due to the repeated sampling, had only a minor effect on the simulations. The HTO diffusion coefficients parallel and perpendicular to the bedding were estimated from the HTO data using the average measured water content and considering the uncertainty of the data regarding their exact vertical position. Thus, for the first time the anisotropy factor could be directly determined in a field experiment. Parameter estimations for the other tracers are ongoing. Parameters similar to those determined in earlier experiments were obtained so far.

Fig. 3.4 shows the measured and simulated 2D distributions of HTO. Fig. 3.5 shows measured and simulated radial HTO profiles in the pore water. Slight, but systematic differences between the measured data and the simulations could not be completely eliminated with reasonable parameter combinations. Improving the match of the borehole simulations very often led to a worse match of the profile simulations, or, improving the match of the profile data near the interval led to a worse match with the data further away. This could be an indication of some processes or heterogeneities that are not yet considered in detail in the simulations, or it could also be due to an unknown bias or a larger uncertainty in the data than has been considered so far. For instance, the measured HTO concentrations of the first samples adjacent to the injection intervals are somewhat lower than the modelled concentrations in all of the simulations. This has been observed already in earlier experiments and might be related to the partial loss of pore water during sampling in this area.

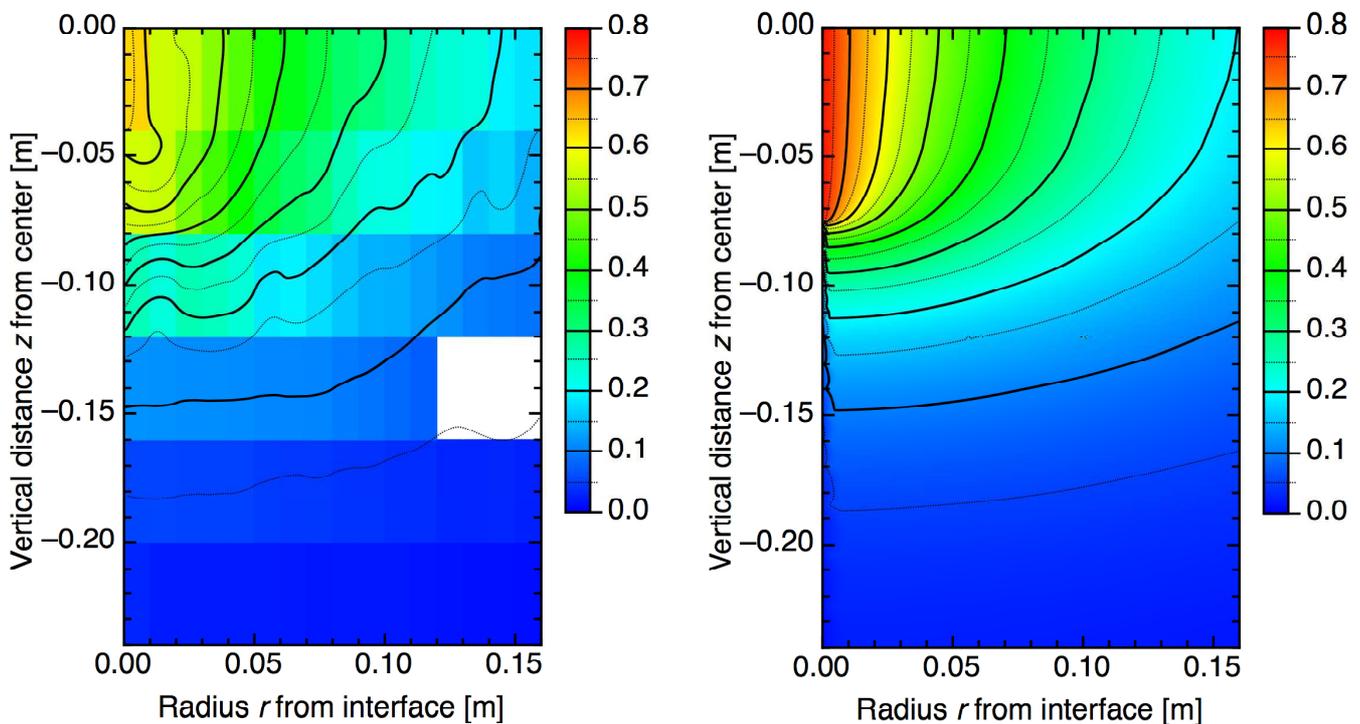


Fig. 3.4: Measured (left) and simulated (right) 2D HTO distributions in the pore water around the lower half of the lower injection interval (located at $r = 0$ m from $0 \leq z \leq -0.075$ m) in the DR experiment. Concentrations normalized with the initial reservoir concentration are shown.

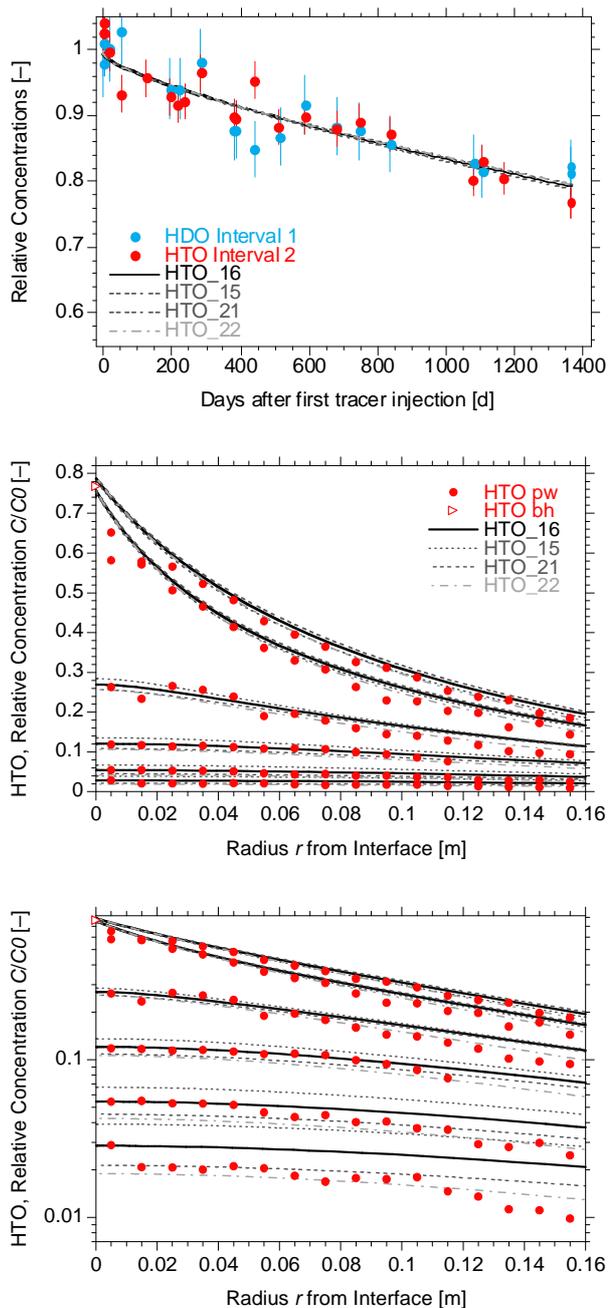


Fig. 3.5: (top) Measured and simulated normalized borehole concentrations of HTO. (middle and bottom) Measured and simulated normalized radial HTO concentration profiles in the pore water (pw), linear and log scale, respectively; the last value in the borehole (bh) is also shown. The solid lines represent the best match with a reasonable parameter set (HTO₁₆). The dashed lines represent alternative sets with lower (HTO₁₅) and larger anisotropy (HTO₂₁). The dash-dotted lines (HTO₂₂) represent a set which matches better the data at larger radii r , but it requires a much too large porosity compared to the measured water contents.

3.2.4 DR-A experiment in the Mont Terri Rock Laboratory

At the beginning of November 2011, a new diffusion and retention experiment (DR-A) was started in the Mont Terri underground rock laboratory. It has a similar set-up to the earlier diffusion experiment with a 1-m long packed-off injection interval. First, HTO, ⁸⁵Sr, ⁸⁰Co, Cs, Eu, I, and Br were added as tracers in an artificial pore water that should match approximately the existing pore water in the rock. It is planned to exchange the tracers later with a somewhat different artificial pore water, again traced, to create a chemical disturbance. The response will then be observed, and the ability of geochemical models to simulate the corresponding changes will then be tested. For this experiment, first scoping calculations were performed in order to define the sampling strategy.

3.3 Interpretation of Co diffusion experiments in OPA with new filters free experimental setup

Results from laboratory in-diffusion experiments with Co, a moderately strongly sorbing radionuclide, performed in a new experimental set-up without filters to avoid filter sorption effects, showed a tracer profile with two concentration components within the clay sample (see Fig. 7.3, LES Progress Report 2010). A strong decrease of the tracer concentration profile is observed at the high Co concentration side and a slow decrease of the tracer concentration profile is detected further within the clay sample. Such a profile was not expected for a simple diffusive transport. MCOTAC was therefore used to model several physical and chemical processes which might explain the observed Co concentration profiles. First, a one-dimensional model setup was used with a multi-site sorption model for Co (BRADBURY & BAEYENS, 2005). Fe-Co sorption competition has been investigated as well as kinetically controlled sorption for the surface complexation reactions. In addition, the influence of a possible mismatch between the clay pore water and the Co doped reservoir water, was investigated with respect to concentration gradients for Fe and pH. None of these variations could explain the observed Co profiles. Information arising out of this modelling exercise indicated that any potential pH gradient existing between the pore water of the 5 mm long clay sample and the reservoir water would not be equalized in the 40 days used for the Co in-diffusion experiments, but would take considerably longer. Finally, a more complex two-dimensional model setup was used to include heterogeneities in sorption site densities. The results obtained assuming a

heterogeneous distribution of sorption sites within the clay sample qualitatively agreed with the measured double front Co concentration profile. However, assumptions regarding heterogeneous sorption site distributions have to be justified experimentally (element mapping or tomography).

3.4 Understanding transport and sorption mechanisms

3.4.1 Up-Scaling diffusive transport in clays

Diffusive transport of ions and water in clay materials results from Brownian motion of solutes and solvent in the interlayer and inter granular space between clay particles. Local pore scale transport is strongly influenced by the proximity of mineral surfaces. These local pore scale effects can be estimated from atomistic simulations. Recently, a concept was developed that allows up-scaling of local pore scale diffusion coefficient for a given pore space model (CHURAKOV & GIMMI, 2011). In order to be able to apply the concept to different clay types, Manav Tyagi (postdoc) developed an operational algorithm which allows the generation of clay pore structural maps based on a mineralogical knowledge of the components and macroscopic properties such as porosity, mean grain size, and grain and pore size distributions (MANAV et al., 2012). The first step in the algorithm is the creation of a representative ensemble of grains. This is achieved in 2D or 3D by a kinetic Monte Carlo (KMC) method which minimizes the interfacial energy starting from an initial grain distribution. The method allows mixtures of different grain types (different minerals) to be created, and also the creation of anisotropic structures with grains of approximately predetermined shapes. The second step consists of introducing pores at the grain boundaries as well as within clay particles e.g. smectite particles. The latter, so called inter-layers or nano-pores, are typically oriented parallel to the main axes of the smectite particles. In this way, representative pore maps consisting of micro- and nano-pores can be generated (see Fig. 3.6). These pore maps can be used to derive up-scaled effective diffusion coefficients for macro-scale models with a homogenization technique. It has to be emphasized, however, that homogenized macro-scale models are valid if scale separation exists and if one is interested in long term behaviour. Nonetheless, the generated clay micro-structure can be used for performing micro-scale simulations irrespective of these limitations.

Fig. 3.7 depicts the effective diffusion coefficient as a function of porosity obtained using the homogenization technique for the 2D multi-scale clay structure shown in Fig. 3.6. A curve for the same pore map, but without nano-pores, is also shown on the same plot. In this case the porosity was varied by changing the width of the micro-pores. It should be noticed from the non-linear curve in the log-log plot that Archie's relationship between effective diffusion coefficients and porosity is not valid if nano-pores are present. This non-classical behaviour is due to the fact that nano-pores become more and more isolated when the micro-porosity is reduced. Thus, nano-pores, though still contributing to the total porosity, start to act like dead-end pores, which increases the tortuosity. Consequently, they may even represent almost closed, inaccessible pore space. On the other hand, at high porosities they are not important.

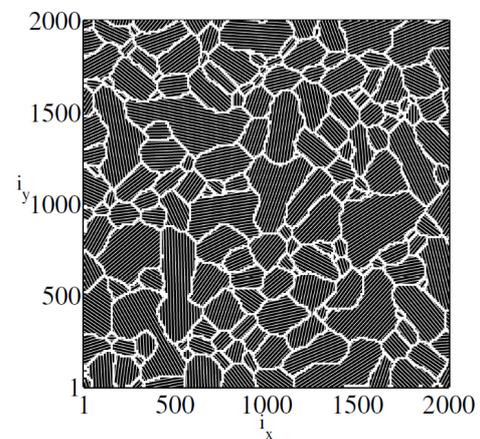


Fig. 3.6: Pore map with micro-pores (shown by thick white coloured contours) and nano-pores (shown by thin white coloured straight lines). Black coloured region are the basic clay layers.

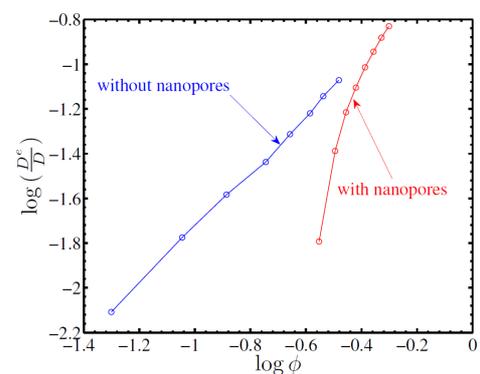


Fig. 3.7: Effective diffusion coefficient (D^e) versus porosity (ϕ), where D is the molecular diffusion coefficient in the pores for the multi-scale pore map shown in Fig. 3.6. Results for the same pore map but without nano-pores are also shown.

3.4.2 Ion uptake by C-S-H phases: Atomistic simulations

The SNF-funded Sinergia project “Stable phase composition in novel cementitious materials: C(-A)-S-H (Calcium-(Aluminium)-Silicate-Hydrate)” is a three year collaborative research program in which ion uptake by cement hydrates is studied experimentally and theoretically. Besides PSI, the other institutions involved are EMPA, EPFL and the University of Bourgogne (Dijon, France). The PSI-hosted sub-project is entitled “Thermodynamic equilibrium in C(-A)-S-H from molecular simulations”, and is being carried out in close collaboration with Dr. Christophe Labbez (Dijon). Within this project Luis Pegado (postdoc) is investigating the influence of aluminium substitution on alkali and alkali earth ion sorption by such materials. The multi-scale molecular modelling approach undertaken involves: ab initio calculations for the study of the mechanism of aluminium incorporation in C(-A)-S-H phases; classical atomistic molecular dynamics (MD) simulations of C(-A)-S-H - electrolyte solution interfaces; and finally, Grand-Canonical Monte Carlo (GCMC) simulations of ion sorption by C(-A)-S-H in the context of the primitive model of electrolyte solutions (implicit solvent model). The incorporation of ion specific and solvent effects in the GCMC simulations requires the calculation of effective potentials (PMF's - Potentials of Mean Force) between different ions and relevant surface groups, obtained through classical atomistic molecular dynamics simulations. MD simulations require a force-field properly describing the interactions between the different components in the system. One central component of this project is therefore the calibration of polarisable force fields for $\text{Si}(\text{OH})_4$ and its different protonation states in aqueous solution. The inclusion of polarisability in molecular force fields is known to be of importance for the description of the specific behaviour of ions at air-water interfaces (JUNGWIRTH & TOBIAS, 2006) and also for the description of the thermodynamic properties of simple electrolyte solutions, where non-polarisable force fields, can predict a completely unphysical ion association (WERNERSSON & JUNGWIRTH, 2010). For the parameterization of classical force fields collaboration with the group of Professor Pavel Jungwirth (Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague) was started, under which a force field for the sulphate ion was developed (PEGADO et al., 2011). The structure of the water around the ion was carefully investigated, in particular its sensitivity to force field parameters, and compared to the results from (first principle) ab initio molecular

dynamics simulations. Polarisable force fields for sulphate were then tested with respect to their thermodynamic behaviour, in the context of sodium sulphate solutions, by comparing the calculated Kirkwood-Buff integrals with those derived from experimental activity data. Work is currently under way to calibrate a classical force field for silicic acid species in aqueous solution by comparison with the water structure around a single molecule as obtained from first principle MD simulations. It is also planned to develop classical force fields for aluminate species in solution, as important models for the other surface groups in C(-A)-S-H phases.

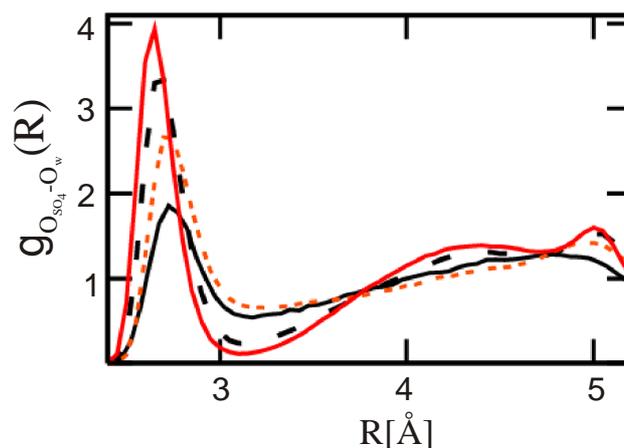


Fig. 3.8: Sulphate oxygens - water oxygens radial distribution functions from classical and first principles molecular dynamics simulations. Full black line is the first principles results. The black dashed line is the result from classical simulations for a sulphate model with charge $+2e$ on the S atom and charges of $-1e$ on the O atoms. Full red and dashed red curves correspond to a model where the O charges are increased and decreased by 20% respectively with respect to the previous model.

3.5 Benchmarking of coupled codes

Benchmarking of transport codes is an important activity which supports the credibility of the numerical simulations. This is true for reactive transport codes describing complex geochemical interactions and/or radionuclide migration in the vicinity of a nuclear waste repository or in laboratory experiments.

3.5.1 Analytical solutions for transport problems with coupling to precipitation/dissolution reactions

Recently, clogging (i.e. the strong reduction of porosity) has received special attention in the transport modelling of cement-bentonite interfaces. Numerous claims that reactive transport codes can solve the reaction transport problem with feedback on porosity need to be validated against analytical solutions. Diffusive transport problems coupled with precipitation-dissolution reactions can be described by non-linear partial differential equations. Finding analytical solutions to such equations is extremely difficult. Therefore, virtually no analytical results were available in the literature until recently.

Over the last two years Mohamed Hayek (postdoc in LES until October 2011) used the ‘‘Simplest Equation Method’’ to derive analytical solutions for 1D coupled reactive transport problems in which there is feedback of strong porosity changes (HAYEK et al., 2011a). In a second step he extended this model for multi-component transport coupled to a single precipitation/dissolution reaction in one, two and three dimensions (HAYEK et al., 2011b). As a special case, he investigated analytical solutions for systems containing one and two solute species that describe the evolution of solutes and solid concentrations as well as porosity. One of the proposed analytical solutions has been used to compare numerical solutions obtained from two conceptually different reactive transport codes: a commercial finite element code COMSOL-Multiphysic and open access finite element code OpenGeoSys. Both codes are extensively used in LES for transport simulations. The numerical results obtained agree well with the analytical solutions for spatial and temporal evolution of concentrations and porosities (Fig. 3.9). A modified version of this benchmark was added to the OpenGeoSys benchmark repository (<http://www.ufz.de/>).

The applicability of the analytical solutions to real world problems is limited, as they contain certain limitations on initial and boundary conditions which are hardly found in nature. However, the comparison between numerical and analytical solutions gives confidence in the use of numerical codes to simulate pore space clogging.

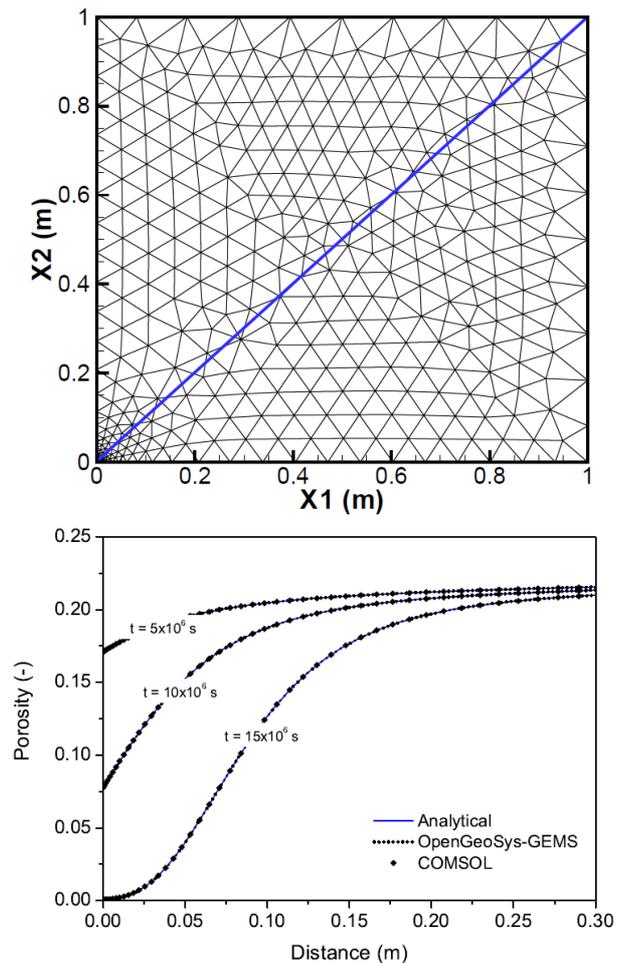


Fig. 3.9: Schematic representation of the computational mesh of a 2D example (top). Comparisons of numerical and analytical solutions for porosity evolution (bottom) were carried out along the diagonal blue line.

3.5.2 COMSOL - MCOTAC benchmark for diffusive transport with a non-linear sorption isotherm

The LES in-house code based on the random walk method, MCOTAC, and a commercial finite element software package COMSOL Multiphysics, were benchmarked (PFINGSTEN & JAKOB, 2011). The benchmark example set up was the diffusion of dissolved Cs through an Opalinus Clay sample taking into account the non-linear sorption of Cs via a look-up table of a tabulated non-linear sorption isotherm (BAEYENS, 2011), which is the most complex sorption process that can be applied in COMSOL.

Results of both codes for Cs through-diffusion in an Opalinus Clay sample whose geometry is related to samples used in laboratory experiments agreed well for a wide range of Cs concentrations (10^{-3} – 10^{-7} mol/l) assumed to be constant at one boundary of the

sample. Through diffusion times as well as C_s concentration values agreed well (Fig. 3.10), although COMSOL and MCOTAC use different spatial discretization schemes, different strategies for solving the diffusion equation and different implementations of the non-linear sorption isotherm – a sorption isotherm (MCOTAC) or a derivative of the sorption isotherm (COMSOL).

It is worth mentioning that the two different algorithms yield very similar results and underline their applicability for modelling diffusion dominated systems and non-linear sorption processes. With COMSOL, complex non-linear sorption isotherms are treated in terms of an analytical function or a look-up table; in MCOTAC, however, multi-species transport (diffusion) in combination with even more complex mechanistic sorption models – more elaborate sorption models such as the 2SPNE SC/CE model (BRADBURY & BAEYENS, 2000) – can be considered. Finally, it should be mentioned that our benchmark example can be used by other modellers for benchmarking their own codes.

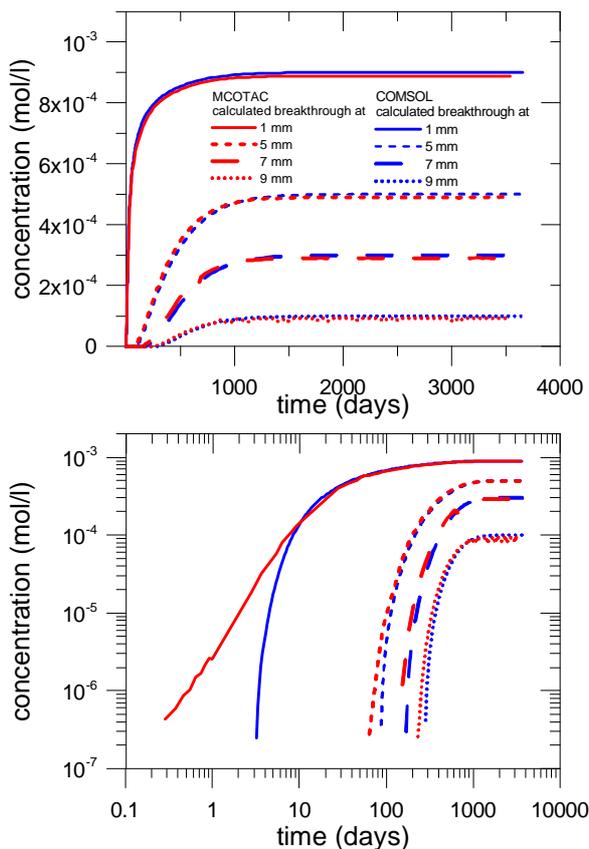


Fig. 3.10: Calculated C_s breakthrough curves at different locations in the Opalinus clay sample calculated with a single species model (COMSOL) and the multispecies model (MCOTAC) both using a tabulated sorption isotherm. The C_s concentration at the “high” concentration boundary was set to be 10^{-3} mol/l.

3.5.3 Fluid-rock interaction modelling

Modelling thermodynamic properties of aqueous solutions is of crucial importance in various fields of scientific, social and economic interest. Examples are the safety assessment and planning of nuclear waste repositories, geothermal applications, petrology, hydrothermal ore deposits, cloud science and climate change, ocean chemistry, environmental remediation, petroleum engineering and chemical process engineering. Since all these applications deal with different aspects of aqueous solutions varying in temperature, pressure and chemical composition, numerous models exist in which each covers only parts of the full set of systems. As part of the Swiss GEOTHERM project financed by Competence Centre for Energy and Sustainability (CCES) (<http://www.cces.ethz.ch/projects/nature/geotherm/>), the PhD project of F. Hingerl deals with the challenge of computing the permeability evolution of an enhanced geothermal reservoir. To do so needs a solution activity model capable of dealing with the high temperature, pressure and salinity. An activity model, ELVIS, has been developed tailored to these demands. Since NaCl is the dominating and virtually omnipresent electrolyte in geothermal fluids ELVIS is parameterised for this system from ambient conditions to 300°C , from 1 to 1000 bars and infinite dilution to 5 molal concentrations. Fig. 3.11 displays the performance of the ELVIS model versus the Pitzer-based Archer NaCl equation of state. The latter presents the current best fit to experimental data of the NaCl system. The ELVIS model reproduces the Archer model within the given errors.

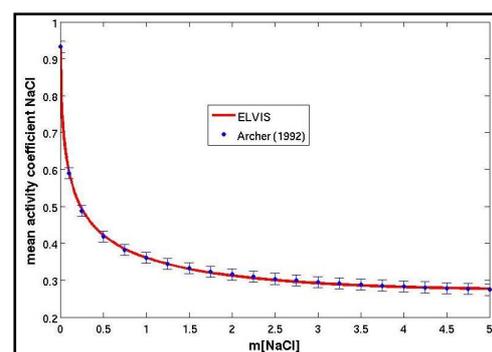


Fig. 3.11: The mean activity coefficient of NaCl in aqueous solution at 300°C , 800 bar as a function of electrolyte concentration. The blue points represent reference values for activities from the Archer NaCl equation of state (ARCHER, 1992). The associated bars give the error of the Archer model with respect to experimental data. The red line indicates the best fit of the ELVIS model. ELVIS reproduces all data points within the given error bars.

Parameterization of the new model to the thermodynamic measurement data was accomplished with the GEMSFIT program which was mainly developed for this purpose. The parallelized open source program GEMSFIT provides a generic interface for fitting thermodynamic activity models, equations of state and solid solution models at varying system compositions, temperature and pressure (Fig. 3.12).

The GEMSFIT is linked to the chemical equilibrium solver GEMS3K for chemical speciation computations which enables fitting of mixed-solutions

systems (solid solutions, mixed solvents). GEMSFIT provides a list of statistical analysis tools which allows thorough evaluation of the fitted parameters. Storage and management of measurement data is accomplished by an external PostgreSQL database server or exported EXCEL sheets. Results from parameter regression as well as from statistical analysis can be visualized in 2D/3D and directly printed to various graphic formats. GEMSFIT is already being used by groups from PSI, ETH Zurich and EMPA.

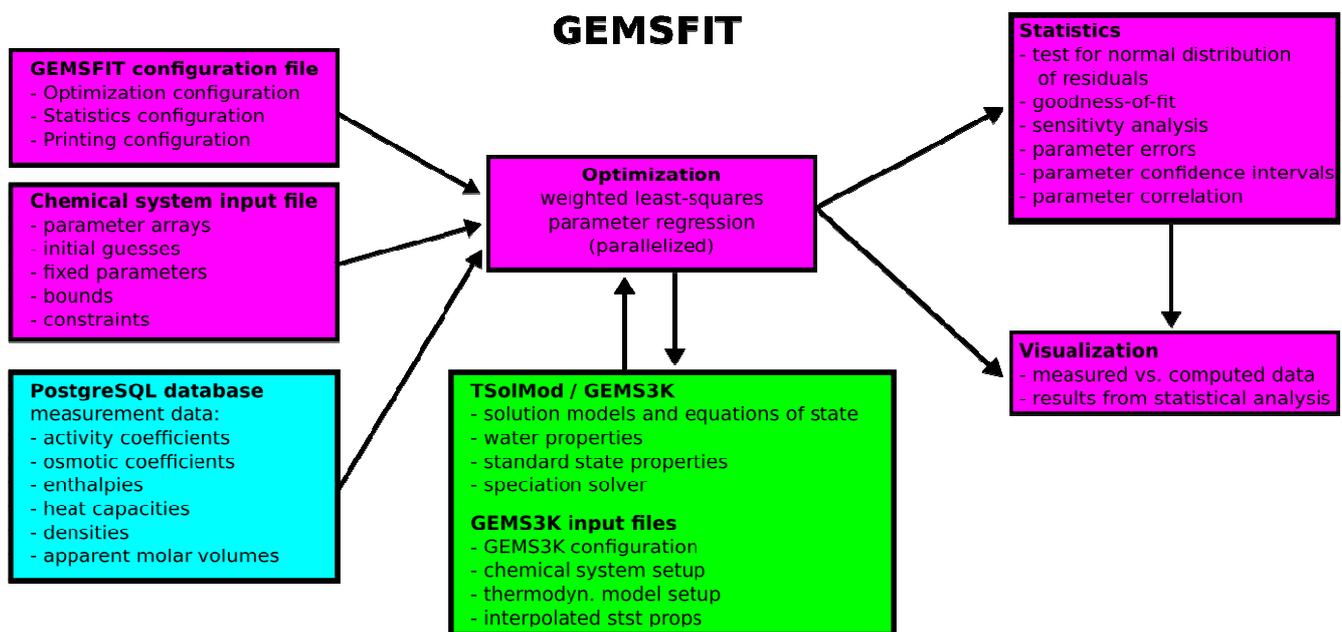


Fig. 3.12: Setup of the GEMSFIT program. Two input files provide all the necessary solver configuration settings and the setup of the chemical system to fit. Measurement data are retrieved from a centralized PostgreSQL database server instance. Weighted least-squares parameter regression is performed on objective functions which interact with the GEMS3K chemical equilibrium solver. Resulting best fit parameters can be subjected to a thorough statistical analysis. Results from parameter regression and statistics can be visualized and printed to various graphics formats.

In a next step, GEMSFIT will be used to extend ELVIS to multi-electrolyte systems to approach the chemical complexity of natural fluids. Once this extension to geologically relevant chemical systems has been achieved, the ELVIS model can then access all thermodynamic properties of electrolyte solutions up to saturation concentration. Temperature and pressure effects are accounted for accurately and independently. This is in favourable contrast to the majority of currently available models because they are usually bound to the vapour pressure saturation curve. Natural and geo-engineered systems often exhibit substantial departures from this curve. Application of a model which does not take this

deviation into account can only lead to approximate solubility predictions. The ELVIS framework is therefore very well suited for mineral precipitation/dissolution modelling in geohydrothermal environments.

3.6 Forthcoming projects

To begin to address high priority questions in performance assessment such as repository re-saturation and clogging, two PhD projects are planned with focuses on transport in partially saturated media and porosity changes at the cement-clay interfaces. The project on transport in partially saturated media,

developed together with the Diffusion Processes Group, has been approved by the PSI Foko. Partial financial support for the project was provided by Nagra. In this project a set of simple well defined experiments will allow the validation of concepts concerning the feedback between chemical reactions, porosity changes and effective transport parameters for saturated and partially saturated conditions. The second project is aimed at the experimental determination of functional relationships between porosity changes and the change of transport properties in the alteration zone near cement-clay interfaces. The project will strongly rely on non-destructive imaging techniques, notably neutron tomography, X-ray tomography, and X-ray diffraction tomography. In order benefit directly from the newest developments in neutron imaging, a collaboration within the PSI CROSS initiative with the Laboratory of Neutron Imaging (NIAG, Group Leader Dr. Lehmann) in the NUM department has been set up. Financial support for this project is provided from the PSI-Directorate and Nagra.

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4 CLAY SORPTION MECHANISMS

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4.1 Overview

Much of the work in the Clay Sorption Mechanisms Group in 2011 was devoted to activities directly related to the Sectoral Plan for Deep Geological Disposal and involved the following topics.

- Effingen Member, “Brauner Dogger” and Helvetic marls have been selected as potential host rocks formations for L/ILW repositories whereas Opalinus Clay is favoured for a HLW repository. The development of sorption data bases (SDB) for these different host rock types is a key activity within the group.
- An experimental programme on the sorption of selected radionuclides i.e. Cs^I, Ni^{II}, Co^{II}, Eu^{III}, Th^{IV} and U^{VI} on the above mentioned host rocks is on going. The measurements on the Effingen Member have been completed.

Mechanistic sorption studies on clay minerals are a continuous ongoing activity. There were three main achievements in the current year.

- The validation of the “bottom up” approach to predict sorption on bentonite and Opalinus Clay for key radionuclides is a very important aspect for the SDB methodology used for the performance assessment.
- Competitive sorption studies on illite.
- An EXAFS study on the uptake of Am^{III} on montmorillonite in the absence and presence of inorganic carbonate was completed.

In the framework of an ongoing PhD project, the interaction of Fe^{II} with clay minerals is being investigated. The first results on the sorption behaviour of Fe^{II} on natural and a synthetic iron-free montmorillonite are presented.

In connection with the “Schweizer Erweiterungsbeitrag DEZA/SECO¹”, a framework agreement between the Swiss Federal Council and the Government of Hungary has been established.

The project “*Development of a macroscopic and microscopic approach to investigate the geochemistry of radioactive waste disposal systems*” started on 15 October 2010. The main focus during the first year was on μ -XRF, -XAS, -XRD investigations on Ni^{II} loaded Boda Claystone Formation samples.

4.2 Activities in support of the Sectoral Plan

4.2.1 Sorption data bases for host rocks

In Switzerland the site selection procedure for both HLW and L/ILW repositories is specified by the Swiss Federal Office of Energy in the Sectoral Plan for Deep Geological Repositories. In the forthcoming Stage 2 of the Sectoral Plan, potential sites will be identified within regions previously selected based on the presence of suitable host rocks, namely Opalinus Clay, “Brauner Dogger”, Effingen Member and Helvetic Marl. Preliminary safety analyses are an integral part of this procedure, and require, amongst other information, the radionuclide sorption properties of the host rock. A methodology to develop sorption data bases for argillaceous rocks and bentonite has been established (BRADBURY et al., 2010) and this method is being applied to compile SDBs for the above mentioned host rocks. Three important components are necessary for the derivation of SDB. The first is high quality source sorption data for illite (host rocks) and montmorillonite (near-field bentonite). The second is the 2:1 clay mineral content of the argillaceous rock, since this parameter best reflects the sorption potential of a given mineral assembly. The third factor influencing radionuclide sorption is the porewater chemistry. With the newly updated Nagra/PSI thermodynamic data base (THOENEN, 2010) the speciation of the radionuclides is calculated in the reference and associated porewater compositions (MÄDER, 2009a,b, 2010) for each individual rock type. The compilations of the SDBs are ongoing and will be used in 2012 in the provisional performance assessments carried out in Stage 2 of the Sectoral Plan.

¹ Direktion für Entwicklung und Zusammenarbeit (DEZA); Staatssekretariat für Wirtschaft (SECO)

4.2.2 Sorption measurements on host rocks

Although the methodology developed to produce sorption data bases for argillaceous rocks and bentonite is relatively new (BRADBURY et al., 2009) there is already substantial evidence indicating that a high degree of confidence can be placed in the results (BRADBURY & BAEYENS, 2010; section 4.3.2). Nevertheless, it was decided to make a whole series of sorption isotherm measurements with representative radionuclides using samples of the proposed host rocks in equilibrium with their respective reference water chemistries so that these measured data could be compared with the predicted data in the SDBs. It is anticipated that these comparative exercises will

substantially increase the confidence in the methodology.

Sorption isotherms for Cs^{I} , Ni^{II} , Co^{II} , Eu^{III} , Th^{IV} and U^{VI} on Effingen Member in the reference porewater ($\text{pH} = 7.7$, $I = 0.7 \text{ M}$) (MÄDER, 2009a) have been completed. The experimental results are shown in Fig. 4.1. Similar series of batch sorption isotherm measurements on “Brauner Dogger”, Helvetic marls and Opalinus Clay are ongoing.

A comprehensive report is planned in which the sorption values predicted in the SDBs for the above mentioned argillaceous rock types will be directly compared with measured values.

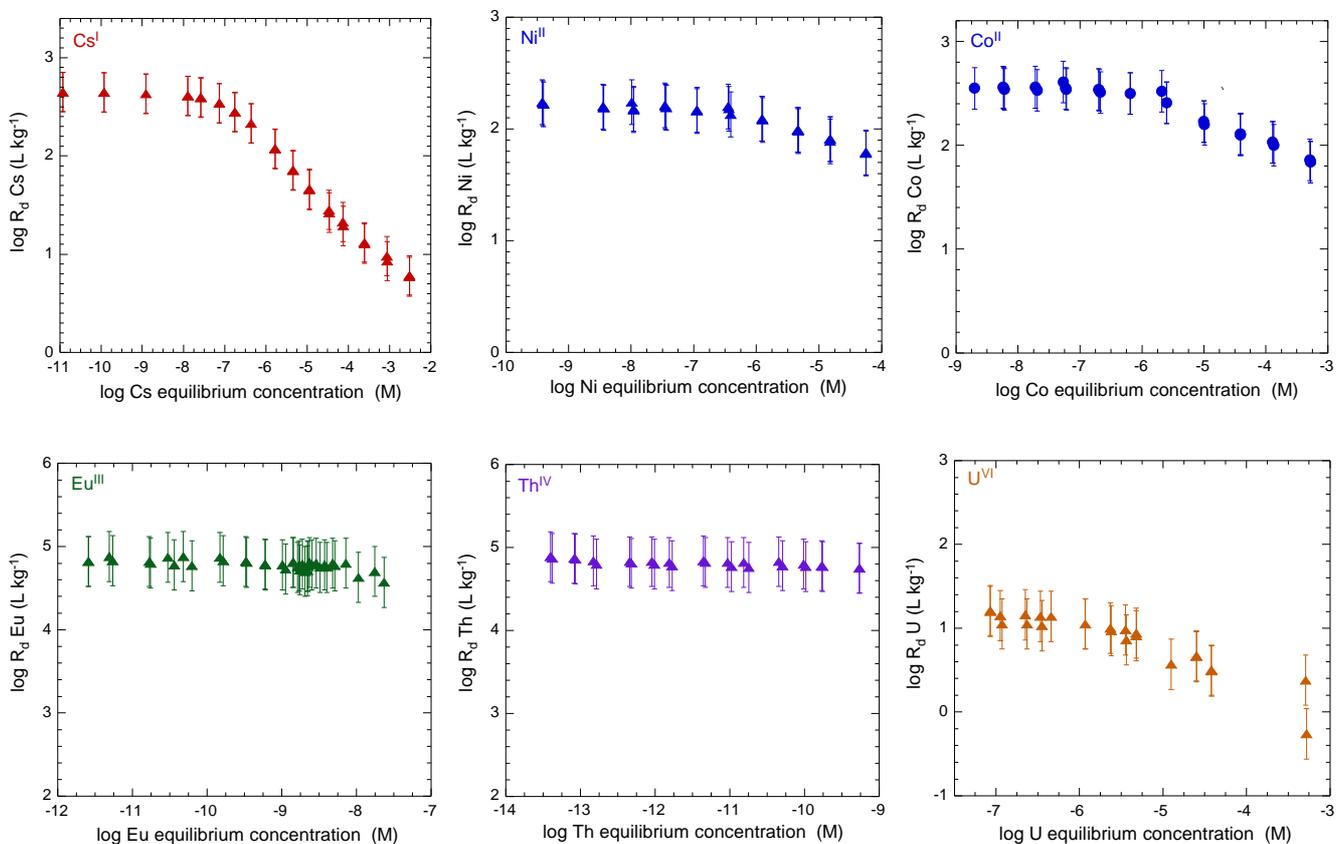


Fig. 4.1: Sorption isotherms for Cs, Ni, Co, Eu, Th and U on Effingen Member (OFT -619.45 m) in the reference porewater (Mäder, 2009a).

4.3 Mechanistic sorption investigations

4.3.1 Competitive sorption

In a deep geological repository for high level waste, stable aqueous metal impurities are present from many different sources e.g. backfill materials, the host rock, the corrosion of steel canister, dissolution of the waste forms. These impurities, which are an integral part of a realistic repository system, can potentially compete with the released radionuclides for the available sorption sites on the backfill materials and host rock and thus reduce their uptake on them. It is clearly an important performance assessment issue to quantify this effect.

Previously investigations on montmorillonite (BRADBURY & BAEYENS, 2005a) were extended to Na-illite, a 2:1 type clay mineral which is omnipresent in argillaceous rocks. The experimental methodology followed was to measure a sorption isotherm for a

chosen sorbate (**blocking element**) in the presence of another sorbate at trace concentration (**trace element**). If the two cations are competitive, the uptake of the trace cation will decrease with increasing blocking element concentration. If they are not competitive, the sorption of the trace cation will remain constant.

The results shown in Fig. 4.2 indicate that the transition metals ($\text{Co}^{\text{II}}/\text{Ni}^{\text{II}}$, $\text{Zn}^{\text{II}}/\text{Ni}^{\text{II}}$) and the trivalent lanthanide/actinide ($\text{Eu}^{\text{III}}/\text{Am}^{\text{III}}$) are mutually competitive i.e. trace cation sorption decreases with increasing blocking element concentration. Note that for illustrative purposes the R_d values for the trace elements are plotted at the equilibrium concentrations of the blocking elements.

The metal ion pairs $\text{Ni}^{\text{II}}/\text{Eu}^{\text{III}}$, $\text{Eu}^{\text{III}}/\text{Th}^{\text{IV}}$ and $\text{Eu}^{\text{III}}/\text{U}^{\text{VI}}$ do not exhibit sorption competition i.e. trace metal ion sorption remains constant as a function of the increasing concentration of the blocking element, Fig. 4.3.

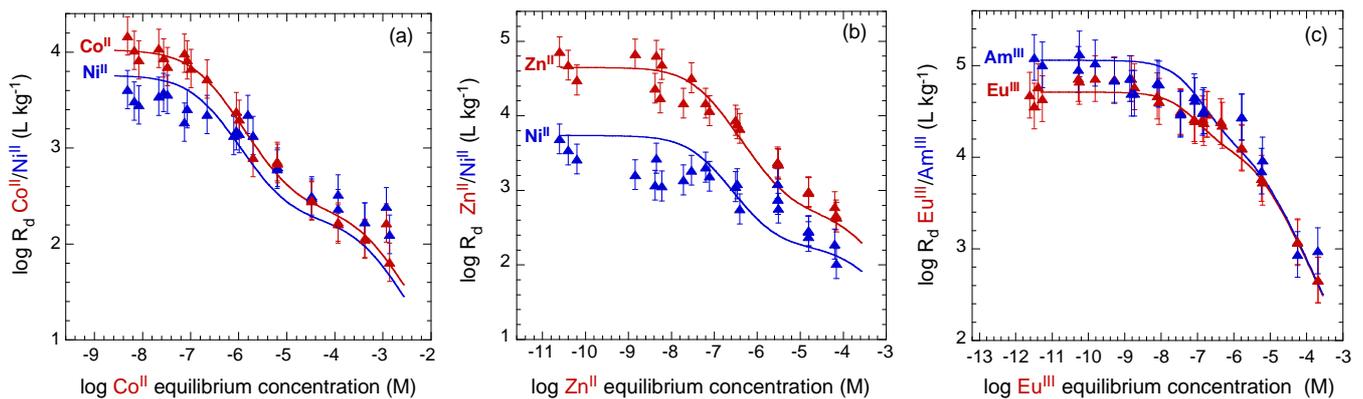


Fig. 4.2: Sorption isotherms measurements (symbols) and modelling (lines) for (a) $\text{Co}^{\text{II}}/\text{Ni}^{\text{II}}$ (pH = 7.0), (b) $\text{Zn}^{\text{II}}/\text{Ni}^{\text{II}}$ (pH = 7.1) and (c) $\text{Eu}^{\text{III}}/\text{Am}^{\text{III}}$ (pH = 6.1) on Na-illite in 0.1 M NaClO_4 .

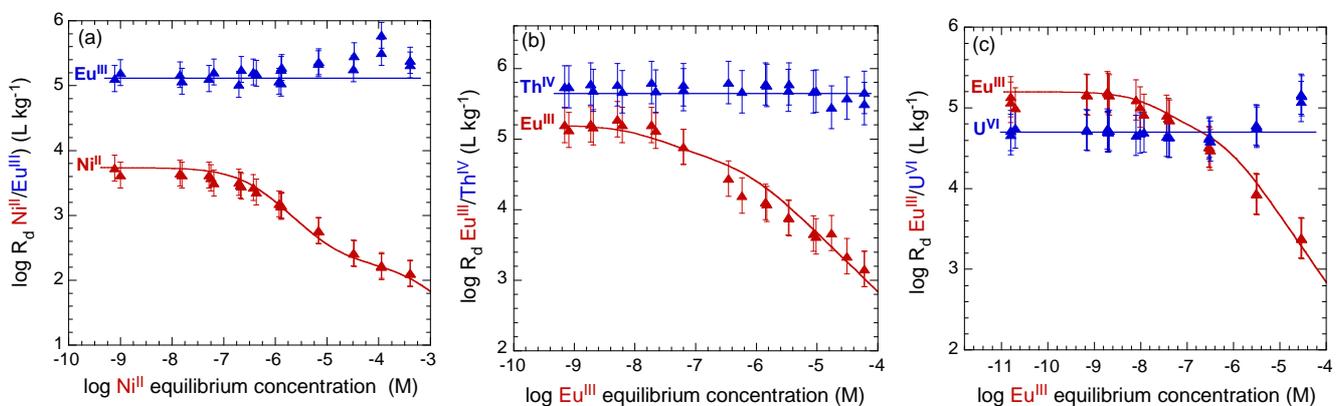


Fig. 4.3: Sorption isotherms measurements (symbols) and modelling (lines) for (a) $\text{Ni}^{\text{II}}/\text{Eu}^{\text{III}}$ (pH = 7.1), (b) $\text{Eu}^{\text{III}}/\text{Th}^{\text{IV}}$ (pH = 7.2) and (c) $\text{Eu}^{\text{III}}/\text{U}^{\text{VI}}$ (pH = 7.2) on Na-illite in 0.1 M NaClO_4 .

Table 4.1: Surface complexation constants used in the modelling. The site types, site capacities and protolysis constants for Na-illite are given in BRADBURY & BAEYENS (2009a).

Surface complexation reaction	log K						
	Ni ^{II}	Co ^{II}	Zn ^{II}	Eu ^{III}	Am ^{III}	Th ^{IV}	U ^{VI}
Strong sites							
$\equiv^{\text{S}}\text{SOH} + \text{Me}^{z+} \Leftrightarrow \equiv^{\text{S}}\text{SOMe}^{z-1} + \text{H}^+$	0.7	0.9	1.6	1.9; 2.2	2.8	7.4	2.2
$\equiv^{\text{S}}\text{SOH} + \text{Me}^{z+} + \text{H}_2\text{O} \Leftrightarrow \equiv^{\text{S}}\text{SOMeOH}^{z-2} + 2\text{H}^+$	-8.2	-7.0	-7.4	-4.6; -4.3	-4.5	2.3	-3.5
$\equiv^{\text{S}}\text{SOH} + \text{Me}^{z+} + 2\text{H}_2\text{O} \Leftrightarrow \equiv^{\text{S}}\text{SOMe}(\text{OH})_2^{z-2} + 3\text{H}^+$	-17.3	-16.5	-17.0	-12.8	-13	-2.4	-10.6
Weak sites							
$\equiv^{\text{W1}}\text{SOH} + \text{Me}^{z+} \Leftrightarrow \equiv^{\text{W1}}\text{SOMe}^{z-1} + \text{H}^+$	-2.4	-2.4	-1.8	0.3	0.3	-	-
$\equiv^{\text{W1}}\text{SOH} + \text{Me}^{z+} + \text{H}_2\text{O} \Leftrightarrow \equiv^{\text{W1}}\text{SOMeOH}^{z-2} + 2\text{H}^+$	-	-	-	-6.2	-6.2	-	-
$\text{Me}^{z+} = \text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{Eu}^{3+}, \text{Am}^{3+}, \text{Th}^{4+} \text{ or } \text{UO}_2^{2+}$							

The 2 Site Protolysis Non Electrostatic Surface Complexation and Cation Exchange (2SPNE SC/CE) model developed for illite was used to model the data. The sorption isotherms for the blocking elements Co^{II}, Zn^{II}, Ni^{II} and Eu^{III} were calculated with the surface complexation constants given in Table 4.1. The trace sorption data for Ni^{II} and Am^{III} in Fig. 4.2 were calculated under the assumption that these elements are competitive. In the case of Eu^{III}, Th^{IV} and U^{VI} in Fig. 4.3 the sorption of these elements is non-competitive.

The main conclusions drawn from this study is that in general, metals ions with the same valence and similar hydrolysis characteristics compete, whereas metal ions with different valences do not compete. For groups of elements which are competitive, the concentration of a particular metal ion does not determine the sorption, but rather the total concentration of all the metal ions present in the given group. Thus, consideration of metal inventories (radioactive and stable) is important in developing sorption data bases for performance assessment studies.

4.3.2 Bottom up approach

The “bottom-up” approach is based on the premise that radionuclide uptake in complex mineral/groundwater systems can be quantitatively predicted from a knowledge and understanding of the mechanistic sorption processes on single minerals,

and the models developed to describe them. The average 2:1 clay mineral contents of MX-80 bentonite and Opalinus Clay are 75 wt. % (montmorillonite) and 40 wt. % (illite and illite/smectite mixed layers), respectively, and these minerals are assumed to be predominantly responsible for sorption.

Sorption isotherms were measured on MX-80 bentonite (BRADBURY & BAEYENS, 2011b) and Opalinus Clay (LAUBER et al., 2000) in the respective synthetic porewater compositions. The isotherms were calculated using the 2SPNE SC/CE model and the Nagra/PSI 01/01 TDB (HUMMEL et al., 2000), assuming that only the free metal ion and hydrolysed species are sorbing. These values were then scaled by 0.75 and 0.40, the respective clay mineral fractions in MX-80 and Opalinus Clay. The results of the blind predictions of the Eu^{III}, Th^{IV} and U^{VI} isotherms measured on MX-80 and Opalinus Clay are shown in Fig. 4.4.

The measurements cover over 4 orders of magnitude of the aqueous metal ion equilibrium concentration. The agreement between experimental results symbols and the blind predictive modelling (lines) is good to very good and the calculated values lie in most cases within the experimental error bars given. The “bottom-up” approach, used in conjunction with some simplifying assumptions, may be regarded as a very promising method for quantitatively calculating radionuclide uptake in complex geochemical systems (BRADBURY & BAEYENS, 2011b).

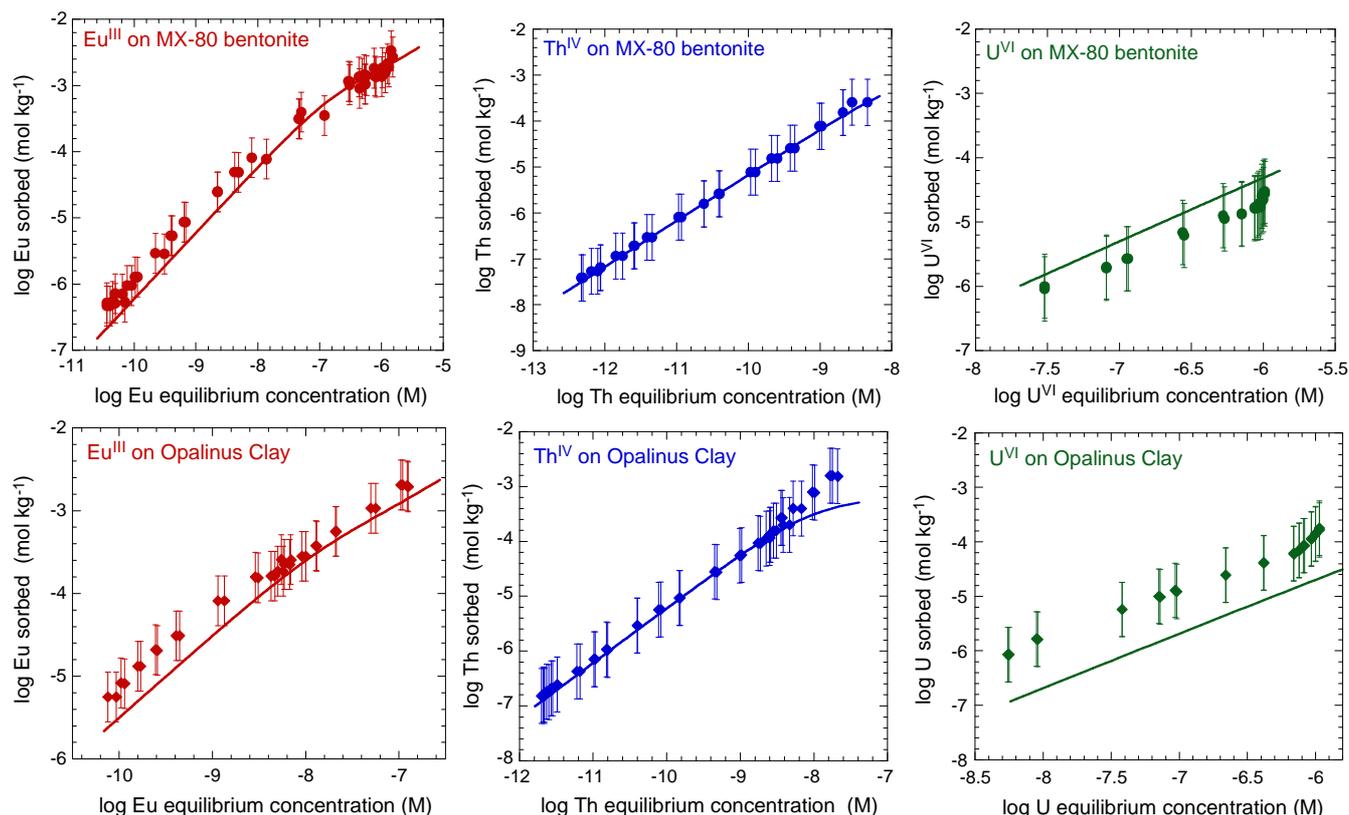


Fig. 4.4: Sorption isotherms on MX-80 bentonite and Opalinus Clay: Experimental results and blind predictions based on the “bottom up” approach (BRADBURY & BAEYENS, 2011a).

4.3.3 Am^{III} sorption on montmorillonite in the presence and absence of carbonate

Previous investigations have suggested the formation of Am^{III} carbonate complexes at the montmorillonite surface (MARQUES et al., 2008). The aim of this study was to further investigate the nature of the surface complexes of Am^{III} at the molecular level using Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy. In the absence and presence of inorganic carbon EXAFS measurements were performed on ²⁴³Am^{III} loaded self-supporting montmorillonite films. Table 4.2 summarizes the

sample matrix together with the experimental conditions. In addition to the clay films, a solid compound, NaAm_{0.005}Gd_{0.995}(CO₃)₂, was synthesized and used as a reference.

Fig. 4.5a shows the Am L_{III} edge k³-weighted radial structure functions (RSFs) of the four Am loaded montmorillonite samples and the reference compound. The spectra obtained clearly show different features.

Fig. 4.5b shows the experimental data as inverse Fourier Transforms (FT⁻¹) together with the corresponding fits. The structural parameters derived from the fits are summarized in Table 4.3.

Table 4.2: Sample matrix for the production of the EXAFS samples (*S/L* ratio = 2 g·L⁻¹, 0.1 M NaClO₄).

Sample	C _{inorg.} (mM)	pH	²⁴³ Am loading (mmol·kg ⁻¹)	log R _d (L · kg ⁻¹)
Am-Mont-carbonate free	-	~8	1.04	4.95
Am-Mont1	7.43	~9.2	1.07	4.01
Am-Mont2	7.43	~9.2	2.78	3.80
Am-Mont3	7.43	~9.2	8.32	4.46
Reference precipitate	NaAm _{0.005} Gd _{0.995} (CO ₃) ₂			

The identification of Am-Al/Si backscattering pairs for both systems (with and without carbonate) is a clear indication for the formation of Am^{III} inner-sphere complexes at the montmorillonite surface. The RSF spectra of the samples Am-Mont1 and Am-Mont2 are similar and the EXAFS parameters obtained by fitting the spectra are consistent with the formation of Am(III) carbonate complexes at the montmorillonite surface. No Am-C shell was necessary to reproduce the EXAFS spectrum. However fitting a weak backscatter such as carbon in our system might be difficult, since the backscattering amplitude produced 1 C ($z = 6$) is much weaker than the amplitude produced by one Si/Al shell ($z = 13/14$)

originating from the montmorillonite surface. Thus, the most reliable structural evidence for the formation of bidentate Am(III) carbonate complexes at the montmorillonite surface is the identification of the distal oxygen O_{dist} shell of the carbonate ligand (4.28 Å) and the associated multiple scattering of Am-C-O_{dis} (4.28 Å) and Am-C-O_{dist}-C (4.28 Å).

The similarity of the RSF spectra of the sample Am-Mont3 and the reference compound (Fig. 4.5a) confirm that precipitation occurred at higher Am^{III} loadings which is in a good agreement with the increased log R_d value obtained for Am-Mont3 (Table 4.2).

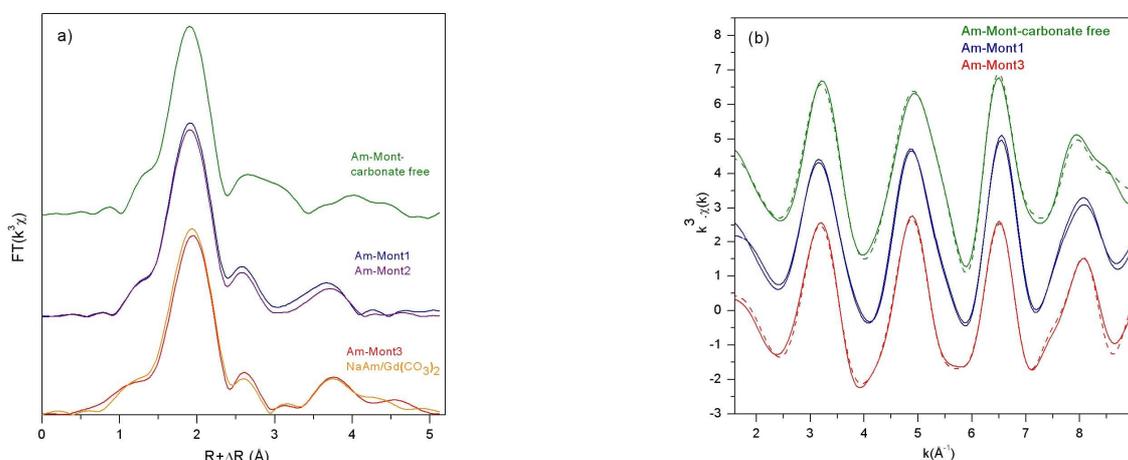


Fig. 4.5: (a) RSF of the experimental EXAFS data obtained for the Am(III) sorption samples and the reference compound NaAm/Gd(CO₃)₂; (b) inverse Fourier transforms (FT^{-1}) of the experimental data (solid lines) and the corresponding least-squares fits (dashed line).

Table 4.3: Structural parameters obtained for the samples Am-Mont-carbonate free, Am-Mont1, Am-Mont3 and the reference compound.

Sample	shell	R (Å)	CN	σ^2 [Å ²]
Am-Mont-carbonate free	Am-O	2.46	8.8	0.014
	Am-Si ₁ /Al ₁	3.20	1.6	0.006 ^{b)}
	Am-Si ₂ /Al ₂	3.75	2.3	0.01 ^{c)}
	Am-Si ₃ /Al ₃	4.72	5	0.01 ^{c)}
Am-Mont1	Am-O	2.45	7.4	0.01
	Am-Si/Al	3.23	1.2	0.003 ^{b)}
	Am-O _{dist}	4.27	1.8	0.004 ^{b)}
	Am-O _{dist} -C	4.27	2 x 1.8 ^{a)}	0.004
	Am-C-O _{dist} -C	4.27	1.8	0.004
Am-Mont3	Am-O	2.51	9.8/10	0.015
	Am-C _{bi}	2.94	3 ^{c)}	0.004
	Am-C _{mono}	3.64	3 ^{c)}	0.008
	Am-O _{dist}	4.29	2 x 3 ^{a)}	0.008
	Am-O _{dist} -C	4.29	3	0.008
	Am-C-O _{dist} -C	4.29	3	0.008

The parameters R, CN and σ^2 of the scatterings paths Am-O_{dist}, Am-O_{dist}-C and Am-C-O_{dist}-C were linked together during the fitting process. ^{a)}Scattering path is two-fold degenerate. ^{b)} fixed at the value obtained freely, ^{c)} fixed. ΔE_0 (eV) = 7 for Am-Mont-carbonate free; = 11 for Am-Mont1,2; = 13 for Am-Mont3 and NaAm_{0.005}Gd_{0.995}(CO₃)₂.

4.4 The sorption of Fe on montmorillonite under anoxic and controlled reducing conditions (PhD project)

Virtually all deep underground repository concepts contain large amounts of iron, and reducing conditions will prevail in the long-term. The influence of reducing conditions on the characteristics of clay minerals, particularly with respect to radionuclide retention in the presence of high aqueous Fe(II) concentrations, is still an open question.

Fe(II) sorption experiments at trace concentrations were carried out in an inert gas glove box on Na-montmorillonite (SWy-2) under (i) anoxic conditions ($O_2 < 0.1$ ppm) and (ii) electrochemically controlled reducing conditions. The experimental results are shown in Fig. 4.6 and indicate that the sorption of iron is more pronounced under anoxic conditions than under electrochemically reducing conditions at pH ~ 7.

The 2SPNE SC/CE sorption model (BRADBURY & BAEYENS, 1997) was used to predict Fe^{II} and Fe^{III} sorption edges on montmorillonite. The surface complexation constants were derived from the linear free energy relationship for the strong site types on montmorillonite (BRADBURY & BAEYENS, 2005b). The Fe sorption edge obtained under anoxic conditions is well reproduced by the model (red broken line) under the assumption that ferric iron (Fe^{III}) is present. On the other hand, the experimental data obtained at pH ~ 7 using the electrochemical cell at a fixed reducing potential (Eh = -0.44 V vs. SHE) are in accord with the predicted sorption of ferrous iron (Fe^{II}). Note that at trace concentrations the redox state of iron in solution cannot be determined experimentally.

An Fe sorption isotherm was measured under anoxic conditions at pH = 6.2 in 0.1 M NaClO₄ on Na-SWy-2, Fig. 4.7. The calculated isotherm using the 2SPNE SC/CE sorption model assuming that Fe^{II} is sorbing (blue broken line in Fig. 4.7) and the measured data (red triangles) clearly do not agree. Also, the data confirm the high sorption values observed in the edge measurements under the same conditions. Measurements made using the phenanthroline method (STUCKI & ANDERSON, 1981) at concentrations $> 10^5$ M showed that the iron in solution was present in the +2 oxidation state.

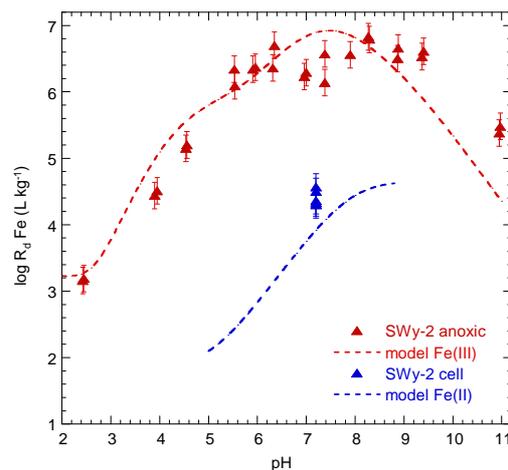


Fig. 4.6: Sorption edge of iron on SWy-2 in 0.1 M NaClO₄ under anoxic conditions (▲) and under controlled Eh conditions (-0.44 V vs. SHE and pH 7.2) (▲). The broken lines are calculated curves using the 2SPNE SC/CE sorption model (see text for details).

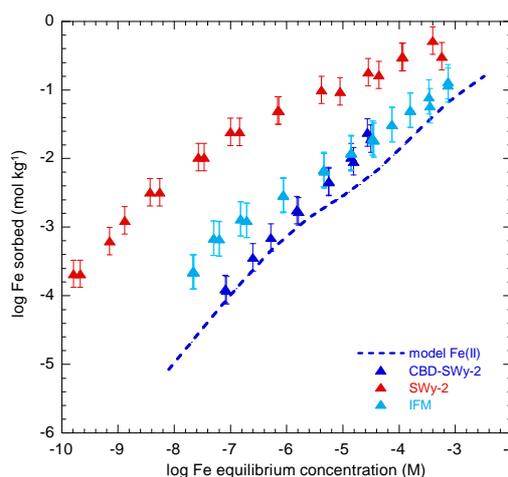


Fig. 4.7: Sorption isotherms of Fe^{II} carried out under anoxic conditions at pH = 6.2 in 0.1 M NaClO₄ on Na-SWy-2 (▲), on CBD-SWy-2 (▲) and on synthetic IFM (▲). The blue broken line is a sorption isotherm calculated under the assumption that iron is present as Fe^{II}.

A possible explanation for the data measured under anoxic conditions in Figs. 4.6 and 4.7 is that the sorbed Fe^{II} is oxidized by an electron transfer reaction with the structural iron (Fe^{III}) of the montmorillonite. In order to investigate such a hypothesis sorption isotherms were measured under anoxic conditions on (i) a citrate/bicarbonate/dithionite (CBD) treated SWy-2 (after STUCKI et al., 1984) and (ii) on a synthetic iron-free montmorillonite (IFM). In the former case the structural Fe^{III} is largely reduced to Fe^{II}. The sorption of Fe^{II} on these treated montmorillonite samples is less pronounced than on

the native SWy-2 and is in much better agreement with the predicted Fe^{II} isotherm (Fig. 4.7). Preliminary EXAFS measurements on Fe loaded IFM samples indicate that the sorbed iron remains in the +2 state on the clay surface. These findings support the hypothesis that the oxidation of the sorbed ferrous iron might occur through an electron transfer process to the structural ferric iron of the montmorillonite.

4.5 Swiss-Hungarian cooperation project

In connection with the Schweizer Erweiterungsbeitrag DEZA/SECO agreement a 3 years cooperation project entitled “*Development of a macro- and microscopic approach to investigate the geochemistry of radioactive waste disposal systems*” has been set up between LES and the Hungarian Academy of Sciences, KFKI Atomic Energy Research Institute. The project started on 15th October 2010. The objectives are to make specific contributions to the safety assessment of future radioactive waste repositories through an understanding of relevant retention mechanisms and processes, and to provide the necessary models and databases. In order to investigate sorption mechanisms on molecular and microscopic scales, high-sensitivity X-ray micro analytical measurements are foreseen. These investigations are strongly linked to macroscopic studies combined with geochemical modelling. The two argillaceous rocks being investigated are Boda Claystone Formation (BCF) and Opalinus Clay.

Three μ -XRF/XAS/XRD beamtime proposals submitted to the HASYLAB (Hamburg, Germany) and ANKA (Karlsruhe, Germany) were approved and the main focus in 2011 was put on the investigations on BCF samples. In a first phase the sample preparation procedures were developed. The aim was to identify the mineral phases responsible for the uptake of Ni^{II} on BCF, and to investigate the uptake process of radionuclides on clays and other minerals present in the argillaceous rock in terms of outer- or inner-sphere complexes or precipitation.

The 2SPNE SC/CE sorption model was used to calculate the sorption isotherm of Ni on BCF samples using the “bottom up” approach. (BCF contains ~ 40 wt.% 2:1 type clay minerals with illite as dominant clay mineral.) Small sections of selected BCF borecore samples from a depth of 540 m were milled down to ca. 30 μ m thickness and mounted onto high purity Si holders and polished. The samples were equilibrated for 72 hours with a 0.1 and 1 mM NiCl₂ solution at pH = 7.1 in a 0.1 M NaCl background electrolyte. Combined μ -XRF/XRD measurements were performed using a multilayer monochromator at a fixed energy of 17.5 keV. μ -XRF maps were recorded on pre-selected areas of the samples using a step size comparable to the beam size (20 μ m at HASYLAB and 5 μ m at ANKA) and 1 s counting time per pixel. The elemental maps served as a basis for the selection of small areas of interest where μ -XRD images were collected using a CCD detector. The μ -EXAFS were measured in fluorescence mode at the HASYLAB beamline L, at 20 μ m lateral resolution of the identified areas of interest.

The distribution maps indicate that Ni is mainly associated with K- and Fe-rich phases, and anti-correlated with Ca. The interpretation is that Ni is predominantly associated with illite (a K-rich 2:1 clay mineral, Fig. 4.8) which has a high K and Fe content.

μ -XRD analyses with a 5 μ m beam diameter indicate that the composition of the argillaceous rock matrix on the micro-scale agrees well with the mineral composition as obtained by bulk-XRD measurements. μ -EXAFS investigations demonstrated that Ni forms inner-sphere complexes on clay minerals at low Ni concentration (0.1 mM), Fig. 4.9. At higher Ni concentrations (1 mM Ni) surface precipitation occurred, Fig. 4.9. The uptake of contaminants on mineral surfaces via inner-sphere complexation strongly reduces the mobility of these metal ions in the geosphere. The results of the analyses showed that for Ni^{II} the clay mineral illite is an effective sink in the BCF sample. The experiments will be continued with other radionuclides, and on Opalinus Clay samples.

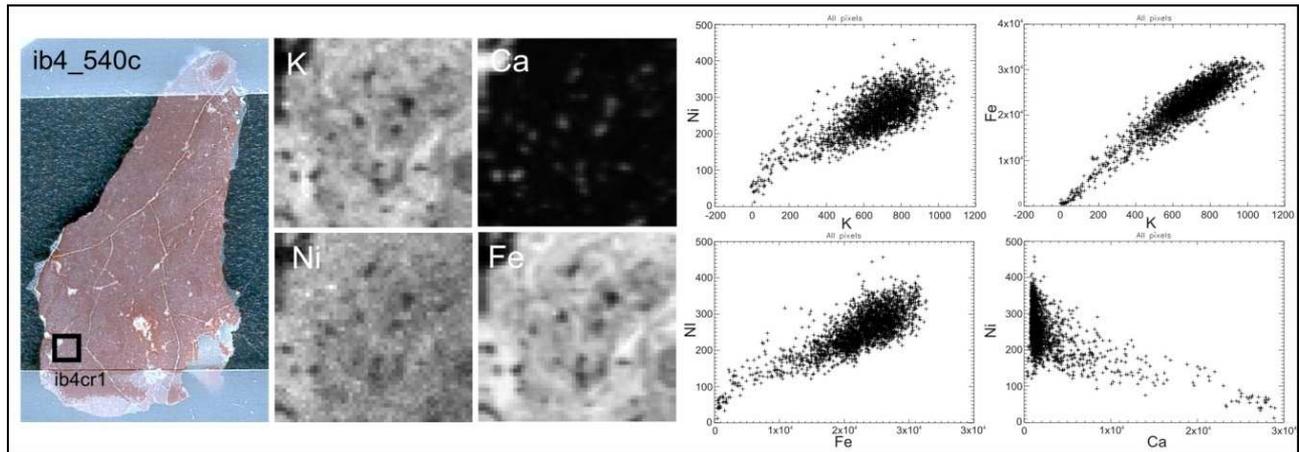


Fig. 4.8: Optical image of the thin section ib4-540c; elemental maps of the selected area ib4cr1 (1x1 mm, indicated as a black square on the optical image) and scatter plots of characteristic X-ray intensities of elements measured at beamline L/HASYLAB.

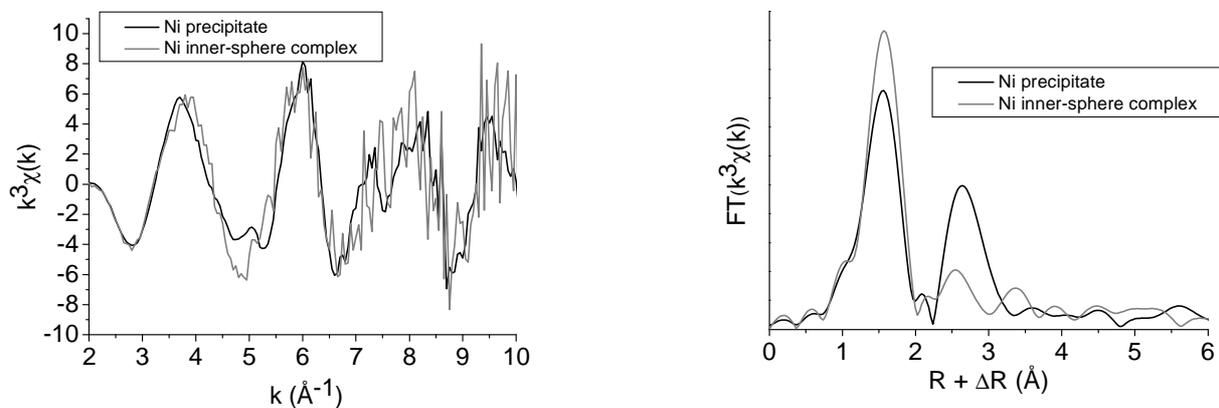


Fig. 4.9: k^3 -weighted Ni K-edge μ -EXAFS spectra representative for the formation of Ni-precipitates and inner-sphere complexes, and the corresponding RSFs, obtained by Fourier transforming the micro-EXAFS spectra in the range from 2 to 10 \AA^{-1} .

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5 CEMENT SYSTEMS

E. Wieland, J. Tits, D. Kunz, A. Laube, P. Schaub (postdoc), B. Dilnesa (PhD, Empa)

5.1 Overview

Cementitious materials are foreseen to be used in the planned deep geological repositories for low-level and short-lived intermediate-level (L/ILW) as well as long-lived intermediate-level (ILW) radioactive waste in Switzerland. A combination of solubility and sorption constraints in the cementitious near field controls the source term for radionuclide migration into the host rock. The research programme carried out by the group "Cement Systems" aims at strengthening the credibility of the sorption values used in performance assessment (PA) for predicting radionuclide retention in the cementitious near field and improving knowledge on the chemical processes in the near field of the planned repositories.

The cement used for the experimental studies is a sulfate-resisting Portland cement CEM I 52.5 N HTS (Lafarge, France), which is currently in use for the conditioning of radioactive waste in Switzerland. Calcium silicate hydrate (C-S-H) phases are considered to be the most important constituent of hardened cement paste (HCP) controlling the immobilisation of metal cations, while AFm ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$) and AFt ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-tri}$) phases of the HCP control anion binding. For this reason complementary sorption studies on radionuclide uptake using C-S-H with different Ca:Si ratios (C:S), AFm and AFt phases have been carried out.

The main lines of research in 2011 were:

- Assessment of the interaction of waste materials with cement and the sorption reduction by complexing ligands in conjunction with activities related to the Sectoral Plan;
- Sorption studies with Cl^- , I^- and SeO_3^{2-} on HCP and cement minerals under saline conditions;
- Wet chemistry experiments and spectroscopic investigations on the interaction of actinides (U(VI), Np(IV,V,VI)) with HCP and C-S-H phases;
- Spectroscopic determination of the Fe speciation in HCP.

The sorption and spectroscopic studies on Np(IV,V,VI) uptake by cementitious materials were carried out in the framework of the 7th EU Framework Programme project "RECOSY" (REdox phenomena

CONtrolling SYstems) in collaboration with Dr. X. Gaona (KIT-INE).

The joint PhD project with Empa on the Fe speciation in cement carried out by B. Dilnesa was brought to a close with the final examination in December 2011. In the last year of this project the main activities focused on completing the spectroscopic studies and preparing the papers required for the submission of the PhD work.

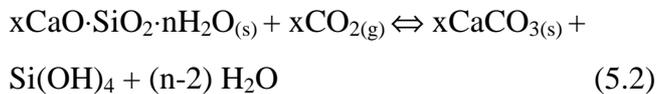
Dr. P. Schaub (postdoc) joined LES on September 1st, 2011. His research activities will focus on further developing the microXRD technique for spatially resolved mineralogical studies at the cement/clay interface. The project will be carried out jointly with the XAFS sub-programme.

5.2 Contribution to the Sectoral Plan

In the framework of the Sectoral Plan a report on the in-situ evolution of the L/ILW repository near field has been prepared in LES ("Chemical evolution of the cementitious L/ILW near field"; for details see Chapter 3). Additional sections to the report were prepared in 2011 concerning the interaction of waste materials with cement (WIELAND & BERNER, 2011). Performance assessment studies carried out within the framework of the Sectoral Plan will require further updates of the existing cement sorption data base (SDB). To this end a re-appraisal of the influence of safety-relevant complexing ligands, e.g. isosaccharinic acid, present in the near field on radionuclide uptake by HCP has been made using information from recent in-house sorption studies and measurements published in the open literature (WIELAND, 2011). Both of the above reports include detailed literature surveys.

In the long term, the waste materials disposed of in the L/ILW repository are expected to interact with the HCP in the engineered barrier. The waste materials and their degradation products can be classified as "reactive" or "inert" with respect to possible impacts on hydrated cement (WIELAND & BERNER, 2011). Materials, such as organics and metals (Al, Mg, Fe), are chemically reactive under the hyperalkaline reducing conditions of the near field. Microbial degradation of organic materials is expected to occur mainly via methanogenesis forming CO_2 and CH_4 , while anaerobic degradation due to respiration, which consumes Fe^{3+} and SO_4^{2-} as electron acceptors, is a

possible alternative pathway of less importance (WIELAND, 2010). Production of CO_2 causes CaCO_3 precipitation in the near field, which depletes the main Ca sources in cement, i.e. portlandite and C-S-H:



Nagra's PA is based on the criterion that the amount of portlandite allowed to transform into calcite by the degradation of organic matter in the L/ILW repository should not exceed 2/3 of the initial portlandite inventory in HCP (SCHWYN, 2008). Waste sorts are denoted as SMA-1/LMA-1 type wastes if the criterion is met, whereas if the above limit is exceeded they are grouped into SMA-2/LMA-2 type wastes (SCHWYN, 2008). The safety criterion ensures that the retention-controlling cement minerals are present in the cement

matrix despite the partial transformation of portlandite into calcite, which further ensures that the barrier function will be maintained during the course of the evolution of the cementitious near field.

The acceptable portlandite transformation due to degradation of organics can be converted into a maximum acceptable loading of the individual organic materials in the near field. The latter loading was estimated on the assumption that 1) all organic materials degrade entirely over time, except graphite for which 20 % degradation was assumed, and b) microbial degradation occurs via the sulfate-reducing pathway or a fermentative process producing CO_2 and CH_4 (Fig. 5.1). A comparison was made with the inventories of organic materials present in all waste sorts (NAGRA, 2008), which revealed that for most organic materials the maximum inventories are well below the maximum acceptable loadings, except for polystyrene, PVC, bitumen, plastic materials, cellulose and graphite.

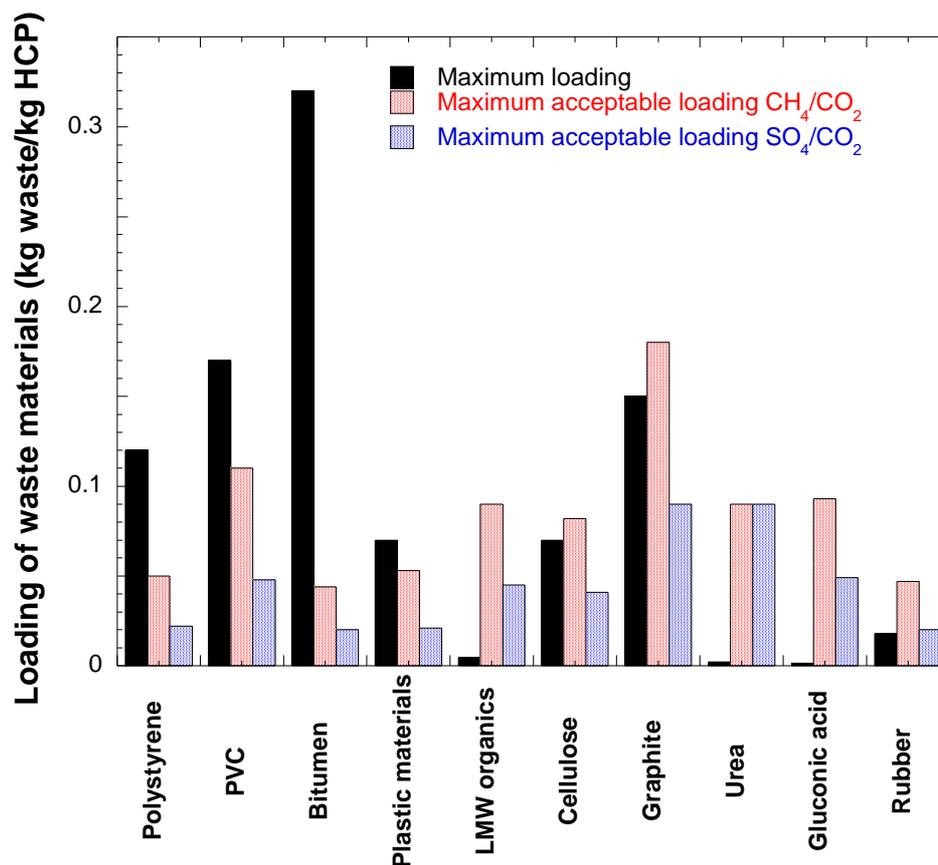


Fig. 5.1: Loadings of organic materials (kg waste/kg HCP) in cement-stabilized waste forms. Maximum loadings were calculated from the compilation of reported inventories in the different waste sorts (NAGRA, 2008). Maximum acceptable loadings were estimated on the assumption that a) sulfate-reducing micro-organisms (SO_4/CO_2) or methanogens (CH_4/CO_2) degrade organic materials and b) a 2/3 reduction of the initial portlandite content of HCP is acceptable.

Metallic materials will be subject to anoxic corrosion, which produces H_2 . Some metals, such as Mg, Al and Fe, are contained in cement minerals, and their release during corrosion into solution may have an impact on the mineral composition of HCP. A literature survey, complemented by thermodynamic scoping calculations, was carried out with the aim of assessing potential impacts (WIELAND & BERNER, 2011). Large quantities of Mg are expected to precipitate as brucite, while only a small amount of Mg is bound as hydrotalcite. Hence, the large Mg inventories of some waste forms are not expected to significantly alter the mineral composition of HCP. High Al loadings give rise to the transformation of portlandite and ettringite into hydrogarnet, calcium hemicarboaluminate or calcium sulfoaluminate solid solutions, respectively. Similarly, under the reducing conditions of the near field, increasing Fe(II) loadings are expected to cause the transformation of ettringite into hydromagnetite and pyrite, along with the simultaneous precipitation of excess Ca as portlandite and calcite. Hence, upper limits of Al and Fe loadings were recommended for SMA-1/LMA-1 waste sorts as the release of these elements can significantly alter the mineral composition of HCP (WIELAND & BERNER, 2011).

5.3 Dose-determining radionuclides

Iodide (^{129}I), chloride (^{36}Cl), selenium (^{79}Se) and ^{14}C species are considered to determine the long-term activity release rate (mSv per year) from the

cementitious near field into the far field (NAGRA, 2002). In 2011 the influence of chloride on the uptake of ^{129}I , ^{36}Cl and ^{75}Se was investigated in multi-tracer experiments. Note that the planned L/ILW repository could be located in a geological formation with significant Cl^- concentrations in the groundwater, for example about 565.9 mmol/kg H_2O in case of the Effingen Member (MÄDER, 2009). In contrast, the Cl^- concentration in cement porewater is generally low (typically $\leq 10^{-3} M$) due to the limited inventory of stable chloride in commercial cements (≤ 0.01 wt%).

HCP exposed to highly saline groundwater is subject to mineral transformations. Chloride was found to readily displace OH^- , SO_4^{2-} and CO_3^{2-} anions in the AFm phases (e.g. BALONIS et al., 2010). In carbonate containing cements, such as HTS cement, chloride binding by AFm phases is controlled by the formation of a solid solution between calcium monocarboaluminate (AFm- CO_3) and Friedel's salt (AFm- Cl_2) (Fig. 5.2) (e.g. BALONIS et al., 2010). Hence, addition of NaCl, simulating a saline groundwater, causes the transformation of calcium monocarboaluminate into Friedel's salt and the precipitation of the released CO_3^{2-} as $CaCO_3$ (Fig. 5.2).

The influence of increasing Cl^- concentrations on ^{129}I uptake by fresh and degraded HCP is significant, while the effect on ^{36}Cl and ^{75}Se binding is much weaker (Fig. 5.3).

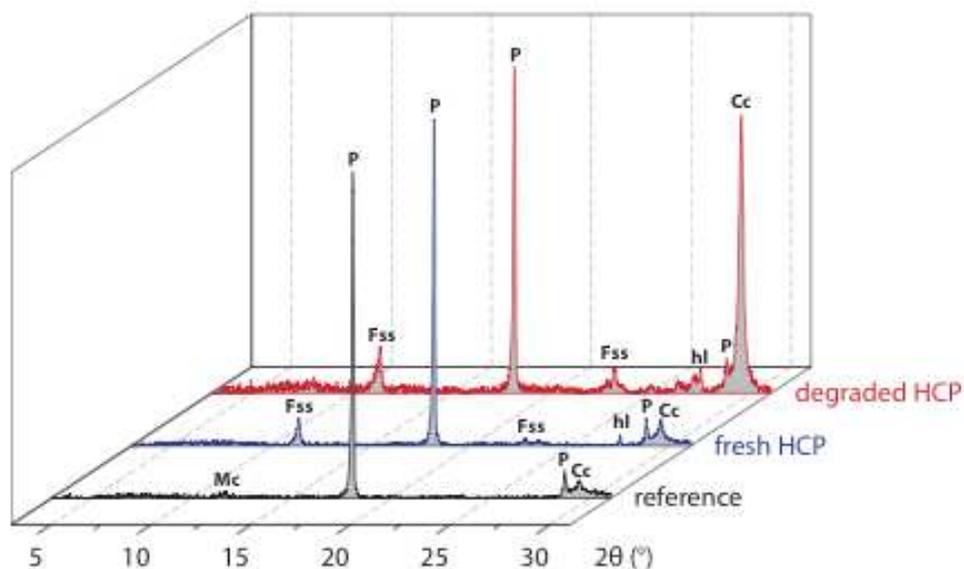


Fig. 5.2: XRD pattern of HCP aged in 1.1 M Cl^- solution at $pH = 13.3$ (fresh HCP) and 12.5 (degraded HCP) for 28 days. P: portlandite, Cc: calcite, Fss: Friedel's salt solid solution, Mc: calcium monocarboaluminate, hl: halite.

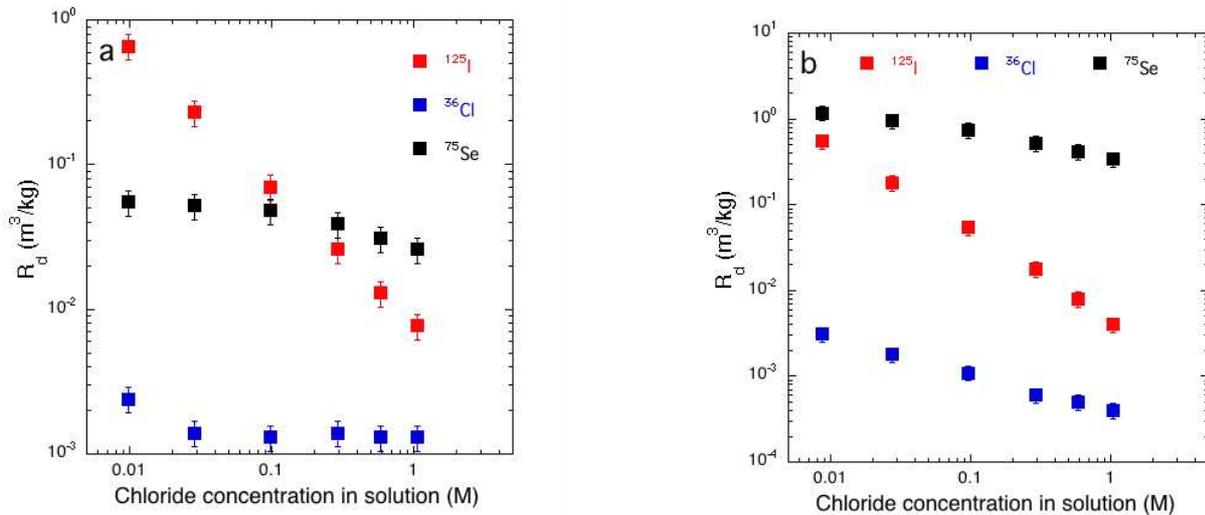


Fig. 5.3: Influence of increasing Cl^- concentration on the uptake of ^{125}I , ^{36}Cl and ^{75}Se by (a) fresh and (b) degraded HCP.

In order to develop a detailed mechanistic understanding, sorption studies with individual cement minerals capable of binding these radionuclides were required. Therefore, additional sorption measurements were carried out on several important cement minerals (Table 5.1).

The measurements show that ^{36}Cl and ^{125}I are taken up selectively by just a few minerals, in particular Friedel's salt (AFm-Cl_2) in the case of ^{36}Cl and calcium monosulfoaluminate (AFm-SO_4) in the case of ^{125}I . Note that the binding of both radionuclides to C-S-H phases, the most abundant phase in HCP, is

only very weak. In contrast, ^{75}Se is taken up by all phases, and even binds strongly to most of them. In the light of these results the dependences shown in Fig. 5.3 can be interpreted as follows: Se strongly sorbs to HCP even at high Cl^- concentrations since the transformation of $\text{AFm-CO}_3/\text{SO}_4$ has no detrimental effect on Se uptake. Isotopic exchange of ^{36}Cl between the stable Cl bound in AFm-Cl_2 and aqueous Cl^- determines ^{36}Cl uptake. The amount of AFm-Cl_2 seems to increase with increasing Cl^- concentration, which results in a constant or slightly decreasing R_d value (Fig. 5.3).

Table 5.1: Sorption values for ^{36}Cl , ^{125}I and ^{75}Se on some important cement minerals in their equilibrium solutions.

Cement phase	R_d * (m^3/kg)		
	^{36}Cl	^{125}I	^{75}Se
C-S-H phase with C/S = 0.75	0	0	0.22
C-S-H phase with C/S = 1.07	0	0.005	1.35
C-S-H phase with C/S = 1.65	0.003	0.008	1.45
Friedel' salt (AFm-Cl_2)	0.23	0	5.75
Calcium monocarboaluminate (AFm-CO_3)	0	0	0.77
Calcium monosulfoaluminate (AFm-SO_4)	0.003	0.03	2.05
Ettringite (AFt-SO_4)	0	0	6.18

* All sorption values are related to the dry weight of the corresponding cement phase.

In contrast, phase transformations caused by Cl⁻ have a pronounced effect on ¹²⁵I uptake by HCP since calcium monosulfoaluminate (AFm-SO₄), which is the most important uptake-controlling phase for I⁻ in HCP (see also Section 2.3.5), converts to AFm-Cl₂. I⁻ uptake by the latter phase is negligibly small.

¹⁴C, possibly in the form of small organic molecules generated during steel corrosion, is a potential major contributor to the dose released from the L/ILW repository. In a recently published status report the relevant research topics have been identified with a view to improving the quantitative treatment of ¹⁴C release in PA (WIELAND & HUMMEL, 2010) as follows: 1) Determination of the chemical nature of the ¹⁴C containing organic compounds released during steel corrosion under reducing conditions, and 2) Determination of the long-term chemical stability of these compounds under the alkaline conditions of a cementitious near field. It was further emphasized in the report that the availability of appropriate analytical tools, which allow low molecular weight (LMW) organic compounds to be identified in the liquid and gas phase at very low concentrations, is a prerequisite for starting an experimental research programme in LES. In 2011 a HPIEC-MS equipment was installed, which allows oxygenated LMW organic compounds to be identified. Analytical protocols for the detection of LMW carboxylic acid and aldehydes (C ≤ 5) using mass spectrometry (MS) and conductivity detection methods are currently being developed and assessed.

5.4 Immobilization of actinides by cementitious materials

5.4.1 Uptake of neptunium by HCP and C-S-H

Neptunium speciation under hyperalkaline conditions

Neptunium is commonly believed to exist in the oxidation states +IV or +V in a cementitious environment under hyperalkaline reducing or oxidizing conditions, respectively. Investigations into the neptunium speciation under hyperalkaline oxidizing conditions were carried out in collaboration with KIT/INE, which show that, in analogy to U(VI), anionic Np(VI) species (NpO₂(OH)₃⁻ and NpO₂(OH)₄²⁻) may also form under these conditions, thus significantly limiting the stability field of Np(V).

In the absence of Na-hypochlorite, used as an oxidizing agent, Np was found to be in the pentavalent state both in the solid and aqueous phases, while in the presence of Na-hypochlorite XANES and EXAFS

data clearly confirmed the presence of Np(VI) in both phases (GAONA et al., 2011a).

Batch sorption experiments with Np(IV), Np(V) and Np(VI) on C-S-H phases

Sorption studies with Np(V) on cementitious materials are sparse, while sorption data for Np(IV) and Np(VI) are lacking in the literature due to experimental difficulties associated with the stabilization of the +IV and +VI redox states. Therefore, sorption values for redox-sensitive actinides, such as Np(IV) and Np(VI), have been estimated on the basis of their chemical analogy with other tetravalent and hexavalent actinides, such as Th(IV) and U(VI) (e.g. WIELAND & VAN LOON, 2002). To verify these analogies, Np(IV,V,VI) uptake by HCP and C-S-H phases under oxidizing, anoxic and reducing conditions was investigated in the framework of the 7th EU FP project "RECOASY".

The effect of pH (10 < pH < 13.3) on Np(IV), Np(V) and Np(VI) sorption to C-S-H phases was investigated and compared with sorption data of the same Np species on TiO₂ (Fig. 5.4).

The experiments were carried out using the short-lived ²³⁹Np isotope (t_{1/2} = 2.355 days), which was separated from its parent, ²⁴³Am, using a standard procedure. The redox state of Np in the experiments was controlled by the addition of Na-dithionite as a reducing agent in case of Np(IV) or Na-hypochlorite as an oxidizing agent in case of Np(VI), respectively. No redox buffer was used in the experiments with Np(V). Preliminary experimental tests showed that neither Na-dithionite nor Na-hypochlorite had any effect on the stability of the C-S-H phase nor any effect on the sorption behaviour of Th(IV) and U(VI).

In the case of C-S-H phases, Np uptake may be influenced not only by the pH changes but also by the C:S ratio. In order to quantify the influence of Np(IV,V,VI) speciation as a function of pH, experiments on TiO₂ in the pH range 10 < pH < 13.3 were performed. Note that the uptake on TiO₂ is expected to occur by surface complexation and this will be influenced by changes in Np(IV,V,VI) speciation as a function of pH.

The results show that the uptake of the tetravalent, pentavalent and hexavalent actinides by either C-S-H phases or TiO₂ are similar (Fig. 5.4). The sorption of Np(IV) and Th(IV) was found to be independent of pH while Np(V) sorption decreases in both cases at pH ≥ 12.

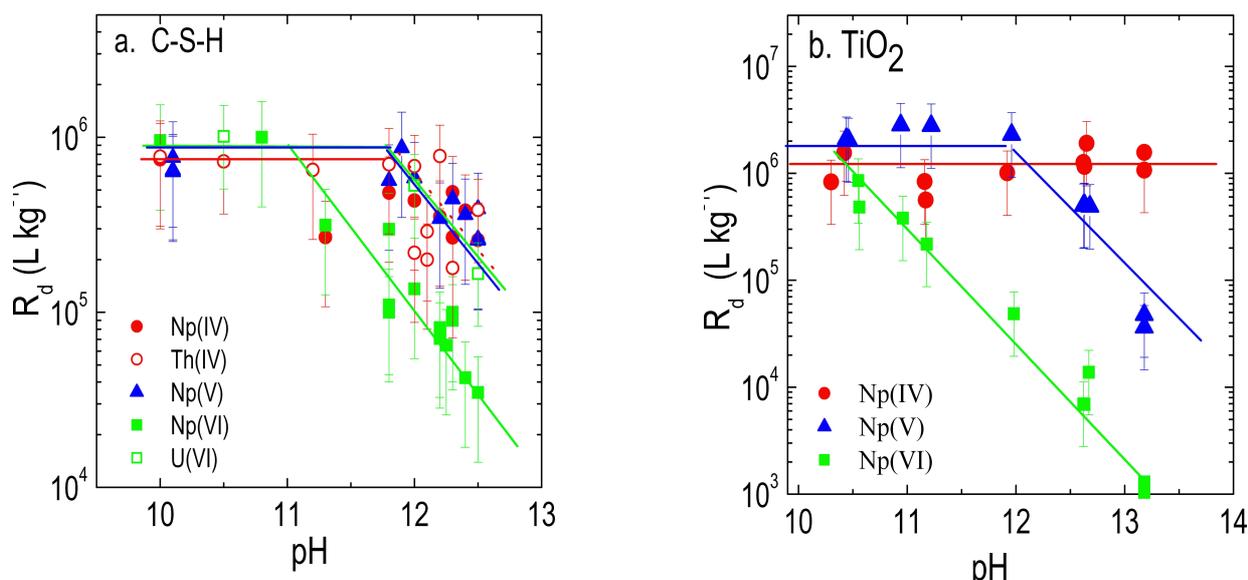


Fig. 5.4: Sorption of actinides on C-S-H and TiO_2 . a) Comparison of the sorption of Np(IV, V, VI) with the sorption values of Th(IV) and U(VI) on C-S-H (C:S = 1.07), b) Np(IV, V, VI) uptake by TiO_2 .

Lower R_d values and a pronounced dependence on pH were observed in case of Np(VI) and U(VI). Differences in the sorption behaviour of the different redox states can be explained by differences in the aqueous speciation. Negatively charged hydroxo species dominate the aqueous speciation of the pentavalent and hexavalent actinides above pH 11, giving rise to a decrease in sorption. In contrast, the aqueous speciation of the tetravalent actinides is independent of pH in the range $10 < \text{pH} < 14$, resulting in constant R_d values over this pH range.

Thus, the observed sorption behaviour of neptunium on C-S-H phases and TiO_2 is predominantly controlled by aqueous speciation.

EXAFS study on Np uptake by cementitious materials

Extended X-ray absorption fine structure (EXAFS) investigations on Np(V, VI) loaded C-S-H and HCP samples were carried out with the aim of determining whether or not pentavalent and hexavalent Np could be incorporated in the C-S-H structure in a manner similar to that of Np(IV) (GAONA et al., 2011b). C-S-H suspensions with C:S ratios 0.75, 1.07

(synthesized in Milli-Q water and in ACW, respectively) and 1.65, and HCP suspensions were loaded with Np(V) in the absence and in the presence of Na-hypochlorite to levels of ~930 ppm or ~2600 ppm, respectively, in the wet paste (Fig. 5.5). EXAFS measurements were carried out at the ROBL beamline at the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

Principal component analysis (PCA) in combination with iterative target-transformation factor analysis (ITFA) of the EXAFS data showed that two components (Np-C-S-H 0.75 and Np-C-S-H 1.65) are sufficient to reconstruct all spectra (Table 5.2). This finding is in agreement with the earlier analysis of Np(IV)-C-S-H/HCP EXAFS data (GAONA et al., 2011b). The Fourier transforms indicate the presence of two different neptunyl moieties (Fig. 5.5). Significantly shorter Np-O_{ax} and Np-O_{eq} distances were determined for samples with Na-hypochlorite (1.79–1.85 Å and 2.24–2.25 Å), indicating the presence of Np(VI), compared to samples under anoxic conditions (1.88–1.89 Å and 2.39 Å), indicating presence of Np(V).

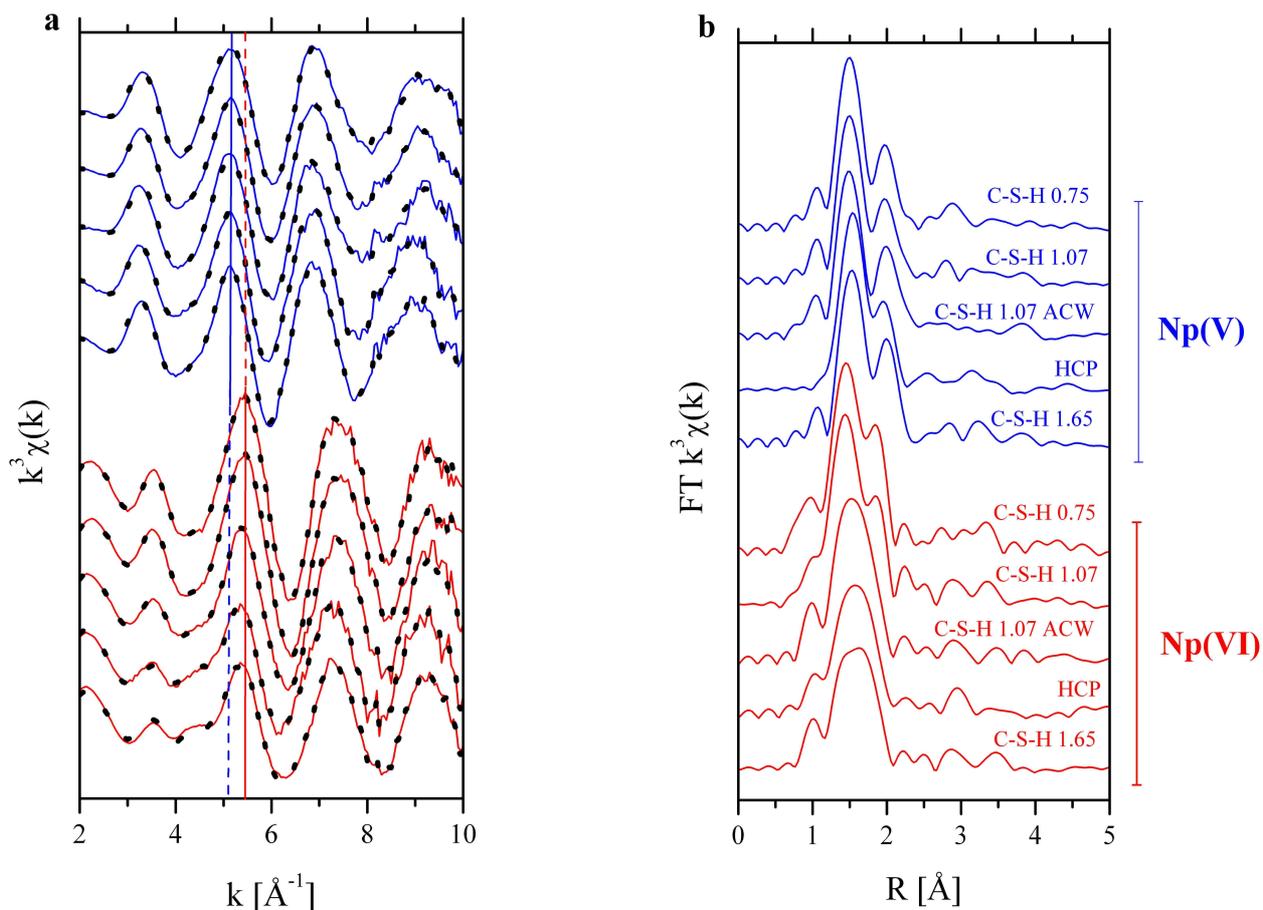


Fig. 5.5: EXAFS measurements of Np(V,VI) loaded C-S-H and HCP samples, a) k^3 -weighted EXAFS spectra (experimental (solid line) and reconstruction by 2 components (dashed line)), b) Fourier transform of Np(V,VI) sorbed on C-S-H (C:S = 0.75, 1.07, 1.07 in ACW, 1.65) and HCP. Vertical lines (solid, dashed) in Fig. 5.5a indicate the phase shift between Np(V) and Np(VI) species.

Table 5.2: Component composition of Np(V) and Np(VI) doped C-S-H (C:S = 0.75, 1.07, 1.07 in ACW, 1.65) and HCP samples as estimated by ITFA. Calculations were performed in $k^3\chi(k)$ space for $2 \leq k [\text{\AA}^{-1}] \leq 10$.

Sample	Np(V)		Np(VI)	
	comp. 1 / comp. 2	total	comp. 1 / comp. 2	total
*Np – C–S–H 0.75	1 / 0	–	1 / 0	–
Np – C–S–H 1.07	0.63 / 0.34	0.99	1 / 0	1
Np – C–S–H 1.07 ACW	0.77 / 0.22	0.99	0.49 / 0.59	1.08
Np – HCP	0 / 1	1	0 / 1	1
*Np – C–S–H 1.65	0 / 1	–	0 / 1	–

* component 1: Np-C-S-H 0.75; component 2: Np-C-S-H 1.65.

Strong interference from the neptunyl moiety significantly limited a detailed analysis of the backscattering contributions from more distant shells. The Np-O_{eq} distance in combination with the presence of a neighboring Si shell, however, suggests that an incorporation mechanism could control Np(V,VI) uptake by C-S-H phases (GAONA et al., 2011c).

5.4.2 TRLFs study on U(VI) uptake by C-S-H phases and HCP

Previous EXAFS studies on U(VI) loaded C-S-H and HCP samples provided conflicting information on the uptake mechanism of U(VI) by cementitious materials (HARFOUCHE et al., 2006, MACÉ et al., 2011). While incorporation of U(VI) was proposed in the earlier study, the more recent study did not unambiguously support this finding. Time-resolved laser fluorescence spectroscopy (TRLFS) measurements were carried out with the aim of resolving this open question concerning the U(VI) sorption mechanism in cementitious materials (TITS et al., 2011). The measurements were carried out on a series of reference samples including the free UO_2^{2+} aquo-ion in 1 M HClO_4 , alkaline uranyl solutions, a solid Ca-uranate, and C-S-H phases with different C:S ratios loaded with U(VI). Details of the measurements are described elsewhere (TITS et al., 2011).

The spectra of the aqueous samples showed strong red shift with increasing pH which was explained by the higher formal charge of the equatorial OH groups of the hydrolysed U(VI) species at high pH compared to the equatorial H_2O groups of the aquo-ion at low pH (Fig 5.6). This results in an increase in the electron density around the U central atom. TRLFS spectra of U(VI) sorbed on C-S-H phases showed that the U(VI) solid speciation continuously changed over a period up to 6 months in contrast to the fast sorption kinetics observed in batch sorption studies (TITS et al., 2008). Decay profile analysis combined with factor analysis of a series of spectra determined for U(VI) - C-S-H suspensions at increasing delay times revealed the presence of four luminescent U(VI) species. Along with the aqueous $\text{UO}_2(\text{OH})_4^{2-}$ species and a Ca-uranate-like precipitate, two different sorbed species were identified (Fig. 5.6). The strong red shift of one of these two sorbed species (species C) originates from the presence of a strong equatorial ligand field, suggesting incorporation into the C-S-H structure. This findings supports the idea that thermodynamic modelling of long-term aspects of U(VI) uptake by C-S-H phases and HCP should consider an incorporation mechanism as proposed by GAONA et al. (2011d).

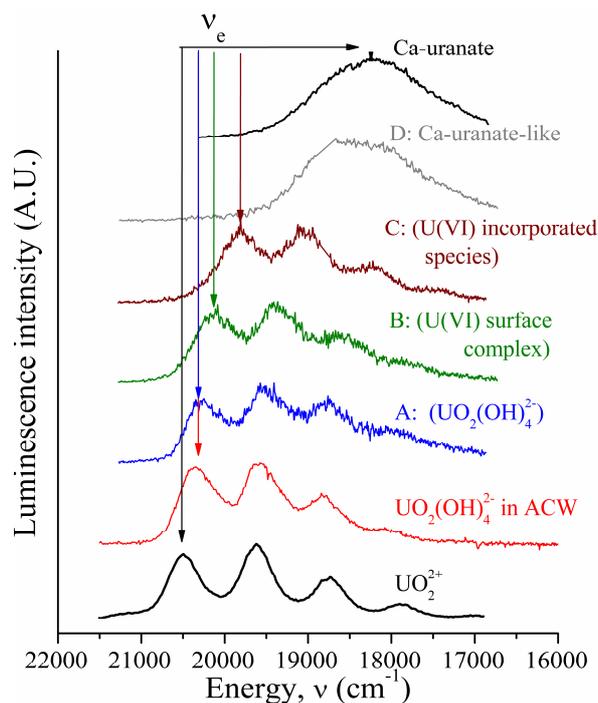


Fig. 5.6: Luminescence spectra of the U(VI) species in alkaline U(VI) solution (ACW: artificial cement pore water of $\text{pH} = 13.3$) and U(VI) loaded C-S-H suspensions after deconvolution by factor analysis. Comparison with two reference spectra: Ca-uranate (top) and free aqueous uranyl in 1 M HClO_4 (bottom).

5.5 Fe speciation in cement paste

The Fe speciation in cement paste is still poorly understood. A PhD study was carried out jointly with Empa with the aim of determining the Fe species formed in hydrating cement. Earlier studies showed that it is difficult to identify Fe-bearing hydrates in cement pastes using standard techniques such as XRD, TGA and SEM due to the overlap of signals from the same compound which contains either Fe or Al. Fe-bearing cement minerals, and some Al/Fe solid solutions, were synthesized and their EXAFS spectra determined at BM26 (DUBBLE) at the ESRF, along with HCP samples aged over different periods of time (Fig. 5.7). The latter spectra were analysed using factor analysis (PCA, ITFA) on the assumption that several Fe species contributed to the overall EXAFS spectra. The latter analysis showed that three main Fe species dominate in HCP: Ferrite (the unreacted Fe-bearing clinker mineral), Fe-hydroxide and Fe-Si-hydrogarnet or the corresponding solid solution with Al-Si-hydrogarnet, respectively (Table 5.3). While Fe-hydroxide forms as metastable phase in the early phase of the hydration process, Fe-Si-hydrogarnet seems to be stable in the long term.

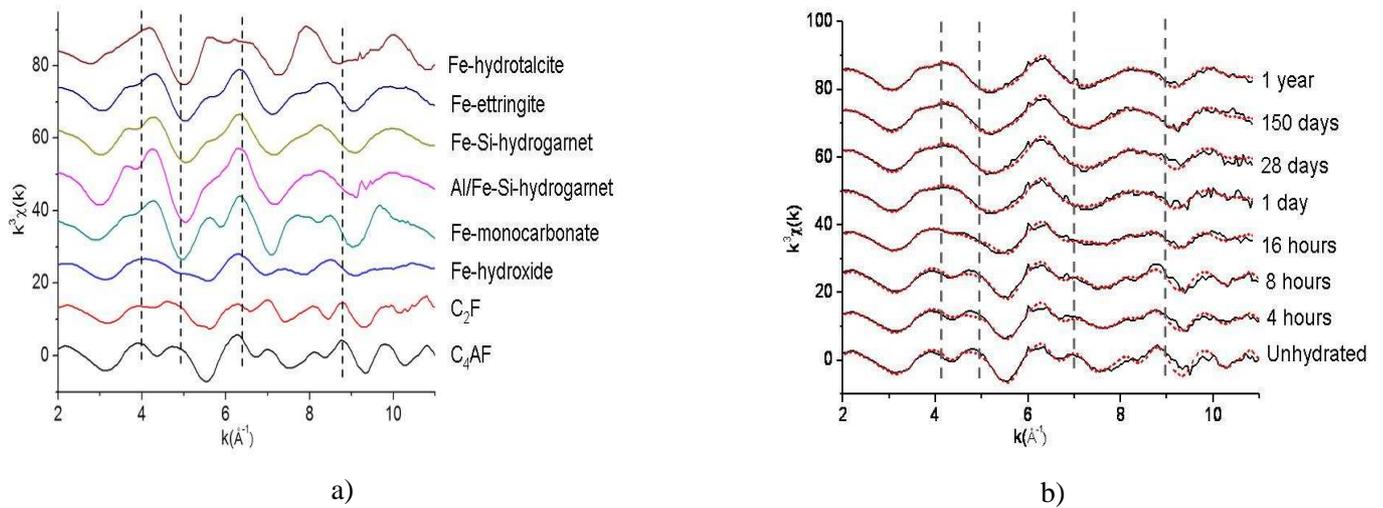


Fig. 5.7: k^3 -weighted experimental bulk EXAFS spectra of a) Fe-bearing phases used as reference compounds and b) OPC hydrated at 20 °C over different periods of time (line: experimental data; dots: modelled data). The broken lines in Fig. 5.7a indicate differences in the spectral features. $C_2(A,F)$ = aluminate/ferrite solid solution, C_2F = ferrite.

Table 5.3: Proportions of Fe-containing phases in OPC hydrated at 20 °C over different periods of time determined with linear combination using the reference spectra.

Age	$C_2(A,F)$	Fe-hydroxide	Fe/Al-Si-hydrogarnet	R-factor
Unhyd	1.00*	-	-	0.15
4 hrs	0.63(3)	0.37(3)	-	0.12
8 hrs	0.70(4)	0.30(4)	-	0.12
16 hrs	0.36(3)	0.64(3)	-	0.10
1 day	0.45(2)	-	0.55(2)	0.08
28 days	0.42(2)	-	0.58(2)	0.07
150 days	0.40(1)	-	0.60(1)	0.05
1 year	0.39(1)	-	0.61(1)	0.04

This is the first time that it has been unambiguously demonstrated that siliceous hydrogarnet is the main Fe(III)-bearing phase in HCP. (The remaining Fe(III) is found in the aluminate/ferrite solid solution $C_2(A,F)$).

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6 COLLOID CHEMISTRY

C. Degueldre, S. Frick, A. Benedicto (PhD student from CIEMAT)

6.1 Overview

The aim of the colloid sub-program is to understand the role of colloids in the migration of radionuclides in the geosphere. The colloid properties studied are their concentration, size distribution and behavior under safety-relevant conditions. This report summarizes the activities over the past year within the framework of the Grimsel colloid project: "Colloid Formation and Migration" (CFM). The focus continues to remain on colloid generation, using single particle counting (SPC) as a characterisation technique. The colloid generation approach followed is a "first" in this area and has the possibility of evaluating clay colloid size distributions not only in batch systems but also under the quasi-stagnant conditions of the CFM system. The knowledge and understanding in groundwater colloid science gained over the last decade allows well founded estimates to be made concerning the potential role played by colloids in the transport of radionuclides in the argillaceous rock formations proposed by Nagra in the frame of the Sectoral Plan.

6.2 Activities in the CFM project

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

The CFM project is the latest project in a series of experiments conducted within the Radionuclide Retardation Program (RRP) of the GTS over the past years. Phase 2 of the CFM project will run for 6 years, from 2008 to 2013, with the aim of studying the in-situ generation and migration of colloids in the Grimsel migration test zone. The main goal of this project is to understand the generation of colloids in quasi-stagnant water at a bentonite block/groundwater flow interface. The LES task is sub-divided into two parts: (i) participation in the in-situ colloid measurement campaigns and (ii) studying colloid generation mechanisms. The breakthrough tests carried out in the CFM project are performed with colloid cocktails that mimic the final colloid tests. SPC measurements were carried out and compared

with other data (INE, CIEMAT ...). INE, who is responsible of the CTM experimental program, collected the latest data together and a paper was presented at the last Migration conference in Beijing, China, September, 2011.

LES/PSI is carrying out transient tests at Grimsel. In quasi-stagnant groundwater aquifers, colloids are found to occur at constant concentration and size distribution under constant flow conditions. In transient conditions induced by water flow rate variations, increases of colloid concentration and size distribution are observed. The transient study focuses on colloids in water from a well-instrumented short bore hole in the water bearing fissure within the mega-packer system around the migration zone of the laboratory tunnel at the Grimsel Test Site.

In the transient tests carried out this year, the flow rate of the water into the short bore hole located in the mega-packer was increased in a controlled way. Following flow rate increases, a new population of colloids was generated and measured (Fig. 6.1). The low ionic strength crystalline groundwater causes the colloid suspension to be stable. In this system, increases in concentration and size distribution by a factor 1.5 to 30, according to the colloid size ($d = 50$ to 2000 nm), are observed when the flow rate increases as a pulse by a factor 20 to 40 in 6 to 10 s (e.g. Fig. 6.1).

Colloid generation by flow transient requires a minimum magnitude impulse (threshold value) which is colloid size dependant. The phyllosilicate mineral phases, micas, chlorite, epidote, display sizes of colloids and particles of a few μm while quartz and the feldspar particle sizes range is predominantly above $10 \mu\text{m}$. These phyllosilicate particles generated during the transients are made up of 10-15 wt. % Al_2O_3 which can be used to detect the particulate phases in suspension during the transients by ICP methods (e.g. see Fig. 6.2). Detection of the colloid using the other elements analysed by ICP was not possible because their concentrations were found to be below the detection limits or because the background concentration of an element in the groundwater is greater than that concentration arising from the colloids. The concentrations were < 1 ppb for Fe, < 0.3 ppb for Mn and Ti. The concentration of Mg was 12.5 ppb and Si was 5.65 ppm.

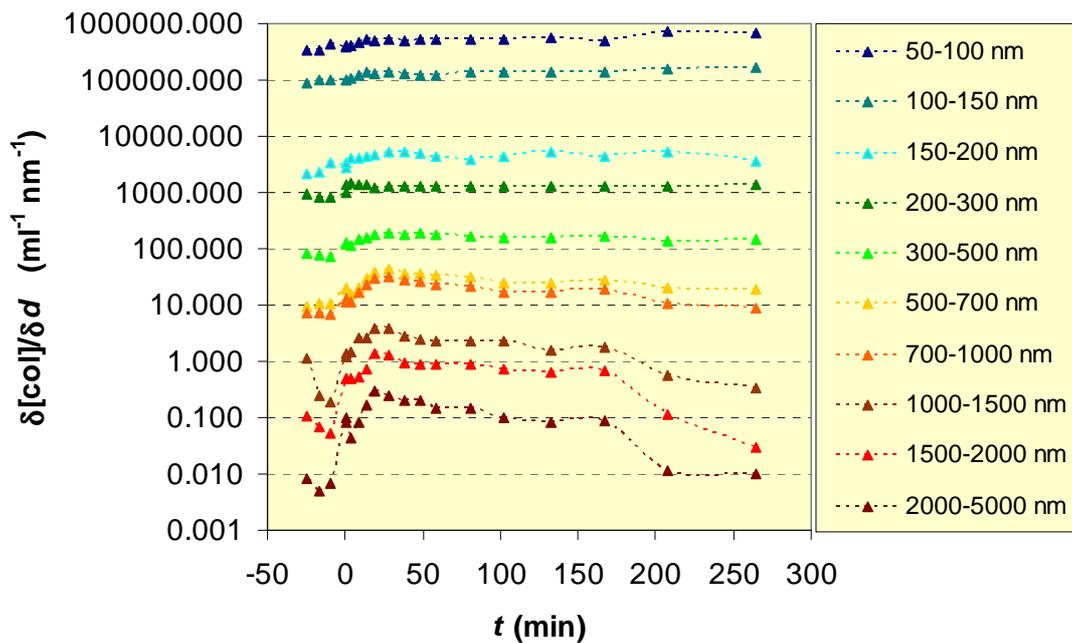


Fig. 6.1: Colloid normalized concentration plot as a function of time t as recorded for all colloid sizes following a flow transient $20 \Rightarrow 950 \text{ ml min}^{-1}$ in 0.1 min ($t = 0$), followed by a relaxation time over hours at a flow rate of 50 ml min^{-1} . Note the generation of large colloids and particles after the flow transient, and the recovery to background concentration levels after relaxation.

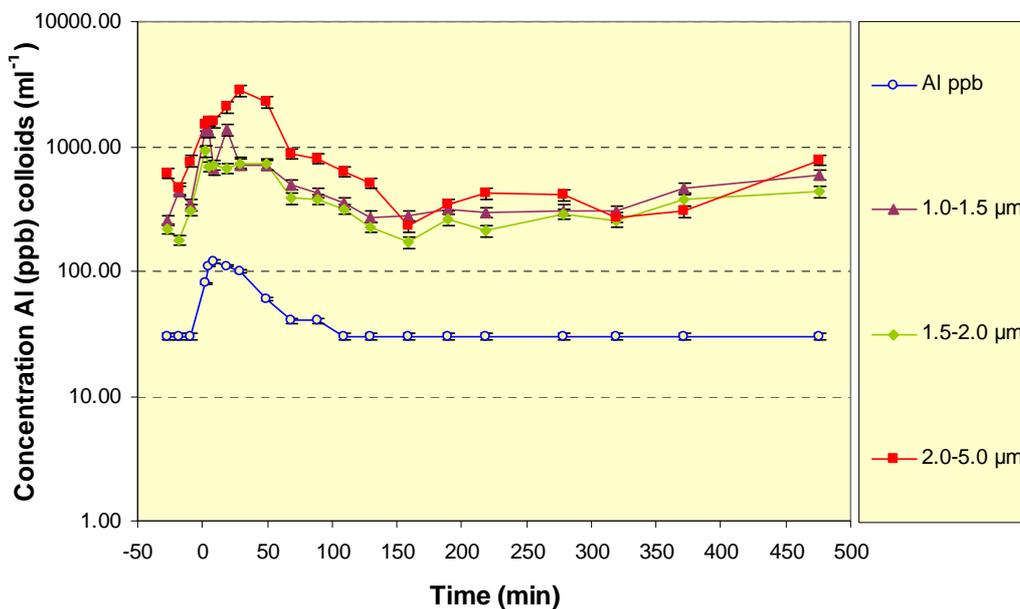


Fig. 6.2: Comparison of colloid concentrations and their Al concentration during a transient $20 \Rightarrow 750 \text{ ml min}^{-1}$ in 0.15 min . Conditions: colloid mass concentration were calculated assuming a spherical colloid model with d (μm) and $\rho = 1 \text{ g cm}^{-3}$

6.3 Other colloid activities

The co-operation with CIEMAT is continuing in a very active manner. The main aim is to optimise the radio-analytical work required to measure colloid breakthroughs in the CFM experiment at the Grimsel Test Site. Colloid labeling was discussed, and it was decided that ^{68}Ge could be used. Since ^{68}Ge decays into ^{68}Ga , a β^+ emitter, it can be utilised for breakthrough tests (in the lab and in-situ) and detected by liquid scintillation and/or by PET during core breakthrough tests allowing a 3D reconstruction of the colloid pathway in laboratory experiments. The PET analysis is foreseen to be carried out at CIEMAT. A Spanish student (A. Benedicto) studied the colloids prior to and after labeling with Ge using the sorption model derived earlier in the colloid program. Emphasis is also given on the sorption of Ga(III) that forms in the process.

6.4 Future work

CFM homologue tests are foreseen in early 2012, and SPC will be used together with other techniques to characterize the colloids during breakthrough in 'in situ' experiments. 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. The LES in-house colloid generation model will be used to systematically describe the colloid generation during the main experiment which is in the process of being designed. Colloid size distributions from the bentonite source (obtained by direct re-suspension) will be compared with those from the groundwater system sampled during the experiment contacting FEBEX bentonite within the groundwater in the Grimsel Test Site.

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

6.5 Reference

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7 DIFFUSION PROCESSES

L.R. Van Loon, M.A. Glaus, W. Müller, S. Frick, N. Diaz (postdoc), H. Wang (PhD), M. Bestel (PhD)

7.1 Overview

The focus of the activities in the “Diffusion Processes” group are i) understanding the diffusion mechanism of radionuclides in compacted argillaceous materials and ii) measuring diffusion parameters (effective diffusion coefficients and rock capacity values) which can be used in performance assessment studies.

Within the framework of the Sectoral Plan (Sachplan Geologische Tiefenlager) final diffusion measurements with HTO, $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ on the potential host rocks Marl of Helveticum, “Brauner Dogger” and Effingen Member were performed. The measurements were used to confirm/check the validity of the extended Archie’s relation over a wide range of porosities for estimating effective diffusion coefficients to be used in performance assessment studies.

In the framework of the EU CatClay project, diffusion measurements with $^{60}\text{Co(II)}$ on OPA were performed using a filter-free in-diffusion technique. The diffusion profiles of $^{60}\text{Co(II)}$ in OPA could only be described by assuming two different independent diffusion pathways. Also diffusion measurements with HTO and ^{85}Sr on illite were performed. The pH and ionic strength of the saturating/contacting solutions were varied in order to test whether “sorption-enhanced” diffusion is an important process in illite.

The work of 2 PhD students, Martina Bestel and Hao Wang, is being carried out to a large extent using the SING and SLS facilities at PSI. The research on dynamics of water in compacted montmorillonite is focused mainly on optimising the sample preparation for QENS measurements, on measuring the water distribution in Na-montmorillonite as a function of bulk dry density using a fixed window scan procedure on a neutron backscattering spectrometer, and on performing diffusion measurements with HTO and $^{22}\text{Na}^+$ as a function of temperature. The work on the use of micro beam techniques to study the transport of contaminants in heterogeneous porous materials has been concerned mainly with the development of a fast “wash-out” ablation cell to improve the sampling time. The results from these two PhD studies have been presented at several conferences and published in peer reviewed journals. Hao Wang was awarded the

Swiss Chemical Society – Metrohm prize for the best oral presentation in the analytical chemistry division during the Autumn meeting of the Swiss Chemical Society (SCS) in Lausanne.

The TRAPHICCS programme on pure clay minerals was continued. Diffusion measurements of HTO, $^{22}\text{Na}^+$ and $^{85}\text{Sr}^{2+}$ were carried out on beidellite. Further measurements with $^{22}\text{Na}^+$ were performed to strengthen the evidence for “sorption-enhanced” diffusion of cations in montmorillonite.

Three PhD proposals, with partial financial support from Nagra, were written in close cooperation with the Transport Mechanisms Group and have been approved by the PSI Research Commission (FoKo). Two of the proposals are concerned with porosity changes induced by dissolution and precipitation reactions occurring at the interface between different materials and the influence on diffusion. Some scoping experiments on precipitation reactions in porous media have been performed. The topic of the third proposal is the migration behaviour of small organic compounds in compacted clay and is strongly related to the C-14 project dealing with the formation of soluble (^{14}C containing) organic compounds produced by the anaerobic corrosion of activated steel.

7.2 Activities in support of the Sectoral Plan

Diffusion measurements with HTO, $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ in potential host rocks such as Effingen Member, Marl of Helveticum and “Brauner Dogger” were continued. By the end of 2011, all measurements will be finished. As already indicated in 2010, all of the data could be described by an extended Archie’s relation (Fig. 7.1). The results were presented at the 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, September 2011, in Beijing, China.

Measurements on samples of Effingen Member from the Oftringen (Canton Aargau) borehole showed that the anion accessible porosity was 50% of the total porosity. This was in contradiction with water activity measurements performed by the University of Bern which yielded an anion accessible porosity of only 25% of the total porosity.

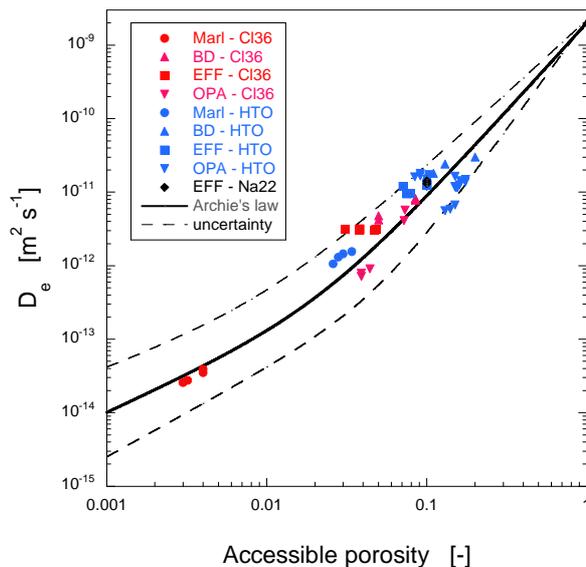


Fig. 7.1: Extended Archie's relation (solid line) describing the relationship between the diffusion accessible porosity and the effective diffusion coefficients together with experimental data for Opalinus Clay, "Brauner Dogger", Effingen Member and Marl of Helveticum.

Additional diffusion measurements on a new sample of Effingen Member from the borehole in Goesgen (Canton Solothurn), however, confirmed the results obtained earlier on the samples from the borehole in Oftringen. The anion accessible porosity values from diffusion measurements have now been accepted as the correct values and were used in the derivation of porewater compositions.

Measurements on new samples of Opalinus Clay and "Brauner Dogger" from a borehole in Schlattigen (Canton Thurgau) are in preparation. A diffusion database based on the extended Archie's relationship is in preparation and will be completed by the end of 2012.

7.3 CatClay

The contribution of LES to WP2 in the EU Catclay project consists of diffusion experiments with Sr^{2+} , Zn^{2+} , and Eu^{3+} in conditioned illite where the ionic strength and pH of the saturating / external solution is varied. The experiments will provide information on the extent of the contribution of "sorption-enhanced" diffusion of these cations in illite to the overall diffusion rates. In order to be able to measure reliably the diffusion of specifically binding radionuclides (Zn^{2+} and Eu^{3+}), suitable experimental techniques and materials need to be developed and evaluated. This is the main focus of the first two years of experimental

work. Besides this, diffusion experiments using HTO and $^{85}\text{Sr}^{2+}$ have already been started because diffusion of these radionuclides can be measured with conventional experimental techniques. All experiments were carried out using Illite du Puy prepared in the Na-form which had undergone a modified acid treatment (BRADBURY & BAEYENS, 2009) using buffered formic acid. This clay material, referred to as Na-IdP, was prepared in a concerted action by all project partners. The conditioned material was then homogenised at PSI and re-distributed to the project partners. The results obtained in the first year can be summarised as follows:

- The effective diffusion coefficients measured for HTO were independent of the salinity of the external reservoir solution, whereas those for Sr^{2+} exhibited a clear dependence, both at pH 5 and 9. With decreasing salinity, effective diffusion coefficients increased. These tests were started at the very beginning of the project using diffusively saturated illite samples compacted to a dry bulk density of $\sim 1900 \text{ kg m}^{-3}$. Later, it was decided that the reference dry bulk density should be 1700 kg m^{-3} . The corresponding diffusion experiments with Sr^{2+} were started and will be completed at the beginning of 2012.
- In order to maintain stable conditions with respect to pH during diffusion experiments, the saturation of the illite samples is a critical issue. Various tests comprising of diffusive and advective saturation, the buffering of pH by the so-called "Good buffers" (GOOD et al., 1966), or pre-conditioning illite by titration with HNO_3/NaOH , were all evaluated. Diffusive saturation turned out to be too slow for obtaining stable pH values throughout the samples within a reasonable time. (Advective saturation could be a viable alternative.)
- A series of sorption tests with chemically modified steel filters were carried out. Out of all the various surface modifications (covalently bound alkyl- or fluorinated alkyl silanes, fluorinated self-assembled monolayers, perfluorinated multi-layers), none were able to prevent the sorption of Eu^{3+} .

The main conclusions from the through-diffusion experiments with HTO and $^{85}\text{Sr}^{2+}$ are:

- Sorption-enhanced diffusion is effective for Sr^{2+} in illite (similar as for montmorillonite).
- The diffusive fluxes for the 0.1 M NaClO_4 case were so high that the use of the "flushed filter technique" was necessary.

- Discrepancies between sorption distribution ratios calculated from through-diffusion experiments and from the tracer profiles in the solid measured after through diffusion (not shown here) were approximately a factor of 2. This is clearly larger than the formal uncertainties involved, but comparable to the discrepancies observed for diffusion of Sr^{2+} in montmorillonite (GLAUS et al., 2007).

The contribution of LES to WP3 of the CatClay project is to perform and interpret the diffusion of Sr, Zn and Eu in a complex matrix such as Opalinus Clay. In a first phase, the in-diffusion technique was modified in such a way that experiments could be performed without the use of confining filters. To this end, in-diffusion experiments with $^{60}\text{Co}(\text{II})$ in OPA were performed. Small cylindrical cores embedded in an epoxy resin were used. After in-diffusion, the tracer profile in the samples was analysed using a modified version of the abrasive peeling technique (VAN LOON & EIKENBERG, 2005). As was already observed in earlier diffusion experiments with OPA, the profiles showed two regions, i.e. it appeared that two independent pathways are involved in the diffusive transport (Fig. 7.2). In view of the sorption mechanisms involved in the uptake of Co on OPA, i.e. ion exchange and surface complexation, both surface diffusion and diffusion in the pore space could be taking place simultaneously.

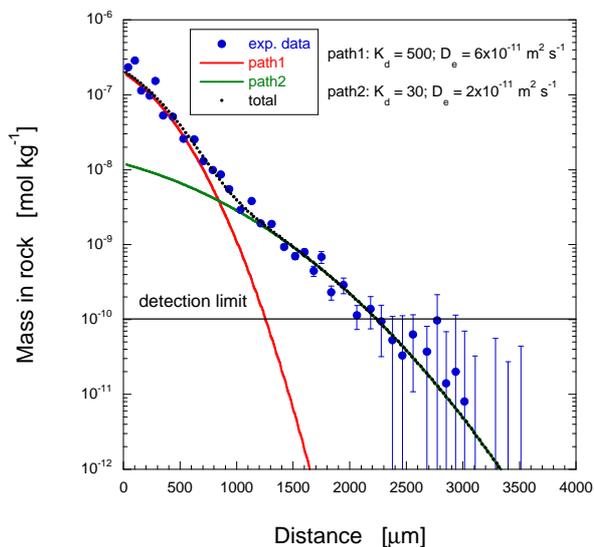


Fig. 7.2: Diffusion profile of $^{60}\text{Co}(\text{II})$ in OPA after 14 days diffusion time. The profile can only be described by assuming two independent diffusion pathways. Both the sorption values (K_d) and the effective diffusion coefficients (D_e) are different (diffusion was parallel to the bedding plane; the concentration of Co(II) in the source solution was 3×10^{-10} M).

The diffusion technique using the small drill cores was shown to give useful results. Some improvements have to be made in order to take into account the sorption of tracers on the epoxy resin. This is especially important for cases where the amount of tracer in the clay is very small, i.e. at larger diffusion distances. Additional diffusion tests with $^{85}\text{Sr}(\text{II})$, $^{65}\text{Zn}(\text{II})$ and $^{152}\text{Eu}(\text{II})$ are planned for 2012.

7.4 Dynamics of water in compacted montmorillonite (PhD project Martina Bestel)

Measurements of the water distribution in compacted Na-montmorillonite showed that at high bulk dry densities the water is mainly located in one or two layers in the interlayer space. At lower densities, macropores are also filled with water and the fraction of water in the interlayer space increases and is mainly present as 3 layers of water. This is in agreement with the conclusions drawn earlier from Cl-diffusion measurements (VAN LOON et al., 2007). This information was used to improve the interpretation of QENS measurements performed on Na-montmorillonite. It was possible to discriminate between diffusion in the interlayer and in the macropores.

Through-diffusion measurements with HTO and $^{22}\text{Na}^+$ were performed for two bulk dry densities, i.e. 1300 and 1700 kg m^{-3} as a function of temperature and ionic strength. The activation energies obtained were very similar for both tracers and indicate a strong coupling between water and charge compensating cations in the interlayer.

7.5 Micro-heterogeneous systems (PhD project Hao Wang)

In 2011 a novel laser ablation cell was designed and is currently under construction. The main aim behind the development was to achieve a fast “wash-out” (low dispersion) of the laser generated aerosol. Low dispersion will clearly improve the signal-to-noise ratio of isotope acquisition (higher sensitivity and a lower limit of detection) and will allow the implementation of efficient imaging schemes which will allow to probe larger areas and to obtain higher spatial resolution simultaneously. In the novel ablation cell, 10Hz ablation pulses could be resolved. Compared to the routinely used cell, faster “wash-out” times of at least an order of magnitude were observed (Fig. 7.3).

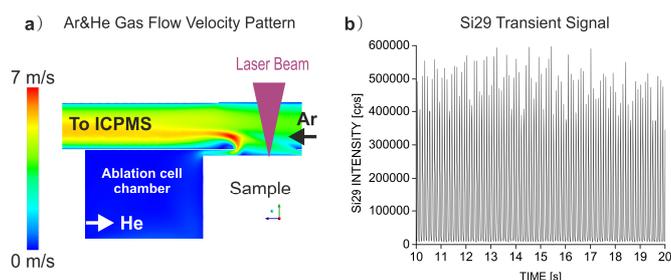


Fig. 7.3: Simulated cell fluid dynamic patterns and experimental results. a) gas flow velocity pattern; b) ^{29}Si signal when ablated a NIST 610 standard material with $10\mu\text{m}$ spot size.

The goal is to further decrease the “wash-out” time, and to couple the cell to a (semi) simultaneous mass spectrometer (MS), e.g. a Time-of-Flight (TOF) MS or a Mattauch-Herzog (MH) geometry based MS, and finally establish a fully quantitative fast LA-ICP-MS technique for chemical imaging.

Improved quantification capabilities for microXRF: The pyMCA software developed by ESRF is currently being implemented at the microXAS beamline. Improved quantitative microXRF imaging based on fast full spectra analysis will be available on a routine basis. The pyMCA quantification algorithms are based on a fundamental parameter approach, consideration of a realistic representation of the experimental setup, and a least squares method to fit full spectra. In order to facilitate knowledge transfer, a pyMCA workshop was organized as an integral part of the Joint Users’ Meeting at PSI in 2011.

A first publication on the combination of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and synchrotron micro-X-ray fluorescence (micro-XRF) for measuring Cs-diffusion in heterogeneous porous media was submitted to and accepted by Analytical Chemistry (WANG et al., 2011). Hao Wang presented his work at several national and international conferences and workshops.

7.6 Transport phenomena in compacted clay systems (TRAPHICCS)

In order to test the effect of isomorphic substitution on the diffusion of cations and anions, through-diffusion experiments with beidellite were performed and compared with diffusion measurements on montmorillonite (GLAUS et al., 2010). In beidellite, isomorphic substitution is mainly in the tetrahedral layer, whereas in montmorillonite the substitution is

mainly located in the octahedral layer. A qualitative overview of the results of through-diffusion experiments with conditioned beidellite (Idaho, Clay Minerals Society) is shown in Fig. 7.4 by the flux curves measured in the target reservoir. The fluxes of HTO were independent of the external salinity, while they increased with decreasing salinity in the case of $^{22}\text{Na}^+$ and decreased with decreasing salinity in the case of $^{36}\text{Cl}^-$. The effective diffusion coefficients and rock capacity factors for HTO and $^{22}\text{Na}^+$ in montmorillonite and beidellite were identical within ~30 to 40 %. In view of these similarities, it can be concluded that any significant differences in molecular mobility of $^{22}\text{Na}^+$ in the two clay minerals cannot be substantiated and that comparative laboratory-scale experiments using these clay minerals are probably not suited as test systems for the verification of intrinsic differences evidenced by simulations on an atomistic scale (GREATHOUSE & CYGAN, 2006; KOSAKOWSKI et al., 2008).

In order to clarify the role of sorption in determining the true driving force for cation diffusion in clay minerals (GLAUS et al., 2007; GIMMI & KOSAKOWSKI, 2011), experiments were carried out under the conditions of a salt gradient across the clay sample.

Briefly, compacted montmorillonite clay plugs were equilibrated in a classical through-diffusion set-up with 0.1 M NaClO_4 on one side and 0.5 M NaClO_4 on the other. After an equilibration phase of ~2 months, $^{22}\text{Na}^+$ was added to both sides of the diffusion cells to give equal activities in the two compartments. The evolution of the $^{22}\text{Na}^+$ concentration in both reservoirs as a function of time is shown in Fig. 7.5.

After a short phase of in-diffusion on both sides, the concentration increased on the 0.5 M NaClO_4 side, while it steadily decreased on the side with the lower salinity. If aqueous phase diffusion were the dominant process, and the external tracer concentration the driving force, the opposite behaviour would have been expected. Consequently, a tracer gradient from the 0.5 M NaClO_4 in the direction of 0.1 M NaClO_4 side would be expected to build up and the diffusive flux would be directed to the 0.1 M NaClO_4 side. As shown by Fig. 7.5, the difference in concentrations of $^{22}\text{Na}^+$ between the 0.5 M NaClO_4 and the 0.1 M NaClO_4 reservoirs increases progressively so that the observed tracer flux is in the direction of the 0.5 M NaClO_4 reservoir.

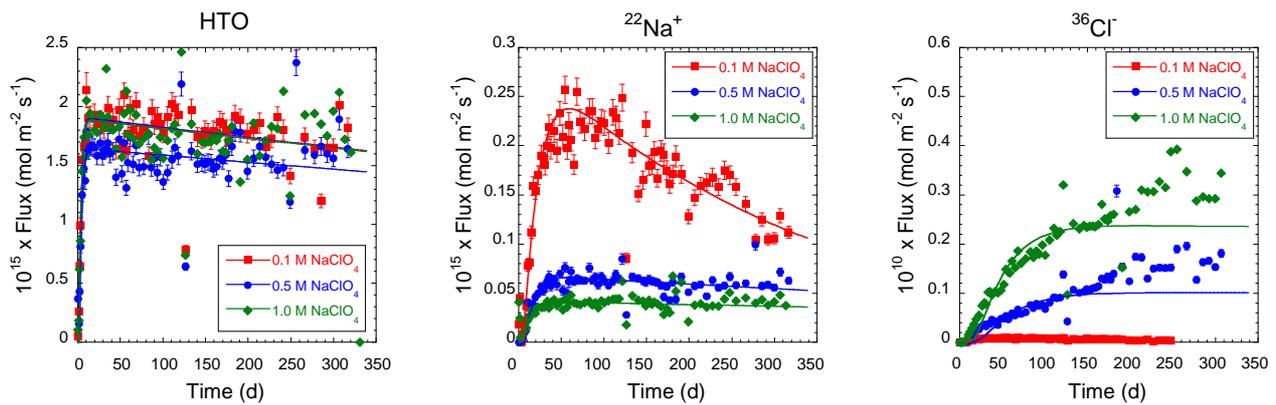


Fig. 7.4: Breakthrough curves of differently charged tracers through beidellite (dry bulk density of $\sim 1900 \text{ kg m}^{-3}$) as a function of the NaClO_4 concentration in the external solutions contacting the compacted clay plug.

The tracer is thus seemingly transported in an “uphill” manner against its own concentration gradient. If, however, the amount of sorbed tracer is anticipated to be the driving force for diffusion, the direction of the tracer flux would be as is observed because the amount of sorbed $^{22}\text{Na}^+$ is larger on the 0.1 M NaClO_4 than on the 0.5 M NaClO_4 side. Such experiments can therefore be regarded as a positive demonstration that the amount of sorbed cations is the driving force for diffusion in montmorillonite, and not the gradient through the aqueous phase. (At least in the case of Na, and possibly other cations whose predominant sorption mechanism is cation exchange.)

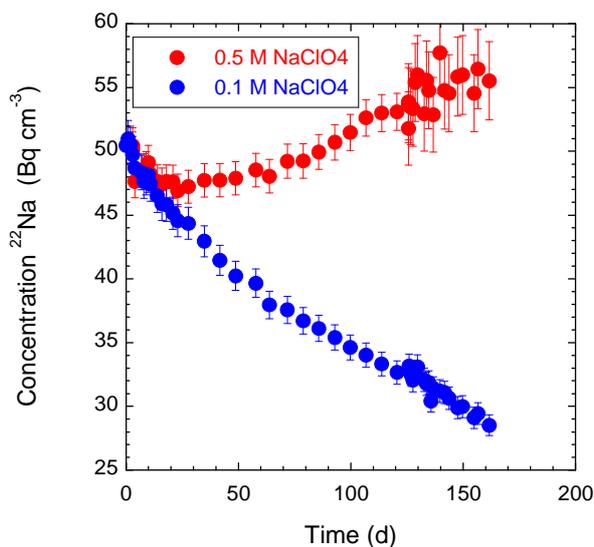


Fig. 7.5: Evolution of the concentration of $^{22}\text{Na}^+$ in the reservoir solutions contacting a compacted sample of montmorillonite (dry bulk density of $\sim 1900 \text{ kg m}^{-3}$). After an initial phase of in-diffusion on both sides, the tracer flux changed direction on the 0.5 M NaClO_4 side after ca. 30 days despite the larger concentration in that reservoir.

In view of the conclusions drawn, it appears to be more appropriate to use the term ‘sorption-enhanced diffusion’ instead of ‘surface diffusion’ for describing the enhanced tracer fluxes of cationic species in swelling clays.

7.7 Porosity changes in porous media

Repository systems have several interfaces where there are strong chemical gradients. The most striking example is the cement-clay interface. Due to dissolution-precipitation reactions occurring at these interfaces, porosity changes can result in changes in the transport properties of solutes and gases. In order to achieve a better understanding of dissolution-precipitation reactions and their effect on solute transport, a new research project will be started in 2012. The project is a co-operation between the Transport Mechanisms Group, the Diffusion Processes Group and the University of Bern. Two PhD proposals were submitted and approved by the PSI Research Commission. First experimental equipment designs have been discussed with the Engineering Department (AMI) at PSI and the equipment will be constructed in 2012. Also, first scoping experiments of precipitation reactions in porous media were performed and preliminary reactive transport calculations were carried out (GEMS-PSI geochemical code coupled with OpenGeoSys transport code). More information is given in Chapter 3.

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NAKARAI K.¹, KOSAKOWSKI G., BERNER U., OWADA H.²

Evolution of cement-bentonite interfaces: Experiments and models, Models – Repositories of Knowledge: Modelcare 2011, Leipzig, Germany, 18-22 September 2011

¹ Gunma University, Gunma, Japan

PFINGSTEN W., VAN LOON L.R.

Modelling diffusion of sorbing radionuclides into clay samples - model assumptions and consequences for experiments and vice versa. 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, China, 18-23 September 2011

ROJO H.¹, TITS J., GAONA X.², GARCIA-GUTIÉRREZ M.¹, MISSANA T.¹, WIELAND E.

Experimental investigation of Np(IV) complexation with gluconic acid under alkaline conditions. 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, China, 18-23 September 2011

¹ CIEMAT, Madrid, Spain

² KIT-INE, Karlsruhe, Germany

SCHÄFER T.¹, HUBER F.¹, HAUSER W.¹, WALTHER C.¹, BOUBY M.¹, GECKEIS H.¹, DEGUELDRE C., YAMADA M.², SUZUKI M.², MISSANA T.³, ALONSO U.³, WOLD S.⁴, TRICK T.⁵, BLECHSCHMIDT I.⁶

The Colloid Formation and Migration Project (CFM) at the Grimsel Test Site (Switzerland): synopsis of the 2008-2010 field experiments. 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, China, 18-23 September 2011

¹ KIT-INE, Karlsruhe, Germany

² AIST, Tsukuba, Japan

³ Ciemat, Madrid, Spain

⁴ KTH, Stockholm, Sweden

⁵ Solexperts, Schwerzenbach, Switzerland

⁶ Nagra, Wettingen, Switzerland

SHAO H.¹, BERNER U., KOLDITZ O.^{1,2}, KOSAKOWSKI G., KULIK D., MÄDER U.³

A reactive transport modeling study on the Maqarin natural analogue for the effects of hyper-alkaline groundwater on sedimentary rock. Models – Repositories of Knowledge: Modelcare 2011, Leipzig, Germany, 18-22 September 2011

¹ Helmholtz Centre for Envir. Research-UFZ, Leipzig, Germany

² TU Dresden, Germany

³ University of Bern, Switzerland

THIEN B., GODON N., AYRAL A.

The double effect of Mg on the long-term alteration rate of a nuclear waste glass. Goldschmidt Conference 2011, Prague, Czech Republic, 14-19 August 2011, Min. Mag. 75(3), 2005

TITS J., GAONA X.¹, LAUBE A., WIELAND E.

Influence of the redox state on the neptunium sorption by cementitious materials: Relationships with the sorption behaviour of Th(IV) and U(VI). 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, China, 18-23 September 2011

¹ KIT-INE, Karlsruhe, Germany

VAN LOON L.R., MIBUS J.¹

On the use of an extended Archie's relation for estimating effective diffusion coefficients in low porosity media. 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, China, 18-23 September 2011

¹ Nagra, Wettingen, Switzerland

VAN LOON L.R., KOSAKOWSKI G., GOUËBAULT E.¹

Precipitation reactions in nanopores of compacted Namontmorillonite. 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, China, 18-23 September 2011

¹ Ecole des Mines, Nantes, France

WANG H.A.O., GROLIMUND D., VAN LOON L.R., GÜNTHER D.¹, BORCA C.N.

Multi-dimensional quantitative microscopic studies with high spatial resolution of contaminant diffusion into Opalinus Clay rock. 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, China, 18-23 September 2011

¹ ETH, Zürich, Switzerland

WANG H.A.O., GROLIMUND D., VAN LOON L.R., BORCA C.N., GÜNTHER D.¹

Quantitative microscopic studies with high spatial resolution of contaminant diffusion into Opalinus Clay rock. Fall Meeting of the Swiss Chemical Society, Lausanne, Switzerland, 9 September 2011

¹ ETH, Zürich, Switzerland

WANG H.A.O., GROLIMUND D., VAN LOON L.R., BORCA C.N., GÜNTHER D.¹

Quantitative microscopic studies with high spatial resolution: the virtue of cross-calibration, Joint Users' Meeting at PSI, Villigen, Switzerland, 15-16 September 2011

¹ ETH, Zürich, Switzerland

WIELAND E., DÄHN R., DILNESA B.Z.^{1,2},
LOTHENBACH B.¹

Synchrotron-based micro-spectroscopic investigations on Al, S, and Fe speciation in cementitious materials, 13th International Congress on the Chemistry of Cement (ICCC11), Madrid, Spain, 3-8 July 2011

¹Empa, Dübendorf, Switzerland

²EPFL, Lausanne, Switzerland

WIELAND E., DÄHN R., GAONA X.¹, MACÉ N., TITS J.
Micro- and macroscopic investigations of actinide binding in cementitious materials, 1st International Symposium on Cement-based Materials for Nuclear Waste (NUWCEM 2011), Avignon, France, 11-14 October 2011

¹KIT-INE, Karlsruhe, Germany

ZEZIN D.¹, HINGERL F.F., DRIESNER T.¹

Experimental data and modeling of the properties of mixed salt aqueous solutions. Russian - Swiss Coordination Meeting, Moscow, Russia, 17-20 May 2011

¹ETH, Zürich, Switzerland

8.5 Invited talks

CHURAKOV S.V.

Multi-scale modelling of ions and water diffusion in clays. (Keynote Lecture) Goldschmidt Conference 2011, Prague, Czech Republic, 14-19 August 2011, Min. Mag. 75(3), 2005

CHURAKOV S.V., GIMMI TH., TYAGI M.

Two step up-scaling of molecular diffusion coefficients in clays. Goldschmidt Conference 2011, Prague, Czech Republic, 14-19 August 2011, Min. Mag. 75(3), 2005

CURTI E., DÄHN R., VESPA M., GROLIMUND D.,
BORCA C.N.

Glass corrosion and secondary clay mineral formation: the fate of Ni and Ce as revealed by μ -XRF/XAS techniques. NEA Clay Club Workshop "Clays under Nano- to Microscopic resolution" Akademie Hotel, Karlsruhe, Germany, 6-8 September 2011

DEGUELDRE C.

Groundwater colloid generation and detection: from pseudo-equilibrium in quasi-stagnant aquifer to transients induced by flow variation or seismic features, Swiss Physical Society meeting, EPFL, Lausanne, Switzerland, 27 June 2011

GIMMI TH., KOSAKOWSKI G.

How mobile are sorbed cations in clays and claystones? University of La Coruña, La Coruña, Spain, 22 June 2011

GROLIMUND D., BORCA C.N., WANG H.A.O.,
VAN LOON R., MARONE F., DIAZ N., JAKOB A.,
CHURAKOV S., GIMMI T., HARTMANN A.,
VONTOBEL P.

Imaging chemistry (and physics) in space and time: Towards a 3D live view on reactive transport. 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, China, 18-23 September 2011

HUMMEL W.

Wohin mit unseren radioaktiven Abfällen?

Universitäre Vorlesungen Winterthur, Switzerland, 9 November 2011.

Senioren-Kolleg Liechtenstein, Mauren, Liechtenstein, 17 November 2011.

Senioren-Universität, Zürich, Switzerland, 6 December 2011

KULIK D.A.

Geochemical Modeling of Aqueous Systems at Moderate Temperatures: Approaches and Tools for Temperature Extrapolations. HITAC Workshop "High Temperature Aqueous Chemistry", KITCampus Nord, Germany, 9 November, 2011

KULIK D.A., KOSAKOWSKI G.

Algorithms and codes for geochemical thermodynamic modelling: Ready for reactive mass transport simulations? In: 1st Russian-Swiss Seminar "Methods for modelling of geochemical processes: algorithms, data prediction, experimental validation, and relevant applications", IGEM RAS, Moscow, Russia, 17-20 May 2011

VAN LOON L.R.

Ion diffusion in low permeability clay rocks: an overview. Goldschmidt Conference 2011, Prague, Czech Republic, 14-19 August 2011, Min. Mag. 75(3), 2005

WIELAND E.

Towards a molecular-level understanding of the immobilization of actinides by cementitious materials, BIGRAD Conference, Leeds, UK, 27-28 June 2011

8.6 Others/teachings

GIMMI TH.

Lecture and examinations 'Geochemical Modelling II: Reactive transport' within frame of Master of Environmental and Resource Geochemistry, University of Bern, Spring Semester 2011

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 2011

KOSAKOWSKI G.

Statistics in Earth Sciences. University of Tübingen, Germany, Summer Semester 2011

KOSAKOWSKI G.

Reactive transport modelling, Helmholtz Interdisciplinary GRADuate School for Environmental Research (HIGRADE), Helmholtz Centre for Environmental Research – UFZ, Leipzig, Germany, 4-7 November 2011

MAZUREK M., CURTIE E.

Geological disposal of radioactive waste. Lecture course with exercises. University of Bern. Spring Semester 2011

PFINGSTEN W.

Modelling of processes in soils and aquifers: 701-1334-00L, Department for Environmental Sciences, ETH Zurich, Spring Semester 2011

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

Nuclear energy systems. Lecture course with exercises, ETH Zurich, Spring Semester 2011

8.7 Awards

The best poster presentation of MIGRATION 2011:

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

Sorption competition on illite: Experiments and modelling. 13th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Beijing, China, 18-23 September 2011

The SCS-Metrohm prize for the best oral presentation in Analytical Chemistry Division:

WANG H.A.O., GROLIMUND D., VAN LOON L.R., BORCA C.N., GÜNTHER D.¹

Quantitative microscopic studies with high spatial resolution of contaminant diffusion into Opalinus clay rock. Fall Meeting of the Swiss Chemical Society (SCS), 9 September 2011, Lausanne, Switzerland

¹ ETH, Zürich, Switzerland

8.8 Participation in expert groups/panels

GLAUS M.A.

Panel expert in the Expert Elicitation Meeting on sorption, diffusion and solubility data used for the Posiva safety case (Finland)

TITS J.

Member of the review panel of the Belgian programme related to the behaviour of spent fuel in a cementitious environment

VAN LOON L.R.

Member of the expert panel on radionuclide migration in Boom Clay.

Member of the review group (SARG) for the extension of the SFR repository in Forsmark, Sweden

WIELAND E.

Member of the Advisory Group for the BIGRAD Consortium in charge of the UK research programme on “Biogeochemical gradients and radionuclide transport”

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