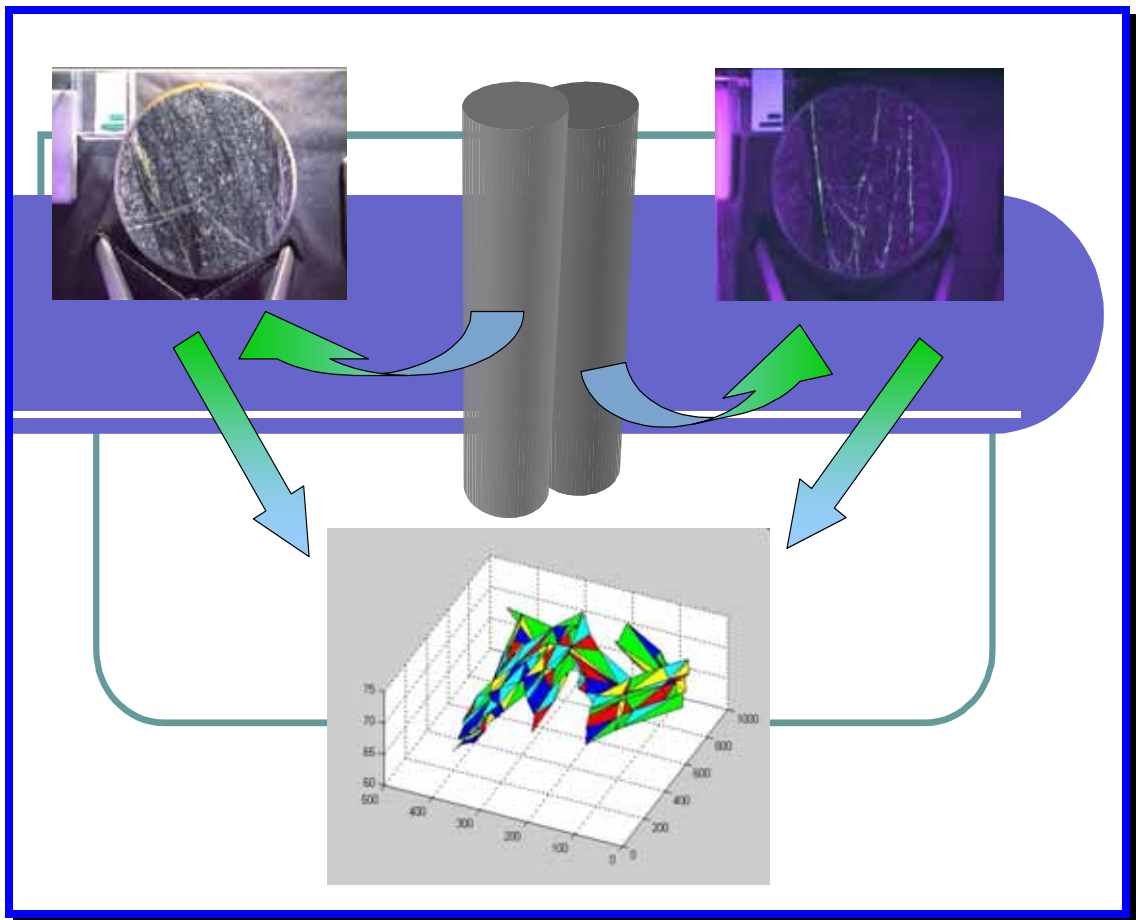


Laboratory for Waste Management



Progress Report

September 2002 to September 2003

Cover Photo

Photographs of sliced bore cores were taken in visible (upper left corner) and ultra-violet (upper right corner) light. They show the traces of fractures. Such photographs were imported into “Matlab”, where the fractures were traced, connected and approximated by triangles. When compared to earlier modelling attempts, the combined set of triangles is a much more realistic representation of the real fracture network. Our future modelling will focus on the effect of small-scale structures on the macroscopic tracer and colloid transport.

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

In its first task, the Laboratory serves an important national role by supporting the Swiss Federal Government and Nagra in their tasks to safely dispose of radioactive wastes from medical, industrial and research applications as well as from nuclear power plants. The activities are in fundamental repository chemistry, chemistry and physics of radionuclides at geological interfaces and radionuclide transport and retardation in geological media and man-made repository barriers. The work performed is a balanced combination of experimental activities in dedicated radioactive laboratories and the field, and theoretical modelling. The work is directed towards repository projects and the results find their application in comprehensive performance assessments carried out by Nagra.

This report summarises the activities and results achieved in the reporting period. It is organised as an overview followed by individual reports on the six waste management sub-programmes and a section on the status of the microXAS beamline.

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

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1 OVERVIEW

Jörg Hadermann

The progress made in the Laboratory (LES) since September 2002 is summarised in this first section. The work within LES is organised in two projects.

The first is the **Waste Management Programme**. Its sub-programmes' achievements are given in sections 2 to 7. These sub-programmes are not isolated units. In fact, there is a strong interaction between them as well as between experimenters and modellers as can be seen to some extent from the list of co-workers on page 20. The results of the XAFS sub-programme are integrated into the other activities. It is also the aim in this first section to facilitate, for the reader, an appreciation of these interactions.

The second is the **MiroXAS beamline project**. The achievements, together with the SLS team, are presented in section 8. The incentive to better understand reactions of atoms at solid surfaces was at the beginning of planning the beamline, and X-ray absorption spectroscopy has become an important tool in the waste management programme.

1.1 General

The current situation of waste management in Switzerland is characterised by a number of important events.

First, in May 2003, the Swiss population and the Cantons clearly **rejected two initiatives**. The first called for a fast phasing-out of nuclear energy, and the second for a moratorium on upgrading or building new nuclear power plants. The votes confirm the Government's position to keep the nuclear energy option open and provide stability to the planning of the concerned institutions.

Second, Nagra has submitted to the Swiss Nuclear Safety Inspectorate the reports for the **Demonstration of Disposal Feasibility** for Spent-Fuel, Vitrified High-Level Waste and Long-Lived Intermediate Level Waste for the Opalinus Clay in Zürcher Weinland at the end of last year. LES contributed considerably to this study. The study is now under national and international review. LES will be engaged in these evaluations. A decision from the Federal Government on how to continue is expected in the year 2006.

Third, the population of Canton Nidwalden rejected – for the second time – a concession to build a reconnaissance tunnel at the **Wellenberg** site. As a consequence the site has been given up. It has to be noted in this context that there is sufficient storage capacity at the ZWILAG facility.

Fourth, a new **nuclear law** will come into force in 2005. The key waste management issues are: fixing the concept of monitored geological disposal for all kinds of wastes, a phased approach with a streamlining of the necessary steps for approval, a stronger commitment of the Federal authorities, a moratorium on reprocessing and the decision to dispose of wastes, in principle, in Switzerland.

Based on the above mentioned events and decisions, the nuclear utilities, as well as the government, are currently preparing a **strategy for the future**. The strategy should be fixed in 2005. Discussion points are, *inter alia*, how to proceed with the two repository programmes, inventories for the low-level and short-lived intermediate-level waste (SMA) repository and organisational structures.

From an **LES point of view** it seems evident that our investigations in connection with the Opalinus clay option will continue in the laboratory and in the Mont Terri Rock Laboratory. The emphasis will be on geochemistry of relevant elements and diffusion processes in compact clays. We have derived sorption and solubility values for the performance assessment which are, in many cases, orders of magnitudes higher and lower, respectively, than have been used in previous assessments, in Switzerland as well as abroad. These values need further corroboration. Furthermore, we will continue with the cement investigations. As a SMA-repository is essentially a cementitious system, these investigations are independent of the specific site and host rock chosen.

The **microXAS beamline** project is essentially on track. The decision to add the FEMTO beam feature will considerably extend the potential of the beam line. It will be possible to investigate chemical reaction pathways from structural information on activated and transient species. On the other hand, the layout has become much more complex when both the undisturbed beam from the undulator, and the sliced FEMTO beam, are going through the same frontend components and mirror. Special care had to be taken with respect to cooling in order to maintain the optical beam quality. All key components have been specified and calls for tenders made. The shielded hutches are installed and the installation of the beamline infrastructure is ongoing. The layout for the active sample holder and the loading box in our Hot Laboratory has been made. We expect "first light" in the experimental hutch in the spring of next year. Commissioning will take place during the second half of 2004 and the beamline will be open to external users early in 2005 (see section 8).

The work within the **5th EU Framework Programme** is proceeding according to plan.

- ACTAF, Aquatic Chemistry and Thermodynamics of Actinides and Fission Products Relevant to Nuclear Waste Disposal (see section 4)
FEBEX-II, Full Scale Engineered Barrier Experiment in Crystalline Rock-Phase II (see section 4)
ECOCLAY-II: Effects of Cement on Clay Barrier Performance – Phase II (see section 5)
GLASTAB, Long-term Behaviour of Glass: Improving the Glass Source Term and Substantiating the Basic Hypotheses (see section 2)
RETROCK, Treatment of Retention Phenomena in Safety Assessments (see section 3)
ACTINET, Establishment of a Network of Excellence in Actinide Science (see section 2 and 4).

The work within the 5th Framework Programme will come to an end very soon.

We were involved in the formulation of three expressions of Interest for the **6th Framework Programme**. The EU call in spring 2003 has been tailored to two of them:

- ACTINET-6, Chemistry and Physics of Actinides in Solution and Solid State (Network of Excellence).
- NF-PRO, Understanding and Physical and Numerical Modelling of the Key Processes in the Near-Field and their coupling for different Host Rocks and Repository Strategies (Integrated Project).

Both have been favourably reviewed by the EU, and the contract negotiations are ongoing. We are expecting that a topic in the second call this autumn will be concerned with radionuclide migration in the far-field. Preparatory work, based on an Expression of Interest, is ongoing.

Bilateral cooperations with external institutions and scientists has continued as before. The long-time co-operation with Nagra was close and enjoyable. Frequent meetings dealt mainly with the ongoing Demonstration of Disposal Feasibility Study, but also with low-level waste disposal. The umbrella agreement with Nagra runs out at the end of this year. A new agreement covering the next five years is ready for signature. We had our yearly meetings with the Institut für Nukleare Entsorgung (INE/FZK), Karlsruhe, the Chemical Physics Department (DPC/CEA), Saclay, and the Institut für Radiochemie (FZR), Dresden, Germany. Co-operation within a formal umbrella agreement also continued with CIEMAT, Spain. Again, we made use of the possibility to perform measurements at the ESRF, Grenoble, at

ALS, Berkeley, and at NSLS, Brookhaven. We continued the co-operation with CRIEPI, Japan, in the field of cementitious systems. On a person to person basis, we have cooperations with the University of Bern, the Federal Institute of Technology ETHZ, EAWAG Dübendorf, EMPA Dübendorf, GFZ, Potsdam, the University of Tübingen, IRSN Paris, Technocentre Kiev, SBRAS Irkutsk, the Nuclear Research Centre Mol, Belgium, the University of Mainz, the Japan Nuclear Cycle Development Institute (JNC), the University of Strasbourg and are participating in various gremia of the OECD/NEA. Within the latter, we mention the Thermodynamic Data Base (TDB) Project. We value these cooperations greatly and consider them indispensable for our work.

On September 23 and 24, 2002, the Waste Management Program Committee met for the yearly meeting. As usual, the work performed and future plans were discussed (AN-44-02-19). On this occasion it was also time to say goodbye to a member of the Committee, Prof. I. Grenthe, Royal Institute for Technology, Stockholm. He has been a member for many years and I would like to take this opportunity to thank him for his co-operation during the meetings and throughout the year. It is a pleasure for the staff of LES to continue the co-operation with Ingmar Grenthe in various gremia also in the future. As a new member we are pleased to welcome Prof. P. Toulhoat, CNRS and University Claude Bernard, Lyon.

Finally, it is noted that we have two new PhD students, M. Vespa and R. Mettier, and a new Post-Doc, M. Harfouche.

1.2 Performance assessment

Our very intensive and direct involvement in specific performance assessment projects is a rather cyclic activity with a time period of six to eight years. It is challenging not only because of the need for comprehensiveness, but also because of the links, upstream and downstream, in a performance assessment chain. For example, a sorption data base has to provide data for all elements present in the waste in noteworthy quantities, it has to take into account site specific groundwater compositions and mineralogies, and it has to provide the data within a concept tailored to, and in a form consistent with, their use. How to deal with uncertainties from incomplete knowledge and with variabilities is an evident and notoriously difficult task. An overview on all aspects of a safety case, proper planning, and provision of time for iterations, are therefore important. For all of these reasons we had, also this year, particularly frequent meetings with the project managers at Nagra.

The largest part of our activities was related to the **Demonstration of Disposal Feasibility Study** (Entsorgungsnachweis) for high-level wastes, spent fuel and long-lived intermediate level wastes. The host rock is Opalinus clay in Zürcher Weinland, northern Switzerland.

A series of **reference reports** has been published during the reporting period. These present the data which have been used in the Safety Report (Nagra Technical Report NTB 02-05, December 2002). The main issue in these reports is to present in a transparent and traceable way, the derivation and selection of the data. As usual, the reports have undergone detailed internal and external reviews.

These reports are on

- Glass corrosion rates of the COGEMA and BNFL glasses (see section 2)
- The reference bentonite porewater composition (see section 2)
- Solubility limits in the near-field of the repository for spent fuel and vitrified high-level waste (see section 2)
- Solubilities in the cementitious environment of the intermediate-level waste repository (see section 2)
- Sorption on MX-80-bentonite (see section 4)
- Sorption on undisturbed Opalinus clay (see section 4)
- Sorption on cement in the intermediate-level waste repository (see section 5)
- Sorption on altered Opalinus clay in the vicinity of the intermediate-level waste repository (see section 4)
- The effects of glaciation and tunnel convergence on flow and radionuclide transport (see section 3).

A report on diffusion in Opalinus clay based on data from laboratory experiments and field investigations, both at the Benken site and the Mont Terri Rock Laboratory, is in preparation.

The most striking feature of our solubility and sorption data bases is that the values differ, for many elements, strongly from those used in the past in Swiss performance assessments, as well as in foreign ones. As a matter of fact, the derived solubilities are lower and the sorption distribution constants higher, by several orders of magnitude in many cases. This is a combined effect of newly developed methodologies, specific in-house measurements, and increased knowledge. In addition, we do not only present lower and upper bounds for solubilities and sorption values, as has been the case in the past, but were confident enough to define realistic expected values.

The **impact of these developments** is fully seen in the new performance assessment for the repository in the Opalinus clay. Most of the radioactive inventory will decay in the man-made

barriers, a tiny fraction will migrate into the host rock, and a very small part only, will return to the biosphere.

1.3 Foundations of repository chemistry

Some time ago we decided to further develop the **GEMS code system** (section 2), a thermodynamic modelling code based on Gibbs energy minimisation. The main reason was flexibility in dealing with heterogeneous multiphase aquatic systems. The code package is now at a stage where it has been possible to place it on our web site for free downloads. We expect that the code will thus become a standard tool, not only at PSI, but also in other institutions. As a quality control check we will get feedback from the users. The code system has indeed fulfilled our expectations. Our thermodynamic data base Nagra/PSI 01/01 has been ported to GEMS to make it useful for geochemical investigations such as speciation, surface complexation, co-precipitation and solid solutions (section 2).

The next step will proceed into the direction of **thermodynamic modelling under uncertainty**. Usually, thermodynamic data and bulk chemical composition of a system are fixed in such calculations. The new idea is to take into account their uncertainty by constructing a so-called payoff matrix. The inspection of this matrix not only allows determinations of uncertainties in speciation to be made, but, and more importantly, yields information on the chemical consistency of the model assumptions for the system considered. For the simple Ca-C-O-H system the feasibility and power of the method has already been demonstrated. This work is being done in co-operation with I.K. Karpov's group in Irkutsk, Russia (see section 2).

In the context of the EU Framework Project ACTAF we investigated the formation of **solid solutions** with europium. Experimental data for co-precipitation with calcite came from the University of Copenhagen, and on uptake in calcite in artificial cement pore water from our own previous experiments. We were able to determine consistent end-members of reactions for both data sets. These results were corroborated by time-resolved laser fluorescence spectroscopy at INE/FZK. The importance and impact of solid solution formation has already been seen during the evaluation of solubility limitations for safety assessments and we will continue in this direction (see section 2).

A further study in the field of thermodynamics investigated the solubility of **portlandite** and the stability constant of the **CaOH⁺** complex. The latter has been measured in a number of electrolyte solutions. The evaluation has led to a consistent picture, and the stability data for portlandite measured over the past 100 years could be reproduced. This work is to be seen within our efforts to better understand and describe cementitious systems (see section 2).

In connection with modelling the sorption of nickel on montmorillonite, it had been noticed that the literature values for **Ni-carbonate** were not reliable. The stability constants for this complex and for **Ni-oxalate** have been carefully measured and the results have been published.

Finally, our work within the **OECD/NEA Thermodynamic Data Base** is mentioned. We chair the experts group for evaluation of data for selected organic ligands with selected elements. The work at LES has been resumed during the reporting period and a final report will be published next year.

1.4 Repository near-field

As in last year's progress report, a division is made between work for the high-level waste and fuel element repository, and work for intermediate-level and low-level wastes. The first has a bentonite backfill, the latter a cementitious environment. However, concerning sorption investigations, the methodology of our investigations is very similar: understand sorption reactions on single mineral components of the bulk system (bentonite, cement), synthesize the latter from the former, and complement macroscopic aqueous chemistry experiments with microscopic, spectroscopic investigations. More artificial is the separation into near-field and far-field (next subsection), since the systems have similar components (e.g. clay) and interactions between them are important (e.g. pH-plume).

Compacted bentonite will be used as backfill material. It contains large quantities of the clay mineral **montmorillonite**. For this reason we have been investigating sorption mechanisms for this clay mineral. This work over the past few years has essentially been done within the FEBEX-II EU project (see section 4).

The sorption of caesium on conditioned Ca-montmorillonite from Wyoming (SWy-1) showed a highly non-linear isotherm which could be explained by taking into account the contribution of a small (~1 %) admixture of illite. At low Cs concentrations the high affinity edge sites in illite dominate the sorption on SWy-1 Ca-montmorillonite. The MX-80 bentonite shows much less non-linearity since sodium is the dominating cation. Experimental data and theoretical curves agree well, and are, again, a point of validation of the previously developed sorption model.

Sorption measurements were also performed for U(VI) on montmorillonite. The data are interpreted in terms of surface complexation and, at pH < 5, cation exchange. Quantitative modelling is planned.

The other clay mineral under investigation is illite, and these results will be summarised in the far-field sub-section since illite is an important component of the Opalinus clay.

The other topic of near-field related investigations is sorption on **cement and cement forming phases**. These also include wet chemistry and X-ray absorption spectroscopy investigations (section 5). As in previous years the main emphasis was on investigations with calcium-silicate-hydrates (CSH). The reason is that CSH phases are important components of cement, and also alteration products resulting from the interaction of alkaline fluids with the Opalinus clay. Part of this work was done in co-operation with CRIEPI, Japan, and part is embedded into the EU project ECOCLAY II (Section 5).

There are different methods of synthesising CSH phases. Work in the past has shown that a synthesis in artificial cement water produces impurities of portlandite. The solution has been to synthesise CSH in pure water, which works well up to high C/S ratios.

Sorption experiments have been performed for different elements: strontium, tin, europium, thorium, uranium and curium. The solid phases used were hardened cement paste and CSH phases. Hardened cement paste was used in order to corroborate the high sorption values which were used in the Safety Assessment based on literature data and some of our own measurements. For Cm(III) measurement were also carried out in co-operation with INE/FZK using time-resolved laser fluorescence spectroscopy to elucidate the sorption mechanisms. One species sorbs on portlandite. The sorption on the CSH component dominates and shows a polynuclear Cm species and a Cm species incorporated into the CSH phase. This conclusion is based on the comparison with sorption on pure CSH phases. For CSH phases sorption studies were also performed at various C/S ratios in artificial cement waters: for Sr there is strong competition with Ca cations. For Eu(III), sorption and desorption experiments show similar results. Th(IV) and U(VI) exhibit the same distribution ratios when comparing sorption and co-precipitation experiments. For U(VI) a linear isotherm results at low concentration ($< 6 \cdot 10^{-6}$ M) whereas at higher concentrations a calcium uranate forms.

The alkaline **degradation of cellulose** seems to be a never ending story. The degradation experiments at 60 °C and 90 °C have definitively falsified the hitherto accepted model concept. We are little interested in the cellulose degradation mechanisms but rather on the impact of degradation products on radionuclide speciation and sorption. For this reason we have decided to investigate the stability of α -isosccharinic acid (the main degradation product) in the alkaline environment. First experiments in this direction are ongoing (see section 7).

1.5 Repository far-field

As in the case of the near-field, sorption is an important immobilisation mechanism in the far-field.

The second type of clay mineral under investigation is **illite** (see section 4). This is an important component of Opalinus clay as well as in other clay rocks. Part of the work performed with illite was done within the EU project ACTAF.

The first step towards a mechanistic understanding of sorption are titration experiments. These yield data for site capacities and surface protolysis constants. It turned out – within the previously developed model – that two weak sites were sufficient to reproduce the titration data for $\text{pH} > 4$. At lower pH values, complex dissolution and exchange reactions dominate. These are not fully understood and are somewhat outside the scope of our work.

The next steps were the measurement of sorption edges and sorption isotherms. This has been done for strontium, nickel, europium and uranium (VI) on Na-illite for different electrolyte concentrations. Cation exchange capacities, selectivity coefficients and surface complexation constants on strong and weak sites were determined for these elements. Edges and isotherms could be well described for Sr, Ni, Eu and U(VI). In order to obtain structural information on the surface complexes, EXAFS measurements have been made for sorbed uranium. These indicate the formation of an inner-sphere complex. A reliable evaluation of the full EXAFS spectrum calls for further measurements at the ROBL, Grenoble. Part of this work was done within the EU ACTAF project.

Diffusion in clay rocks is a focal point in our transport investigations. Investigations are ongoing in the lab and in the field along with modelling. (see sections 3 and 7).

Diffusion in Opalinus clay is not isotropic because of preferential layering during its formation as a marine sediment. Therefore, experiments are being performed to measure diffusion parallel and perpendicular to bedding. A second point to consider is that the overburden induces a pressure perpendicular to the bedding. For this reason new diffusion cells have been developed in which the confining pressure could be simulated. Also in the past reporting period these diffusion cells have functioned very well.

A third point to note is that we perform measurements with material from the Mont Terri Rock laboratory and from the deep drilling at the Benken site. The reason is that field experiments are being performed at Mont Terri and a plentiful supply of material is available, whereas the quantity is restricted for the Benken material. Of course, the aim is to extrapolate the characteristics from the former to the latter. The tracers which were measured in the reporting period are ^{85}Sr (perpendicular to bedding), ^{36}Cl (parallel to bedding) and ^{22}Na (both principal components of the diffusion tensor). As had been seen before, there is a factor

of ~5 difference between the effective diffusion coefficients in the two orientations. The differences in diffusion coefficients and rock capacity factor between Mont Terri and Benken material are due to the different degrees of compaction. Out-diffusion experiments (which are done immediately following the through-diffusion experiments) are much more sensitive to the diffusion processes. They clearly exhibit two diffusion pathways with the exception of Cl-diffusion through Benken Opalinus clay. The reason might be ion exclusion.

In the past, we had tentatively interpreted the slow diffusion component as diffusion through the interlayers of the clay platelets. Based on the new results, especially those for Cl-diffusion, we are not so sure about this interpretation any longer. In order to obtain microscopic information we have started neutron spectroscopy measurements at the FOCUS instrument at SINQ. This would yield local diffusion coefficients. Scoping experiments have been done with Opalinus clay, bentonite and sandstone. In the last case we do not expect to see bound water. The method looks promising and measurements will continue. (see section 7). Furthermore, we made some first steps to take into account heterogeneities in the material where the diffusion processes are operative (see section 3). It may be the case that the different diffusion pathways are a consequence of such heterogeneities.

First steps have begun towards the measurement of **diffusion in pure compacted clay minerals** (see section 7). The idea behind this new approach is to take advantage of our relatively good understanding of sorption mechanisms (section 4) and to investigate the behaviour of reactive tracers in a dynamic diffusion situation.

During the reporting period the results of the Mont Terri diffusion **field experiment**, DI-A, became available and were interpreted. Most tracers behaved as expected. The interpretation of caesium diffusion was somewhat hampered by the numerical tools at our disposal.

A few, smaller scale activities were concerned with transport in **fractured media**. These are almost completely related to the Grimsel Test Site. The first point to mention in this context is a PhD thesis project whose aim is to obtain realistic fracture networks from information gained in the Excavation Project. The second is that predictions and subsequent analyses of data from the Colloid and Radionuclide Retardation Experiment at the Grimsel Test Site were made (see section 3). In connection with this we also did some experimental investigations (see section 6), measuring the stability of colloids from backfill material in the Grimsel water and the breakthrough of colloids. For the actinides Am(III) and Pu(IV) we indeed see colloid mediated tracer transport. Finally, an overview of the impact of, and reliance on, matrix diffusion in performance assessment has been performed within the EU RETROCK project (see section 3).

Waste Management Laboratory: Sub-Programme Structure

Waste Management Programme	
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MicroXAS Beamline Project

Management 445xxx

Design and Construction 4451xx

Infrastructure 4452xx

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2 THERMODYNAMIC MODELLING

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

2.1 Overview

In the period September 2002 to September 2003, covered by this progress report, a large fraction of the activities of the thermodynamic modelling group was devoted to finalising the documentation of work done for Nagra's project for demonstrating disposal feasibility (*Entsorgungsnachweis*). Besides the Nagra/PSI Chemical Thermodynamic Data Base 01/01, available as book-on-demand since September 2002 (HUMMEL et al. 2002), a series of reports has been published, discussing in detail

- the application of the Nagra/PSI TDB for estimating the solubility of tetravalent actinides (HUMMEL & BERNER 2002),
- the solubility limits of 36 elements potentially relevant in the near-field of a repository for spent fuel and vitrified high-level waste (BERNER 2002)
- and in the cementitious environment of an intermediate-level waste repository (BERNER 2003),
- the modelling work performed to define a reference bentonite porewater composition (CURTI & WERSIN 2002),
- and the glass corrosion rates of the two Swiss reference glasses (CURTI 2003).

The ongoing work on thermodynamic databases and software comprises three topics:

- Extensive review work has been done for the international project OECD/NEA TDB Phase II: Selected Organic Ligands.
- The GEM-Selektor program package has been documented and a web release is now available. The Nagra/PSI TDB 01/01 has been ported to GEMS.
- A re-evaluation of the solubility of portlandite $\text{Ca}(\text{OH})_2(\text{s})$ and the stability of the CaOH^+ complex, key compounds in cement chemistry, has been started.

A considerable amount of modelling work was performed in the context of the EU projects ACTAF (solid solutions) and GLASTAB (long-term glass corrosion rates).

A new project, thermodynamic modelling under uncertainty, has been started with a pilot study undertaken in collaboration with Prof. Karpov's group in Irkutsk, Russia.

2.2 Work for demonstrating the disposal feasibility (*Entsorgungsnachweis*)

2.2.1 Solubility limits in cementitious environments

Cement pore waters are strongly alkaline with pH values ranging from 12.5 to 13.5, they contain almost no carbonate and only small amounts of sulphate. Thus, elemental solubilities under such conditions are mainly determined by oxide and hydroxide solids. Using the Nagra/PSI Chemical Thermodynamic Data Base (HUMMEL et al. 2002), solubility and speciation were evaluated for 36 potentially PA relevant elements at the reference pH of 12.5 (portlandite saturation) (BERNER 2003).

The pH sensitivity of the solubility limits was examined by performing calculations at pH 13.4, in accordance with the pH of non-altered cement pore water. Solubility increases predominantly for elements that tend to form anionic hydroxide complexes, such as Sn, Pd, Zr, Ni, Eu, Cd, Mo and Co.

Oxidizing conditions around +350 mV might be expected in the environment of nitrate containing wastes. In such cases, significant solubility increases are calculated for U, Np, Pu, Se and Ag.

Based on the contents of the updated Nagra/PSI TDB, the elements Cs, Cl, I, Tc, Nb and Sb turned out not to be solubility limited in cementitious environments, which could, in part, be an artefact from insufficient data and may call for specific database work focusing on high pH environments.

Special attention was paid to the uncertainties of evaluated maximum concentrations. These uncertainties were expressed as upper and lower limits, mainly derived from uncertainties of solubility products and formation constants using error propagation methods. However, this is by no means a straightforward procedure. Other features such as “detailed system understanding”, “system history” or “relevance of limiting phase” may cause additional uncertainties. Such features need to be assessed case-by-case.

2.2.2 Bentonite reference porewater

In the past year, time has been devoted to prepare the final documentation of the modelling work performed to define a reference bentonite porewater composition (CURTI & WERSIN 2002).

2.2.3 Glass corrosion parameters

Reference glass corrosion rates were updated based on the kinetic data obtained from long-term leaching experiments (12 years) of the two Swiss reference glasses. In contrast to the preceding safety assessment KRISTALLIN-I, the new results allowed us to define distinct long-term rates for the two types of glass ($1.5 \text{ mg m}^{-2} \text{ d}^{-1}$ for BNFL glass and $0.2 \text{ mg m}^{-2} \text{ d}^{-1}$ for COGEMA glass). The procedure and methods used to determine the rates have been documented in detail (CURTI 2003).

2.3 Thermodynamic databases and software

2.3.1 OECD/NEA TDB review on selected organic ligands

The international project “OECD/NEA TDB Phase II: Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Zr, Ni and Se with Selected Organic Ligands” consumed a large fraction of the time of its chairman (W. Hummel) in the period September 2002 to September 2003.

An important milestone has been reached: Two out of three major chapters, concerning the ligands citrate and edta (ethylenediaminetetra-acetate) and comprising about 700 reviewed references and more than 500 draft manuscript pages, are now (September 2003) ready for external peer review.

However, the third major chapter concerning the ligand oxalate caused unexpected problems. Despite all the efforts of the chairman and another experts to help the two reviewers responsible for the main part of this chapter, no substantial progress was reached in the period October 2002 to July 2003. In May 2003 some sections of the oxalate chapter were re-allocated to other experts of the review team. At the end of July 2003 the two reviewers announced their resignation from the project, and subsequently their unfinished work had to be redistributed to the remaining experts of the review team.

2.3.2 Portlandite and CaOH^+ : Key compounds in cement chemistry

We described the thermodynamics of hydrogarnet-like cement phases based on 60 year old experimental data in the last progress report. This work aims at a quantitative thermodynamic model for cement phases. As a prerequisite for such a model, basic characteristics, like the solubility of portlandite $\text{Ca}(\text{OH})_2(\text{s})$ and the stability of the CaOH^+ complex, which are key compounds in cement chemistry, must be known very well.

DUCHESNE & REARDON (1995) presented a comprehensive portlandite solubility model based on the Pitzer formalism. They do not need to define a CaOH^+ complex; instead they adopt a large number of Pitzer interaction coefficients to mimic experimental systems up to very high electrolyte concentrations. The NEA (GRENTHE et al. 1992) proposes a simpler ionic strength correction model, the specific ion interaction theory (SIT), for deriving basic thermodynamic data, and we decided to perform our in-house database work on the basis of this SIT approach. Hence, we could not directly use the DUCHESNE & REARDON (1995) model, but we had to re-evaluate the available data.

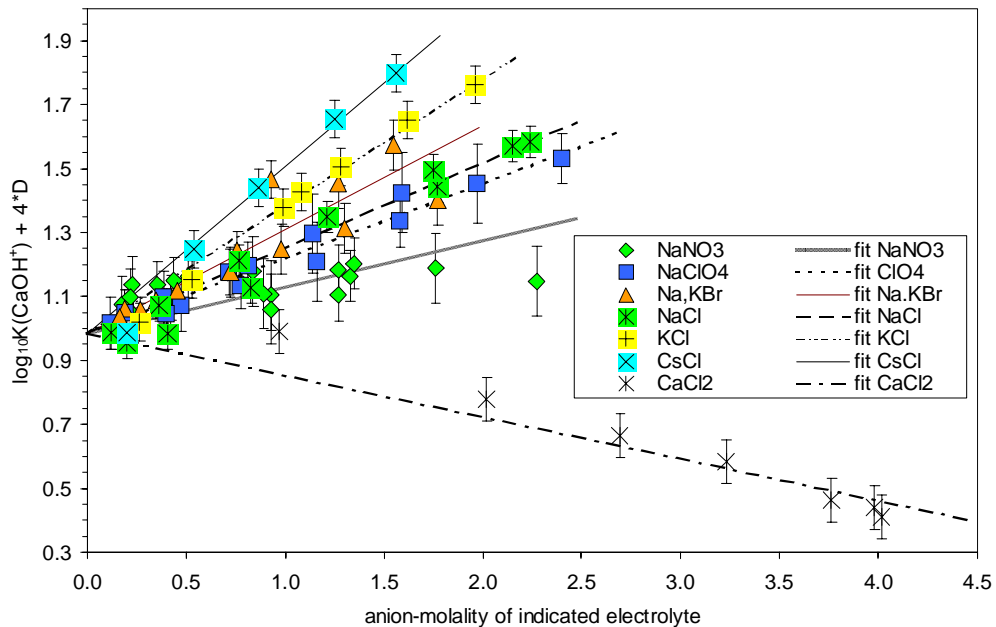


Fig. 2.1: SIT multi-dimensional linear regression of the CaOH^+ formation constant yielding $\log_{10}K^{\circ}_{\text{CaOH}^+} = 0.98 \pm 0.02$.

The formation constant of CaOH^+ is one of the key issues in this re-evaluation, as it cannot be assessed independently of the portlandite solubility product. We assumed that $\log_{10}K^{\circ}_{\text{sp}} = -5.19 \pm 0.04$ at $I = 0$ evaluated by DUCHESNE & REARDON (1995) is reliable, and then re-evaluated portlandite solubility data in different electrolytes from MILIKAN (1916), JOHNSTON & GROVE (1931) and YEATTS & MARSHALL (1967). Using published SIT interaction coefficients (GRENTHE et al. 1992), $K_{\text{sp}}(I)$ and $K_{\text{CaOH}^+}(I)$ at variable electrolyte concentrations were determined for every reported experiment. Since $\log_{10}K^{\circ}_{\text{CaOH}^+}$ at $I = 0$ must be independent of the electrolyte type, a multi-dimensional linear regression of $\log_{10}K_{\text{CaOH}^+}(I)$ versus the corresponding anion molality was performed for seven different electrolytes (Fig. 2.1) forcing all straight lines to share one single point at $I = 0$.

The extracted parameters were in turn used to describe the solubility of portlandite in hydroxide electrolyte media. The comparison with experimental work from the last hundred years (D'ANSELME 1903, FRATINI 1949, JOHNSTON & GROVE 1931, YEATS & MARSHALL 1967, DIAMOND 1977, DUCHESNE & REARDON 1995, TITS & WIELAND 2003) is shown in Fig. 2.2.

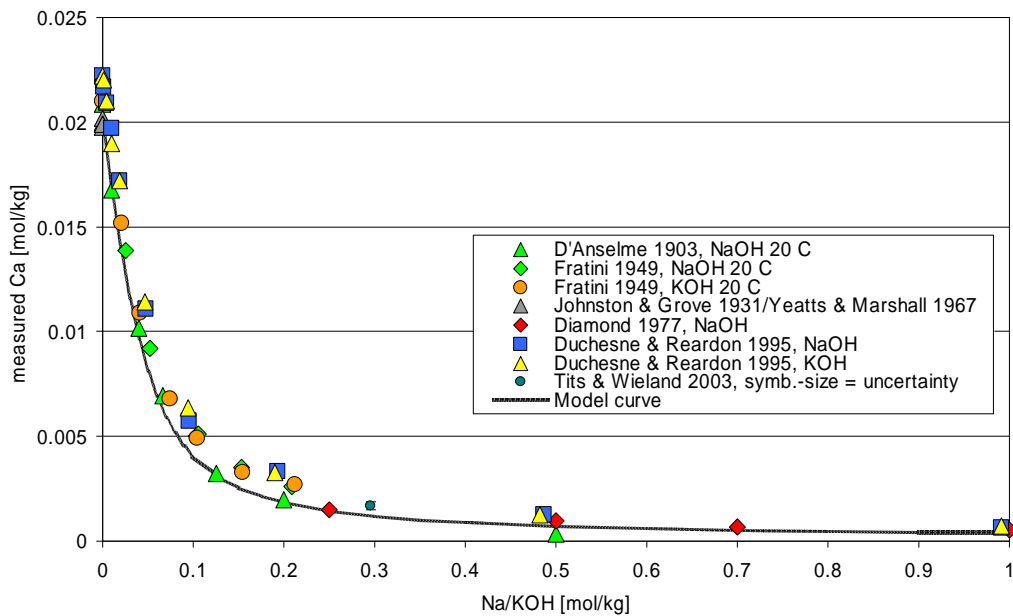


Fig. 2.2: The solubility of portlandite $\text{Ca}(\text{OH})_2(\text{s})$.

2.3.3 GEMS database

The original Nagra/PSI TDB 01/01 (HUMMEL et al. 2002) was designed to be used with geochemical modelling codes that apply the law of mass action algorithm (e.g., MINEQL and PHREEQC). The essential thermodynamic data at standard conditions (1 bar, 25°C) are equilibrium constants ($\log_{10}K^\circ$) for the formation reactions of product species from master species. Since GEM-Selektor (GEMS) has taken over as our workhorse for geochemical modelling, the Nagra/PSI TDB 01/01 has been ported to GEMS. GEMS is a geochemical modelling code based on a Gibbs energy minimization algorithm. The essential thermodynamic data are molar Gibbs energies of formation from the elements ($\Delta_f G^\circ$) for all chemical species. Therefore, the main task in porting the Nagra/PSI TDB 01/01 to GEMS was to derive $\Delta_f G^\circ$ of each aqueous species, solid, and gas from the equilibrium constant of its formation reaction and $\Delta_f G^\circ$ of all master species taking part in that reaction. With these values for $\Delta_f G^\circ$ any $\log_{10}K^\circ$ contained in

the Nagra/PSI TDB 01/01 is perfectly reproducible at the standard conditions (1 bar and 25°C).

In addition to the $\Delta_f G^\circ$ data for standard conditions, the Nagra/PSI TDB 01/01 GEMS also includes data for the extrapolation of $\Delta_f G^\circ$ (and thus $\log_{10} K^\circ$) to temperatures above 25°C. GEMS uses the revised HKF (Helgeson-Kirkham-Flowers) equation of state for calculating the change in $\Delta_f G^\circ$ of aqueous species as a function of pressure and temperature. We decided to adopt published HKF parameters, if available, although without any critical evaluation. If HKF parameters were missing, we used 1- and 2-term temperature extrapolations for isocoulombic or isoelectric reactions.

Note that all these additional data given in order to extend calculation of chemical equilibria to elevated temperatures should not be considered as part of the official Nagra/PSI TDB 01/01 GEMS. The official data for GEMS are restricted to those required for the calculation of chemical equilibria at standard conditions.

2.3.4 The GEM-Selektor program package: Documentation and web release

The GEM-Selektor v.2-PSI code, written in C/C++, combines the high-precision GEM IPM-2 algorithm (CHUDNENKO et al. 2002) with tools and thermodynamic database for physicochemical modelling of heterogeneous multiphase aquatic systems. The code appears more suitable for simultaneous modelling of aqueous speciation, surface complexation, co-precipitation and solid solution formation than the commonly available LMA speciation codes. In March 2003, the continuing development of GEMS-PSI program package has reached the stage when a release candidate (for Win32) could be put on the LES web site for free (registered) download, in order to make it available to a broader research community and eventually improve the code and documentation after collecting users feedback. Even though extensive on-line documentation is yet to be finished, and the official advertising has yet to be done, more than 80 downloads were registered in March-August 2003, indicating a considerable interest in the geochemical community.

The main emphasis in extensive and tedious work on writing the adequate and precise documentation files has been made on functionality of GEMS productivity modules (such as Process Simulator), and especially, on built-in calculations of thermodynamic data and activity coefficients. In parallel, the on-line screenshot tutorial has been developed that gives an easy step-by-step introduction into GEMS modelling of aquatic equilibria. Programming work was limited to testing, bug fixing and improving some dialogs and built-in functions, as well as incorporating some third-party contributions

(subroutines for thermodynamic calculations provided by M. Gottschalk, GFZ Potsdam, Germany, and S.V. Churakov, CSCS ETHZ, Manno, Switzerland). Preparation of a GEMS release for Linux, final documentation and tutorial examples is under way.

The GEM-Selektor v.2.0.0-PSI program package for (Win32) with Nagra/PSI TDB 01/01-GEMS (THOENEN & KULIK 2002; 2003) is available as a release candidate for download from <http://les.web.psi.ch/Software/GEMS-PSI/>.

2.4 Thermodynamic modelling under uncertainty

In geochemical modelling, all input data are usually treated as deterministic values, though in reality neither the standard molar Gibbs energy of components nor the bulk chemical composition of the system are known precisely. Without a sensitivity study, geochemical modelling may potentially lead to serious misinterpretations or totally wrong conclusions, - a grim perspective in applications relevant to performance assessment in nuclear/toxic waste disposal. This motivated our pilot study undertaken in collaboration with Prof. Karpov's group (Institute of Geochemistry SB RAS, Irkutsk, Russia), aimed at a new approach to geochemical modelling under uncertainty of input data (KARPOV et al. 1999) and applied to PA-relevant chemical systems (CHUDNENKO, KARPOV, KULIK, BERNER, HUMMEL, ARTIMENKO 2003, PSI report in preparation).

Briefly, the new approach combines (i) Gibbs energy minimization (GEM) algorithm for calculation of heterogeneous chemical equilibria (KARPOV et al. 1997; 2001); (ii) sampling the multi-dimensional "uncertainty space" using a uniform probing grid; (iii) advanced statistical analysis based on the "decision-making" criteria adopted from game theory. "Sampling" means here GEM calculations of $n(Q)$ (scores to thousands) equilibrium states at different combinations of uncertain input data, located within an uncertainty space made of the respective uncertainty intervals taken as coordinates. Statistical analysis is needed because of a vast sampled output (full chemical speciation at each point) and, mainly, because the correct phase assemblage (or experimental concentration) may not be the most frequent one(s) among sampled results.

The key part of uncertainty space analysis lies in constructing a *payoff matrix* $E = \|e_{tq}\|$ of size $n(Q) \times n(Q)$, with rows referring to different GEM solution variants and columns related to different combinations of input parameters for the sample variants. Each e_{tq} value would then *measure a general chemical inconsistency* between q -th input data combination and t -th calculated equilibrium speciation. As the number of sample points $n(Q)$ is typically set above 100, the payoff matrix would contain more than

10000 elements and be difficult to interpret. Hence, a further statistical processing is done, e.g. by computing the arithmetic mean \bar{e}_t of each t -th row of the payoff matrix E .

Independent experimental information about any calculated equilibrium parameter can be used for checking how the analysis of payoff matrix reduces initial uncertainty intervals. This procedure can be called “filtering”; in the simplest case, it utilizes an independent knowledge about the stable phase assemblage. Filters can also be set using known total dissolved concentrations, or measured pH or pe. Regions of the uncertainty space where no filtered sample points occur can be safely cut off, thus making some initial uncertainty intervals smaller. Then, the whole modeling run can be repeated, eventually leading to the smallest possible uncertainties and robust modeling results.

In PA model applications, not only a correct phase assemblage is of interest but reliable solubilities (e.g. actinides) must be obtained. This motivated our selection of the Ca-C-(N)-O-H system with an objective to demonstrate the efficiency of the new approach in reconstructing the *a priori* known phase assemblage and solubility of portlandite $\text{Ca}(\text{OH})_2(\text{s})$ in the presence of calcite $\text{Ca}(\text{CO}_3)(\text{s})$. In this system, it was possible to visualize a 2D uncertainty space with two coordinates – the G_{298}^0 values of portlandite $\text{Ca}(\text{OH})_2$ and the CaOH^+ hydroxocomplex. Literature data on portlandite solubility yield a well-established experimental bracket $19.5 < [\text{Ca}] < 22 \text{ mmol}/(\text{kgH}_2\text{O})$ (BERNER 2003) to be used for filtering. Thermodynamic data were taken from the Nagra/PSI TDB (HUMMEL et al. 2002), recently ported into the GEM-Selektor code (THOENEN & KULIK 2002). An *ad interim* Selektor-W code (from Prof. Karpov’s group) was used in calculations.

The imposed uncertainty of $\pm 1 \log_{10}K$ unit ($\pm 5.708 \text{ kJ/mol}$) yielded the intervals $-902.720 < G_{298}^* < -891.305 \text{ kJ/mol}$ for $\text{Ca}(\text{OH})_2(\text{s})$ and $-722.732 < G_{298}^* < 711.316 \text{ kJ/mol}$ for CaOH^+ , comprising a 2-D uncertainty space sampled at $n(Q)$ values of 11, 53, 153 and 601. In each case, the payoff matrix was computed and mean absolute values $|\bar{e}_t|$ were plotted against input G_{298}^0 values for each sample point, thus creating contour images of “inconsistency” in the uncertainty space. A similar pattern (Fig. 2.3) was found at all sample sizes $n(Q)$, with the smallest $|\bar{e}_t|$ values lying in a “valley” covering the “deterministic” point $(-717.024; -897.013 \text{ kJ/mol})$.

Applying the “Ca filter”, $19.5 < [\text{Ca}] < 22 \text{ mmol}/(\text{kgH}_2\text{O})$, removes the ambiguity of the shallow “valley” revealed in Fig. 2.3 and suggests that “consistent” combinations of input G_{298}^0 values should lie within intervals $[897 \pm 1.5] \text{ kJ/mol}$ for portlandite and $[717 \pm 1.5] \text{ kJ/mol}$ for CaOH^+ , thus reducing the initial uncertainty from 1 to 0.3 pK units.

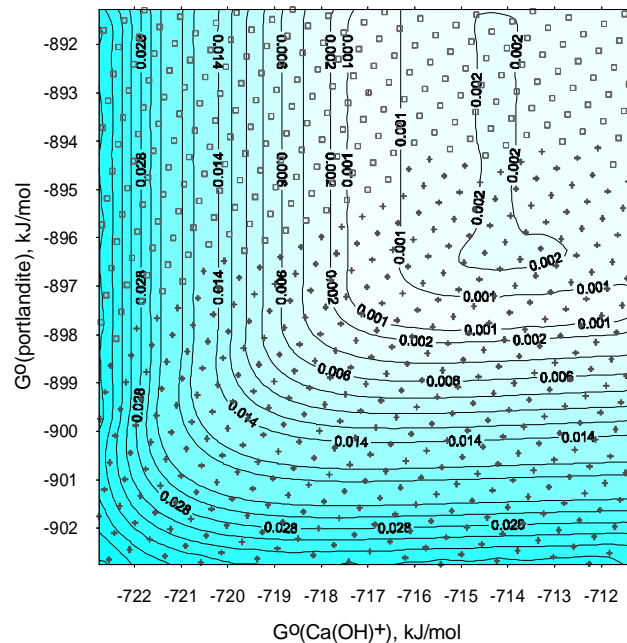


Fig. 2.3: Contour plots of the $|\bar{\epsilon}_t|$ surface at $n(Q) = 601$, obtained from a payoff matrix. Sample points yielding the AGCP phase assemblage are shown as crosses, and those yielding the wrong AGC phase assemblage are shown as squares (A: aqueous, G: gaseous, C: calcite and P: portlandite phases present in non-zero mole amount).

Our pilot study on geochemical modelling in the uncertainty space (part of which is presented above) opens an exciting research perspective, posing many questions to be answered. Does this new technique based on decision-making criteria work equally well in multi-dimensional uncertainty spaces, which are difficult to visualize? How efficient will it be in more complex chemical systems? How reliable are the adapted uncertainty intervals in the absence of experimental data? We hope to answer these and other questions in future collaborative projects, beginning with incorporating the necessary software tools and algorithms into the GEM-Selektor code.

2.5 EU projects

2.5.1 GLASTAB

The European project GLASTAB (3rd and last project year), deals with the dissolution kinetics and alteration mineralogy of nuclear waste glasses. Our laboratory contributes with the evaluation of kinetic long-term experiments, now running for 12 years. Most of the work due for this project has been completed in the first two project years. In the last year an additional regular solution sampling was carried out, and samples of alteration products (extracted after 11 years leaching time) were supplied to our partners in

Strasbourg for TEM analyses. The modelling work focused on the precise evaluation of long-term glass corrosion rates for the demonstration of the disposal feasibility (see section 2.2.3).

2.5.2 ACTAF

In the context of the European project ACTAF (last project year), a considerable amount of work was performed to model solid solution formation of trivalent lanthanides and actinides with calcite. The work was carried out in co-operation with our project partners at FZK and University of Copenhagen.

In this study, we were concerned with solid solution formation through heterovalent substitution, exemplified for the special case of Eu(III) incorporation in calcite. The interest in such systems is not purely academic since Eu(III) is a chemical analogue of the trivalent actinides Am, Cm and Pu(III). Heterovalent solid solutions are by far more complex than the case of substitutions of like-charged ions, due to the introduction of a local charge excess or deficit. The requirement for electroneutrality in the mineral structure precludes simple isomorphous substitutions and alternative substitution mechanisms must be found in order to model thermodynamic equilibrium between such solid solutions and aqueous solutions successfully.

At least 3 mechanisms providing local charge balance were considered: Eu^{3+} incorporation adjacent to octahedral vacancies, coupled substitutions (e.g. $\text{Eu}^{3+}\text{-Na}^+$ or $\text{Eu}^{3+}\text{-H}^+$), or the formation of a neutral “complex” through appropriate lattice deformations. This resulted in a considerable number of possible end-member stoichiometries.

We carried out a systematic thermodynamic analysis to model the uptake of Eu(III) in calcite for (1) recrystallization experiments in synthetic cement pore water (pH 13.3) (TITS et al. 2003) and (2) coprecipitation tests in a diluted NaClO_4 aqueous solution (pH 6), conducted at the University of Copenhagen. Solid solution formation between seven possible end-member pairs was modeled with the Gibbs energy minimization (GEM) method following two alternative strategies: (1) “forward” and (2) “inverse” modeling.

The first strategy (“forward” modeling) is the classical approach, involving the direct calculation of the equilibrium Eu concentrations in the aqueous and solid phase (mole fractions) from the bulk composition of the experimental system and independently

measured end-member solubility products. This method was applied to model ideal calcite solid solutions of calcite with $\text{Eu}_2(\text{CO}_3)_3$, $\text{EuNa}(\text{CO}_3)_2$, $\text{EuOH}(\text{CO}_3)$ or $\text{Eu}(\text{OH})_3$.

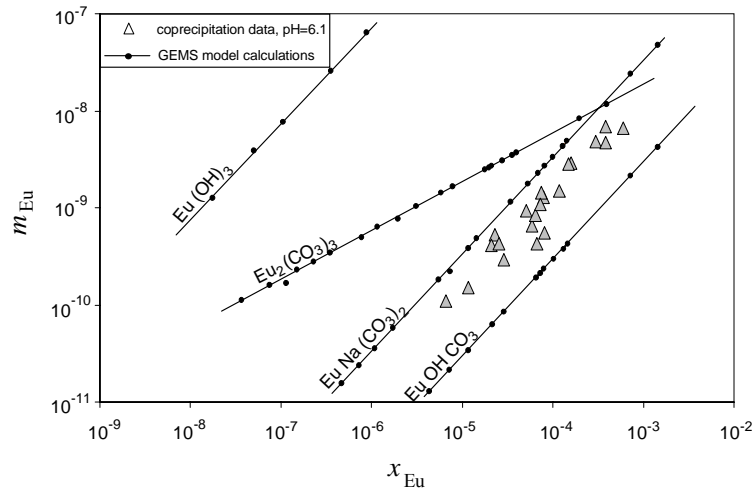


Fig. 2.4: Comparison of ideal solid solution model calculations with the experimental data from Eu coprecipitation experiments with calcite carried out in a 0.025-0.1 m NaClO_4 medium at $\text{pH} \sim 6.1$. Each line represents the model calculations for the specified Eu end-member. Single GEMS calculations are represented by dots on the model lines. The plot shows Eu equilibrium molalities (m_{Eu}) as a function of mole fractions (x_{Eu}).

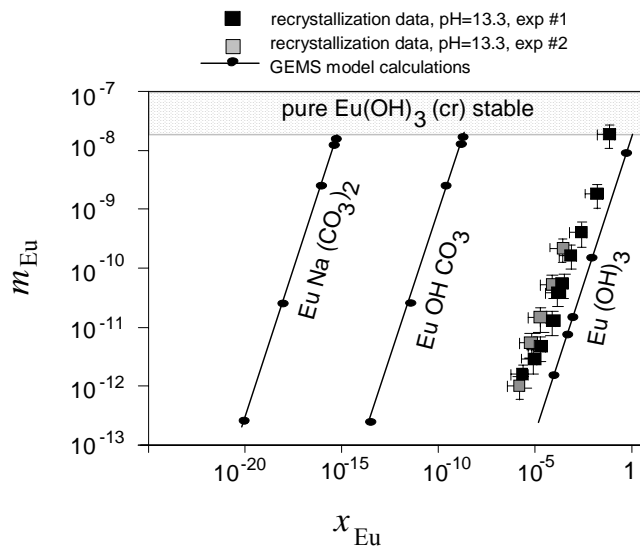


Fig. 2.5: Comparison of ideal solid solution model calculations with the data of Eu uptake experiments carried out in ACW water ($\text{pH} 13.3$). Calculations with the $\text{Eu}_2(\text{CO}_3)_3$ end-member yield physically unreasonable mole fractions $< 10^{-20}$ to the left of the plot, indicating total exclusion of Eu from the calcite lattice.

The comparison of the predictions with the experimental data led us to exclude all four end-members (Figs. 2.4 and 2.5). Solid solution formation with $\text{Eu}_2(\text{CO}_3)_3$ could be ruled out based on the discrepancy of predicted (+ 1/2) and observed (+1) slope in the isotherm plot ($\log m_{\text{Eu}}$ vs. $\log x$). The remaining Eu poles were discarded because none were capable of reproducing simultaneously *both* datasets.

Our results are consistent with TRLFS data obtained at FZK, which indicate that Cm(III) loses completely its hydration sphere during incorporation into the calcite lattice. Hence, all hydroxyl-bearing end-members are excluded by the spectroscopic measurements as well as by our thermodynamic analysis.

The second strategy (“inverse” modeling) must be applied when the solubility product of a candidate end-member is not known. It involves the calculation of the end-member thermodynamic properties (free energy of formation plus the inherent activity term, G_{α}^*) from the experimental data, through so-called dual-thermodynamic calculations. We applied this method to three potential Eu end-members, $\text{EuO}_{1.5}$, $\text{EuO}(\text{CO}_3)_{0.5}$ and $\text{EuH}(\text{CO}_3)_2$, for which solubility products are not available. Such calculations were performed for each end-member at all points of the isotherm, yielding a statistical mean for G_{α}^* .

An end-member is considered to be acceptable if the standard deviation over all isotherm points is in the order of $\pm 2 \text{ kJ mol}^{-1}$ or less, and if the G_{α}^* values of a given end-member coincide for both datasets. These requirements were found to apply approximately only for a solid solution with $\text{EuO}(\text{CO}_3)_{0.5}$ as end-member. Further refinements allowed us to define a model with a slightly different stoichiometry and mean free energy ($\text{EuO}_{9/8}(\text{CO}_3)_{3/8}$, $G^* = -1015.9 \pm 2.1 \text{ kJ mol}^{-1}$) that reproduces both datasets within the analytical uncertainties. In Figs. 2.4 and 2.5 this model would produce two lines perfectly matching the linear trends defined by the experimental data.

2.6 Other activities

Together with scientists from EMPA (Swiss Federal Laboratories for Materials Testing and Research; an Institution of the ETH domain) a workshop entitled “porosity of cement materials” was organised for about 40 participants on April 10, 2003, at EMPA. We believe that the primary objectives of this workshop, namely to initiate scientific discussions and to establish personal contacts among researchers in the field of cementitious materials, were successfully achieved.

2.7 References

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3 GEOSPHERE TRANSPORT MODELLING

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

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

Geosphere transport modelling is one of the key activities of the Waste Management Laboratory LES and, hence, the working activities of the group cover - despite the very restricted man-power - a wide range of important scientific questions. Our main goal is to arrive at an increased understanding of the most important transport mechanisms and processes and to quantitatively estimate their effects on the mobility of migrating radionuclides. For this purpose we develop state-of-the-art models whose quality is investigated thoroughly by modelling experiments on the laboratory and field scale. Furthermore, we require that the predictive quality of such models is tested in new experiments. Such a procedure leads to refined models which are highly reliable and can be used periodically for safety assessment purposes.

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

- **Reactive transport modelling** applying MCOTAC;
- the analysis of **diffusion** experiments on the laboratory and field scale through Opalinus clay from the Benken and Mont Terri area;
- predictions and subsequent analyses of the **colloid and radionuclide retardation experiment** (CRR) performed in the Grimsel test site;
- the derivation of **more realistic fracture geometries** from the analysis of Grimsel bore cores which can be used in transport modelling;
- work for the **Opalinus clay performance assessment** and
- work in the frame of the EU-Concerted Action **RETROCK**.

In February 2003 Ralph Mettier joined the group as a PhD student. His background is geophysics and he completed his studies at ETH in Zürich. His supervisors during the next three years are G. Kosakowski (PSI/LES) and Prof. O. Kolditz from the University of Tübingen, Germany. His main activities will be 1) the evaluation of bore cores from the Grimsel excavation experiment with special emphasis on the derivation of detailed 3D fracture networks and 2) the investigation of the effect of small-scale structures, as observed in these bore cores, on the macroscopic transport of dissolved radionuclides and colloids. A critical comparison of his forthcoming modelling results will be done with former results from the migration and colloid experiments performed in the rock laboratory at Grimsel.

3.1 Overview

3.1.1 Reactive transport modelling applying MCOTAC

The MCOTAC modelling, related to the high pH-plume experiment performed at the Grimsel test site, has come to its final state. A series of lay-out predictions for the spatial and temporal distribution of Cs, Co and Eu as tracers was made. In a final experiment these radionuclides will be injected simultaneously into the static dipole flow field of the shear zone altered by a high-pH plume. Values for the transport parameters deduced from a former fit of the results of a dye tracer dipole experiment in the unaltered shear zone were applied. However, since no results from experiments with sorbing tracer were available, our predictions are associated with large uncertainties because the porosity distribution and the effects of the high-pH on the rock alteration and, consequently, on tracer transport could only be roughly estimated.

For modelling short-term laboratory and field experiments it is often necessary to account for kinetically controlled mineral reaction. (However, such processes may be less important for safety assessment purposes.) That is why we had to extend MCOTAC to include kinetics of mineral reactions. Our efforts have recently come to an end, and the necessary code verification was done by a comparison of MCOTAC results with those from an analytical solution, including kinetically controlled mineral dissolution in a column, according to Xu and Pruess, 1998.

In order to model successfully the breakthrough curves from through- and out-diffusion experiments using Opalinus clay samples from the Benken and Mont Terri area, it is necessary - for diffusion parallel to bedding - to account for two different porosities and two different values for the apparent diffusion coefficient. So far, only uncoupled transport pathways with independent transport properties have been considered (see also sub-section 3.1.2). With the present version of MCOATC however, it is possible to quantitatively investigate the validity of such a simplification. Furthermore, structured porosities and diffusivities representing being natural clay samples are presently being investigated (Fig. 3.1). In the near future we will also account for heterogeneous mineral distribution, sorption sites and various reactions, all of them will be important in order to understand diffusion processes in natural, heterogeneous clay.

In order to also run MCOTAC on much cheaper and wider spread PC/Windows systems than more expensive UNIX-based workstations, some effort was made to evaluate appropriate FORTRAN and C-compilers and to generate a 1D version of MCOTAC. The inevitable code verification was also done and successfully finalised.

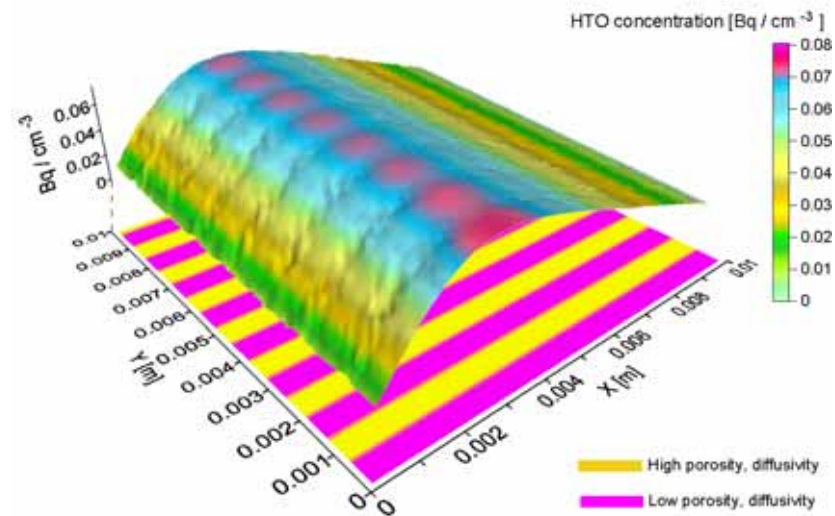


Fig. 3.1: Inhomogeneous but periodic HTO distribution in a 2D stripe-structured clay after $t = 49$ days after starting through-diffusion and 2.4 hours after switching to the out-diffusion phase initialised by replacing the (constant) traced solution in the reservoir at $x = 0$ m. Hence, during tracer out-diffusion both line-boundaries are represented by a constant zero-concentration boundary condition.

The hypothetical Opalinus clay sample with quadratic shape extends from $x, y = 0$ to $x, y = 0.01$ m and consists of eight parallel stripes, each of them extending parallel to the x -direction with homogeneous and isotropic transport properties. However, the values for the porosity and diffusivity change alternating from zone to zone in y -direction, and the tracer diffusion takes place in two dimensions.

3.1.2 Modelling small-scale through- and out-diffusion experiments using Opalinus clay

During this year, too, new experimental results from small-scale diffusion experiments became available for inverse modelling purposes. (For more detailed information concerning the experimental background see chapter 7.) These experiments were performed with samples stemming either from the Benken deep-drilling or from the Mont Terri underground facility. Tracers were sodium and chlorine and the diffusion direction was either parallel or perpendicular to bedding. The experiments consisted of two different phases: 1) a through-diffusion phase until near steady-state with regard to the diffusive tracer flux across the down-stream boundary; and 2) an out-diffusion phase where the sample, loaded with tracer from the previous through-diffusion phase, is leached. By inverse modelling both, tracer through- and out-diffusion, values for the

apparent diffusion coefficient and further information concerning sorption processes and sample homogeneity can be deduced.

The breakthrough curves for diffusion perpendicular to bedding showed no irregularities for both the through- and out-diffusion phase, for both investigated tracers and independent from which location the samples derive. However, the temporal evolution of the diffusive tracer flux during the out-diffusion phase with diffusion parallel to bedding generally showed a more complex behaviour. Consequently, it was not possible to reproduce the breakthrough data based on a single porous medium. Only when accounting for a second independent transport porosity, could a satisfying reproduction of the data be achieved. With these investigations we now have detailed information for three different tracers: a neutral species (HTO), one cation ($^{22}\text{Na}^+$) and one anion ($^{36}\text{Cl}^-$). However, we still do not have an adequate picture of the two types of preferential transport pathways. In order to shed light on the nature of the two different types of transport relevant porosities, we will perform detailed mineralogical investigations, especially with regard to the finer details of the fabrics of the samples. In addition, we will continue with this type of combined diffusion experiments using further cationic and anionic tracers.

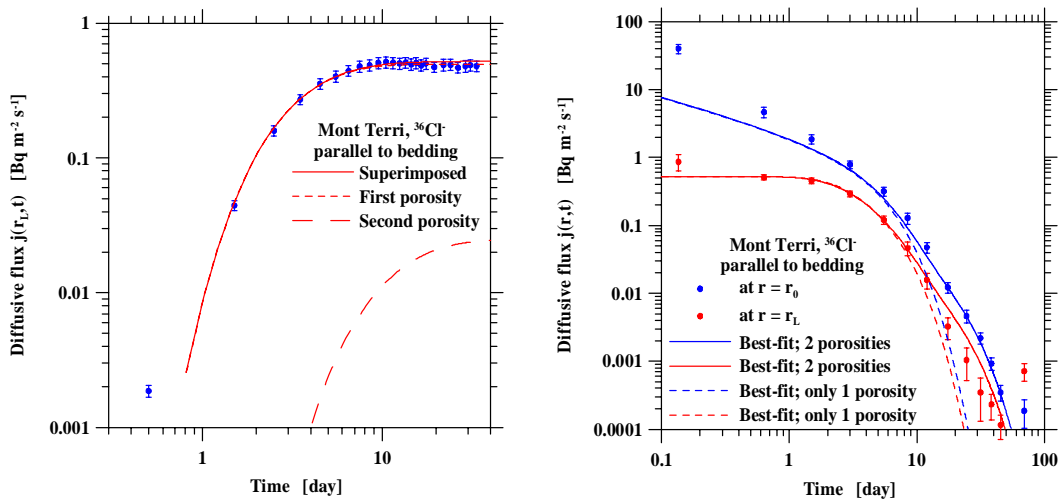


Fig. 3.2: Measured and calculated breakthrough curves for the anion $^{36}\text{Cl}^-$. Plotted is the diffusive flux versus time through an Opalinus clay sample from the Mont Terri facility. Tracer diffusion happened within a cylindrical sample with inner radius r_0 and outer radius r_L parallel to the fabric. The left figure shows the result for through-diffusion. As can be recognised, a diffusion model in terms of a single porous medium is sufficient to reproduce the data with high precision. However, when fitting the out-diffusion phase things look different. Although its contribution to total flux is only on a very small level and only at late times, a second type of transport porosity is imperatively needed in order to reproduce the measurements.

3.1.3 DI-A experiment Mont Terri

Modelling the results of the DI-A experiment carried out at the Mont Terri rock laboratory was a major task in the last year. For this purpose, the code HYDRUS2D was implemented and tested. Unfortunately, the modelling is not straightforward since the code does not allow material-specific pore diffusion coefficients or tortuosities to be set directly. Only an empirical tortuosity relation based on the porosity can be used. To avoid this problem, an auxiliary linear sorption has to be introduced and the porosity values have to be adapted accordingly. Moreover, such a procedure does not work in the case of non-linear sorption, as encountered especially for caesium. Thus, only calculations for HTO, Γ^- , and Na^+ , but not for Cs^+ , could be performed in this way. For Cs^+ an appropriate calculation was carried out using the implemented empirical tortuosity relationship. The agreement with the measured data in the borehole for HTO, Γ^- and $^{22}\text{Na}^+$ was generally good, if the parameters previously determined in the laboratory were used.

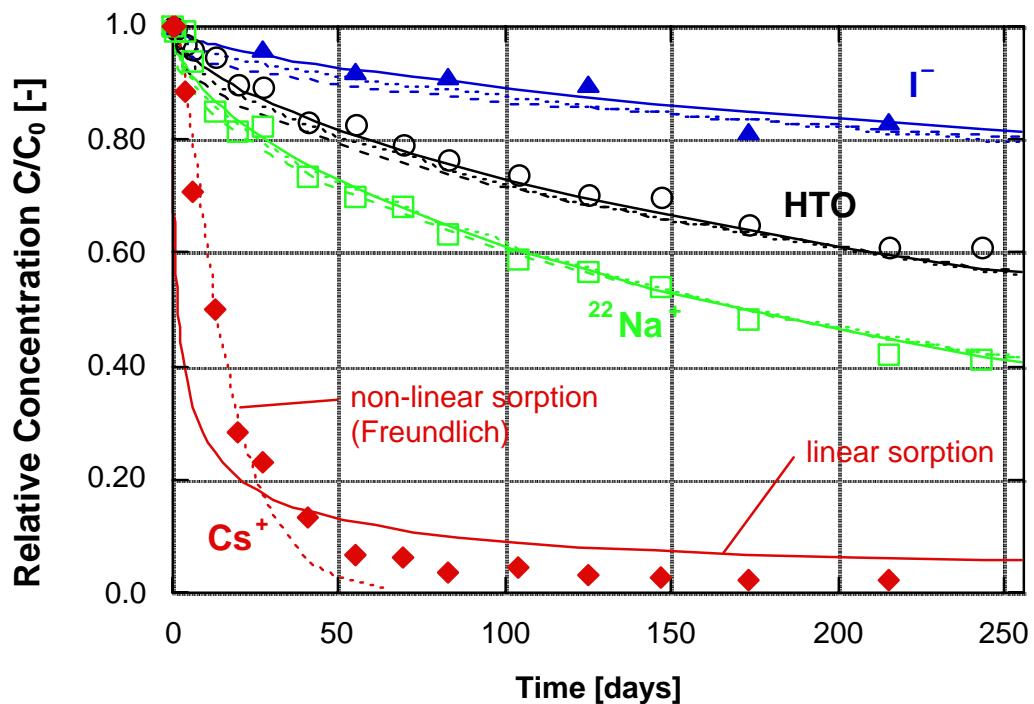


Fig. 3.3: Comparison of experimental data (individual symbols) with an analytical solution of a simple 1D-diffusion/linear sorption model considering cylindrical co-ordinates (solid lines) and with numerical solutions of the code HYDRUS2D (dashed lines) for HTO, Γ^- and $^{22}\text{Na}^+$ as tracers. Also shown are the values for the temporal Cs^+ concentration in the borehole and two different HYDRUS2D calculations accounting either for linear or non-linear (Freundlich) tracer sorption on the Opalinus clay.

As a check, and to circumvent some of the numerical problems of HYDRUS2D, a code based on the numerical inversion of the Laplace transformed solution for the radial system was written and tested. Calculations for a linearised isotherm of caesium are similar to the measured data, but show, as expected, some systematic deviations.

After excavating the rock surrounding the borehole, data for the concentrations in the rock also became available. The agreement between measurements and calculations for HTO, I⁻ and ²²Na⁺ as tracers is generally very good, hence, corroborating our modelling assumptions.

Some scoping calculations for the next phase of the DI-A experiment, where strongly sorbing tracers such as Co or Eu shall be used, were performed. These calculations showed that the concentrations of the strongly sorbing tracers will drop relatively quickly in the borehole, and that the tracers will stay very close to the injection borehole. This will make a quantitative analysis very difficult, unless high resolution measurement techniques can be used. In addition, sorption onto the equipment will presumably be a major problem additionally complicating a careful analysis of the data.

3.1.4 Modelling the colloid and radionuclide retardation (CRR) experiment

The CRR experiment terminates in 2003 at the end of Grimsel Phase V. Our modelling work therefore concentrated on the analysis of the experimental breakthrough data. These fits were then compared with the former predictions and resulted in subsequent model refinements. It was shown that bentonite colloids can, at least potentially, affect the transport of some safety-relevant radionuclides.

The details of our modelling work and its results will be published in a PSI/Nagra technical report. A first draft is currently under external review; an extended summary of this report will be incorporated as part of the final modelling report of the CRR project. The results will also be published; a manuscript has already been submitted to *Journal of Contaminant Hydrology*.

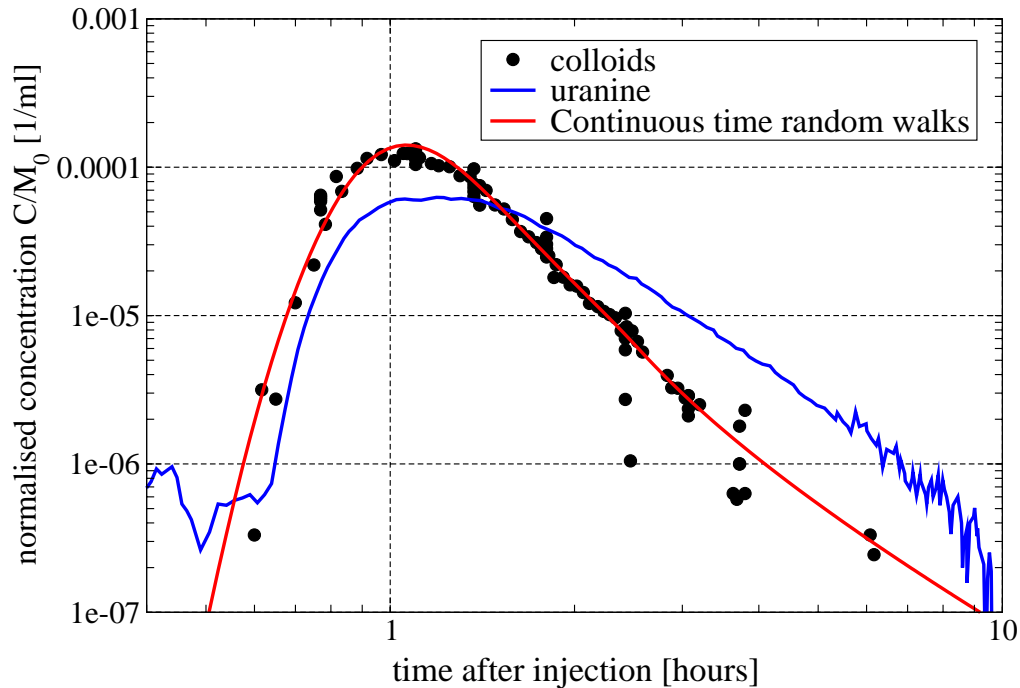


Fig. 3.4: The breakthrough data for uranine and bentonite colloids from run #6a of the CRR experiment and our best-fit of the bentonite colloid data applying the non-Fickian dispersion (continuous time random walk) model. As can be seen, colloid breakthrough is slightly earlier than that of dissolved uranine.

3.1.5 Obtaining realistic fracture geometries from observation on crystalline bore cores

The photographic data provided by the excavation project experiment (EP) at the Grimsel shear zone give us a possibility to study the geometry of a fracture network down to rather small scales. The spatial resolution that can be achieved is determined mainly by the spacing of the photographed surfaces. The available photographs from the EP yield a vertical resolution of roughly 3 cm.

Over a total length of over 3 m, the two overlapping cores with diameters of 30+ cm present a complex network of fractures with a wide range of characteristics and opening widths.

The process of determining the spatial distribution of the fractures is, however, hampered by several technical problems, particularly with missing geometric information. Therefore, the vertical positioning of each image within the cores, as well as the fitting together of the overlapping images, was strongly subjected to personal judgement.

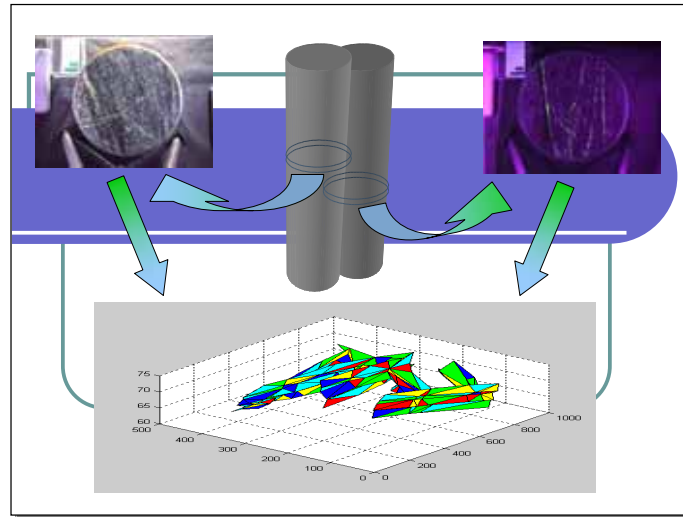


Fig. 3.5: Photographs of the slices from both sides of bore cores were provided in visible lighting (upper left corner) and ultra-violet (upper right corner). Such photographs were imported into “Matlab”, where the fractures were traced, connected and approximated by triangles. When compared to earlier modelling attempts, the combined set of triangles is a much more realistic representation of the real fracture network. Our future modelling will focus on the effect of small-scale structures on the macroscopic tracer and colloid transport.

The task of extracting the relevant circular portions of each image was performed semi-automatically with a “Matlab” script. Further scripts allow for the picking of multiple connected points along the length of each fracture visible in the images, thereby effectively linearising the shape of the fractures. These layers of intersection lines between fractures and slice surfaces are then connected to form 3D representations of the fracture planes in the actual rock cores. By building these polygons up from triangles, the need for triangulating the model fracture planes is mostly eliminated.

In the immediate future it is intended to use the 3D fracture system for flow and transport modelling. The more realistic fracture geometry should enable us to perform valuable comparisons between our simulation results and the breakthrough curves recorded from experiments carried out earlier. Special attention will be given to fracture junction geometries and matrix diffusion processes.

3.1.6 Work related to the Opalinus clay performance assessment

A series of geosphere calculations using FRAC3DVS for the safety assessment of the planned Swiss repository for high-level radioactive waste in the Opalinus clay formation was performed. These geosphere calculations were based on the final geosphere dataset and they confirmed the results of the calculations with the preliminary datasets. The calculations concentrated on the two safety-relevant cases:

- 1) consolidation driven flow due to glaciations and
- 2) the fluid flow driven by tunnel convergence.

Our results are part of a forthcoming document; a first draft of the PSI Report/Nagra Technical Report is currently being reviewed externally.

The draft of the report 'Projekt Opalinuston, Synthese der geowissenschaftlichen Untersuchungsergebnisse' went through a second, external review process. The classification and (documented) incorporation of the review comments took place during the second half of the year 2002; the report was finally printed at the end of 2002.

At the same time, the reference reports ('Untersuchungsberichte'), which were the basis for the above synthesis, had to be compiled and written.

3.1.7 Work performed in the frame of the EU-concerted action RETROCK

The overall objective of the project is to develop a common basis for incorporating geosphere retention phenomena in safety assessments with regard to deep geological repositories for radioactive waste. The main focus is to examine whether simplifications frequently adopted in safety assessments are based on sound conceptualisations and can be defended with more complex process models, experiments and other sources such as data from natural analogue studies. The project concentrates on saturated fractured hard rocks such as crystalline bedrock.

The focus of the second project year was on work package 2 (WP2) entitled "Examination of concepts". A first draft of a comprehensive report was produced by all the members describing the retention and transport processes as they are broadly understood currently. It also presents the principal methods for accounting for the retention processes and relevant geometrical aspects in research models and their simplified consideration in contemporary performance assessment models.

Our contribution to WP2 was a lengthy article concerning matrix diffusion; the in-depth examination of the current understanding and approaches of different sub-processes associated with matrix diffusion, such as channelling, anion exclusion or pore plugging

- reactive transport. Other important aspects such as the consequences of a possible limited extension of the porous rock accessible for matrix diffusion, or the question how to deal with possible time-dependencies in transport modelling, etc. were discussed in detail too.

3.1.8 Other (short term) activities

PhD research proposal, time-of-flight (TOF) neutron scattering

Together with Luc van Loon (PSI/LES) some preliminary TOF neutron scattering measurements on clay samples were performed at the SINQ at PSI. Based on the results of these experiments and with the additional support by F. Juranyi and S. Janssen (PSI/Laboratory for neutron scattering), L. Diamond from the Institute for Geological Sciences of the University of Bern and N. Skipper from the Department of Physics and Astronomy of the University College in London, in spring a research proposal for a PhD project entitled 'Structure and Dynamics of Confined Water in Compacted Clay Systems' was submitted to the PSI research commission. The PhD student, who will be registered at the University of Bern, will investigate the diffusion properties of clay samples with through-diffusion experiments on the macroscopic and with neutron scattering experiments on the microscopic scale. These results will be interpreted with suitable models and with regard to results of forthcoming molecular modelling studies.

Modelling flow and transport in heterogeneous porous media

A manuscript describing a method to derive the structure of a heterogeneous sand tank by image analysis was finalized and submitted to a journal. The structure detection described in this manuscript was the basis of extensive numerical simulations of flow and transport through the heterogeneous sand tank. The results of these simulations, which are compared with previously obtained experimental results, were described in details in a further submitted paper.

Fracture networks

Our work concentrates on the effect of local flow cells on the transport in fracture networks and the transfer of disc shaped fractures into a network of pipes. This work is done in close co-operation with colleagues from the University of Waterloo, Canada, and the Weizmann Institute, Israel.

Molecular modelling

Our activities in the area of molecular modelling started with the investigation of the software packages "Moldy" (Molecular Dynamics approach) and "Monte" (Monte

Carlo approach). In the near future it is planned to investigate the diffusion of various ions through bentonite with both tools.

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¹ Nagra, Hardstrasse 73, Wettingen, Switzerland.

² Rock Rock-Water Interaction (RWI), Institute of Geological Sciences, University of Bern, Baltzerstrasse 1, Bern, Switzerland.

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¹ Dipartimento di Ingegneria, Idraulica, Marittima e Geotecnica (IMAGE), University of Padova, Italy.

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¹ Enviro, Cerdanyola del Vallès, Spain.

² Japan Nuclear Cycle Development Institute (JNC), Japan.

³ Institute for Nuclear Waste Management (INE), Forschungszentrum Karlsruhe, Karlsruhe, Germany.

⁴ SAM Ltd, Edinburgh, Scotland, United Kingdom.

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¹ Institute Rock-Water Interaction (RWI), Institute of Geological Sciences, University of Bern, Baltzerstrasse 1, Bern, Switzerland.

² Ground-Water Geochemistry, 411 East Front Street, New Berne, North Carolina, USA.

³ Nagra, Hardstrasse 73, Wettingen, Switzerland.

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² Department of Nuclear Chemistry, Chalmers University of Technology, Göteborg, Sweden.

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⁵ Geotechnisches Institut, Gartenstrasse 13, Bern, Switzerland.

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³ CIEMAT, Madrid, Spain.

⁴ Paul Scherrer Institut, Villigen, Switzerland.

⁵ ENRESA, Madrid, Spain.

⁶ IRSN, Fontenay-aux-Roses, France

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4 CLAY SYSTEMS

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4.1 Introduction

The near- and far-field sorption data bases (SDBs) for the performance assessment (PA) of a high-level waste and spent fuel repository in an Opalinus Clay (OPA) host rock (Entsorgungsnachweis) have been published. In addition, a further report has been published on a comparative study between apparent diffusion coefficients (D_a) measured in compacted bentonite and those calculated on the basis of batch sorption measurements. These three reference reports are of key importance for the currently on-going international peer review (NEA) of the Safety Report (NAGRA, 2002).

Mechanistic sorption studies are continuing on montmorillonite and illite mainly within the current 5th EU framework projects. In the ACTAF project titration and Eu sorption data on illite have been modelled. Sorption studies of U(VI) on illite are on-going. In the FEBEX II project porewater chemistry modelling for compacted Febex bentonite has been completed. The sorption/modelling studies for Cs are finished whereas the Sr and U(VI) sorption studies on montmorillonite are continuing.

Within the 6th EU framework project LES is participating in NF-PRO in 2 subprojects, and is a member of the ACTINET network of excellence consortium. (Both of these programmes have been accepted.) In addition LES is actively participating in the preparation of FUNMIG for the second EU call expected in October 2003.

EXAFS measurements at the European Synchrotron Radiation Facility (ESRF) in Grenoble have been performed on Eu and Nd montmorillonite systems at the GILDA and DUBBLE beam lines, and U(VI)/illite at the ROBL beamline. First micro-XAS measurements of metal sorbed onto heterogeneous OPA clay samples took place at the Advanced Light Source (ALS) in Berkeley.

The Ni carbonate and oxalate complexation studies have been published.

4.2 Performance assessment

Three important PA related reference reports have been published so far in the first half of this year. SDBs on MX-80 bentonite (BRADBURY & BAEYENS, 2003a) and OPA (BRADBURY & BAEYENS, 2003b) for the PA of the near- and far-field respectively. A SDB for a disturbed/altered OPA for a long-lived intermediate-level waste repository is in preparation (BRADBURY & BAEYENS, 2003c). A third report concerns a study in which D_a values measured in compacted bentonite are compared with those calculated

from batch sorption measurements and the effective diffusion coefficient of tritiated water (BRADBURY & BAEYENS, 2003d). Good agreement between measured and calculated D_a values was obtained for the elements Cs(I), Ni(II), Sm(III), Am(III), Zr(IV) and Np(V). This is an important result supporting the use of sorption values measured in dispersed systems for calculating D_a values in compacted material.

Fig. 4.1 shows a pictorial representation of the selected R_d values together with their respective uncertainties for the MX-80 bentonite. The data in this plot are compared with the corresponding R_d values selected by STENHOUSE (1995) and used in the Kristallin-I PA (Nagra, 1994). The selected values in the current SDB are, in general, distinctly greater. In this SDB work a large number of “in house” measured data were available and the strategy in the selection procedure was to use the actual measured “in house” or literature sorption values, and not some arbitrarily reduced (conservative) values. In the current SDB the new Nagra/PSI thermodynamic data base (TDB) (HUMMEL et al., 2002) was used to calculate element speciation.

MX-80 BENTONITE SORPTION VALUES

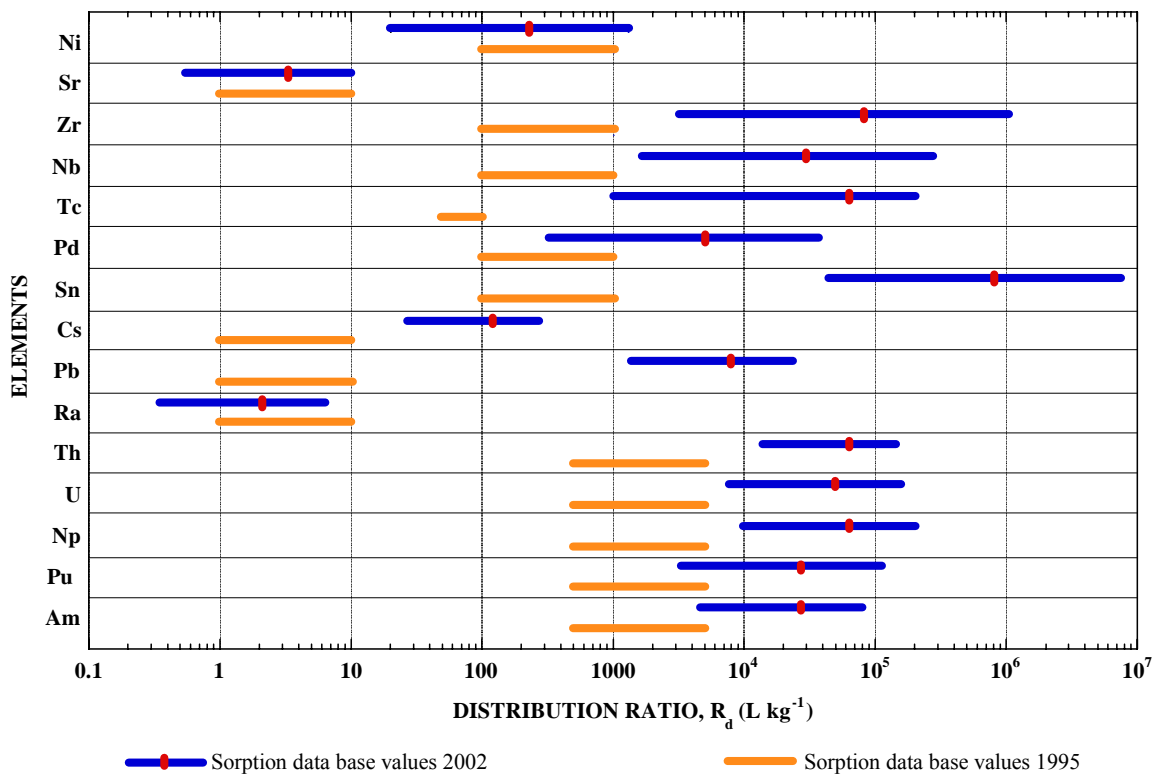


Fig. 4.1: A comparison of sorption data selected for MX-80 bentonite in the current PA (BRADBURY & BAEYENS, 2003a) and the PA of 1995 (STENHOUSE, 1995).

4.3 Mechanistic sorption studies

Argillaceous rocks are being viewed with continuing interest in many European waste management programmes as suitable host formations for the deep geological disposal of radioactive waste (Opalinus Clay, Switzerland; Boom and Ypresian Clay, Belgium; Spanish Reference Clay, Spain; Callovo-Oxfordian and Toarcian, France). Clay minerals such as illite, smectite, illite/smectite mixed layers and kaolinite are important components in such rock types and can often make up 50 wt. % or more of the total mass. One of the most important characteristics of many clay minerals, as far as repository PA studies are concerned, is their generally strong radionuclide retention properties. A knowledge of sorption processes and of the system parameters which influence them is becoming an increasingly essential requirement.

In a series of papers BRADBURY & BAEYENS (1997, 1999, 2002) developed and applied a relatively simple two site non electrostatic surface complexation model combined with cation exchange (2SPNE/CE model) to describe the uptake of Ni, Zn and Eu on Na- and Ca- montmorillonites. The aim was to extend these investigations to another important clay mineral system, illite. Because the unit cells of montmorillonite and illite are similar the initial expectation was that the 2SPNE/CE model with suitable parameter value changes, could also be used to model the titration behaviour and the radionuclide uptake on illite.

4.3.1 Illite

As part of the 5th EU framework programme, ACTAF, batch back titration measurements on Na-illite were performed in a NaClO₄ background electrolyte at three ionic strength, 0.01, 0.1 and 0.5 M. The modelling of these data is presented in following section.

Also as part of the ACTAF programme, sorption edges and isotherms for Eu and U(VI) were measured. In addition, similar measurements were also made for Ni and Sr. The experimental data for Eu, Ni and Sr have been successfully modelled in the pH range 4 to 11. As an example, the modelling results for the Eu sorption data are given in section 4.3.1.2. Two sorption edge and two isotherm data sets for U(VI) on Na-illite have almost been completed.

4.3.1.1 Modelling Na-illite titration data

The 2SPNE-model was used to describe the protonation and deprotonation of the amphoteric surface hydroxyl groups (sites) situated at clay platelet edges on illite. The

titration curves are modelled in terms of protonation ($\equiv\text{SOH} + \text{H}^+ \rightleftharpoons \equiv\text{SOH}_2^+$) and deprotonation ($\equiv\text{SOH} \rightleftharpoons \equiv\text{SO}^- + \text{H}^+$) reactions on the two types of weak sites, ($\equiv\text{S}^{\text{W}1}\text{OH}$ and $\equiv\text{S}^{\text{W}2}\text{OH}$) described in terms of intrinsic stability constants and mass action relationships without an electrostatic term.

The starting point for the modelling of the titration data in the illite system was the premise that a similar model and similar model parameters as used in the case of montmorillonite might also be appropriate to illite. The dotted curve in Fig. 4.2 was obtained by taking the site capacities and protolysis constants for montmorillonite (BRADBURY & BAEYENS, 1997) applying them directly to model the illite titration data. As can be seen the basic shape and form of the calculated curve approximates that of the measured one.

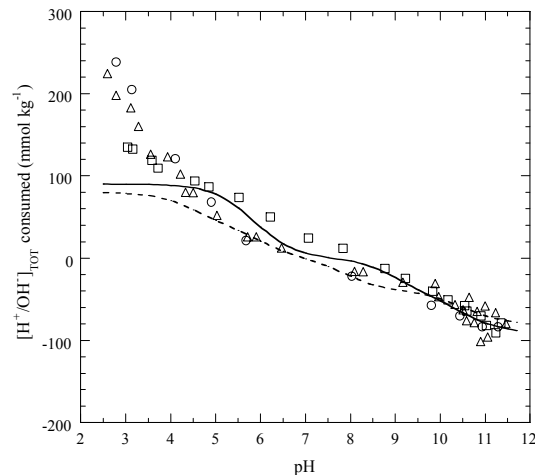


Fig. 4.2: Titration data on Na-illite at (O) 0.01 M; (Δ) 0.1 M and (\square) 0.5 M. The curves are model calculations. (See text for details).

A series of iterations then followed in which the first step was to find a “best set “ of parameter values for the $\equiv\text{S}^{\text{W}1}\text{OH}$ sites which fitted the acid region of the plot. This was followed by a similar procedure for the $\equiv\text{S}^{\text{W}2}\text{OH}$ sites and the alkaline region of the curve. These parameters were then preliminarily fixed for the modelling exercise for the sorption edges and isotherms. This, i.e. consideration of the titration and sorption results together, was an integral part of the iterative procedure for finally being able to fix weak site capacities and protolysis constants. The outcome is shown in Fig. 4.2 where the continuous line has been modelled using the site types, site capacities and protolysis constants determined for Na-illite given in Table 4.1. The measurements below pH 4 deviate from the curve. The processes occurring here are complex and driven by dissolution and exchange reactions. Although a relatively good system understanding has been achieved, especially with respect to the cation exchange processes, as

evidenced by the modelling of the Sr sorption data (not given here), nevertheless the very low pH data could not be quantitatively corrected.

Table 4.1: Summary of site types, site capacities and protolysis constants determined for Na-illite.

<u>Site types:</u>	<u>Site capacities:</u>
$\equiv\text{SOH}$	$2.0 \times 10^{-3} \text{ mol kg}^{-1}$
$\equiv\text{S}^{\text{W1}}\text{OH}$	$4.5 \times 10^{-2} \text{ mol kg}^{-1}$
$\equiv\text{S}^{\text{W2}}\text{OH}$	$4.5 \times 10^{-2} \text{ mol kg}^{-1}$
Surface complexation formation reactions	$\log K_{\text{int}}$
$\equiv\text{SOH} + \text{H}^+ \Leftrightarrow \equiv\text{SOH}_2^+$	5.5
$\equiv\text{SOH} \Leftrightarrow \equiv\text{SO}^- + \text{H}^+$	-6.2
$\equiv\text{S}^{\text{W1}}\text{OH} + \text{H}^+ \Leftrightarrow \equiv\text{S}^{\text{W1}}\text{H}_2^+$	5.5
$\equiv\text{S}^{\text{W1}}\text{OH} \Leftrightarrow \equiv\text{S}^{\text{W1}}\text{O}^- + \text{H}^+$	-6.2
$\equiv\text{S}^{\text{W2}}\text{OH} + \text{H}^+ \Leftrightarrow \equiv\text{S}^{\text{W2}}\text{H}_2^+$	9.0
$\equiv\text{S}^{\text{W2}}\text{OH} \Leftrightarrow \equiv\text{S}^{\text{W2}}\text{O}^- + \text{H}^+$	-10.5

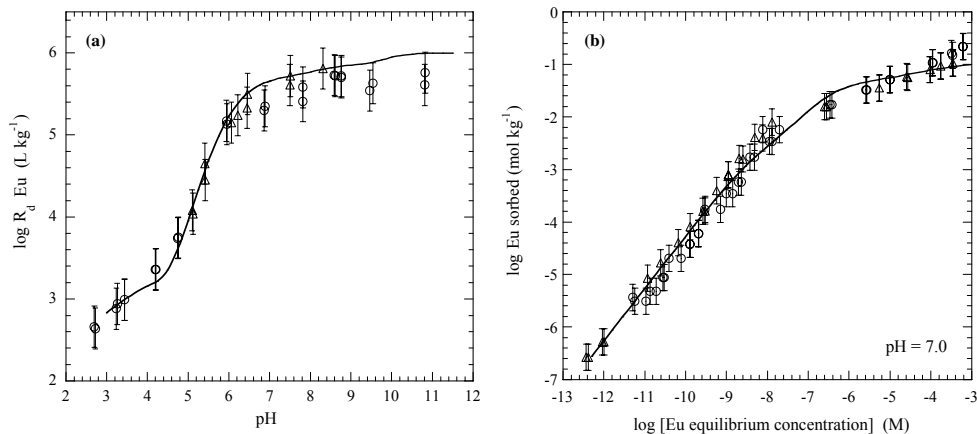
4.3.1.2 Modelling radionuclide sorption on Na-illite

The aim is to produce a (quasi) mechanistic sorption model describing metal ion uptake in the illite system. Sorption edge (sorption at trace concentration determined as a function of pH at a fixed ionic strength) and sorption isotherm measurements for a number of radionuclides (Sr, Ni, Eu, U(VI)) have been performed on Na-illite. A report with the experimental and modelling investigations is in a first draft form (BRADBURY & BAEYENS, 2003e). The results from the Eu study are presented below together with the modelling.

Sorption edges for Eu on Na-illite were determined at trace concentrations in 0.01, 0.1 and 0.5 M NaClO₄. Two isotherms in 0.1 M NaClO₄ were measured at pH 5.5 and 7. The Eu sorption data modelling was carried out with the site types, site capacities and protolysis constants for the amphoteric edge sites, Table 4.1, and the illite CEC of 225 meq kg⁻¹, determined in this study using a Cs isotope exchange method. The additional parameters required for the modelling of the three sorption edges and two isotherms are summarised in Table 4.3. An intensive iterative methodology was required to satisfactorily model all data sets. Surface complexation, cation exchange and competition from elements released through the interactions between the illite/background electrolyte system (particularly at low pH) were taken into account. Fig. 4.3 presents an example of a sorption edge and an isotherm together with the modelled curves.

Table 4.2: Mass action equations and associated constants used in the modelling of Eu uptake on Na-illite.

Cation exchange reaction	K_C
$3 \text{ Na-illite} + \text{Eu}^{3+} \leftrightarrow \text{Eu-illite} + 3 \text{ Na}^+$	76
Surface complexation formation reactions on strong sites	
$\log K_{\text{int}}$	
$\equiv\text{SOH} + \text{Eu}^{3+} \leftrightarrow \equiv\text{SOEu}^{2+} + \text{H}^+$	3.1
$\equiv\text{SOH} + \text{Eu}^{3+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{SOEuOH}^+ + 2 \text{ H}^+$	-5.0
$\equiv\text{SOH} + \text{Eu}^{3+} + 2 \text{ H}_2\text{O} \leftrightarrow \equiv\text{SOEu}(\text{OH})_2^0 + 3 \text{ H}^+$	-14.5
$\equiv\text{SOH} + \text{Eu}^{3+} + 3 \text{ H}_2\text{O} \leftrightarrow \equiv\text{SOEu}(\text{OH})_3^- + 4 \text{ H}^+$	-24.0
$\equiv\text{SOH} + \text{Eu}^{3+} + 4 \text{ H}_2\text{O} \leftrightarrow \equiv\text{SOEu}(\text{OH})_4^{2-} + 5 \text{ H}^+$	-34.5
Surface complexation formation reaction on weak sites	
$\log K_{\text{int}}$	
$\equiv\text{S}^{\text{W}}\text{OH} + \text{Eu}^{3+} \leftrightarrow \equiv\text{S}^{\text{W}}\text{OEu}^{2+} + \text{H}^+$	0.1
$\equiv\text{S}^{\text{W}}\text{OH} + \text{Eu}^{3+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{S}^{\text{W}}\text{OEuOH}^+ + 2 \text{ H}^+$	-5.7

**Fig. 4.3:** Eu sorption (a) edge and (b) isotherm on Na-illite at 0.1 M NaClO₄. The solid lines are calculated using the model parameters given in Tables 4.1 and 4.2.

4.3.1.3 Surface analysis

Four samples of Na-illite with U(VI) loadings between 750 and 1650 ppm were prepared at pH = 5 and pH = 6 in an 0.1 M NaClO₄ background electrolyte with reaction times of 7 days for EXAFS investigations at the Rossendorf beamline (ROBL), ESRF. The radial structure functions (RSFs, uncorrected for phase shift) of k^3 -weighted L_{III}-edge EXAFS spectra of uranyl treated illite are shown in Fig. 4.4. The figure shows that there are peaks at $R + \Delta R \sim 1.4 \text{ \AA}$ and $\sim 1.8 \text{ \AA}$ (peak A and B), $R + \Delta R \sim 2.5 \text{ \AA}$ (peak C), and at $R + \Delta R \sim 3.0 \text{ \AA}$ (peak D). The intensity and position of the peaks remain essentially unchanged by varying the pH and U(VI) loadings on the clay

indicating that the uptake mechanism under the chosen experimental conditions is not affected by these parameters.

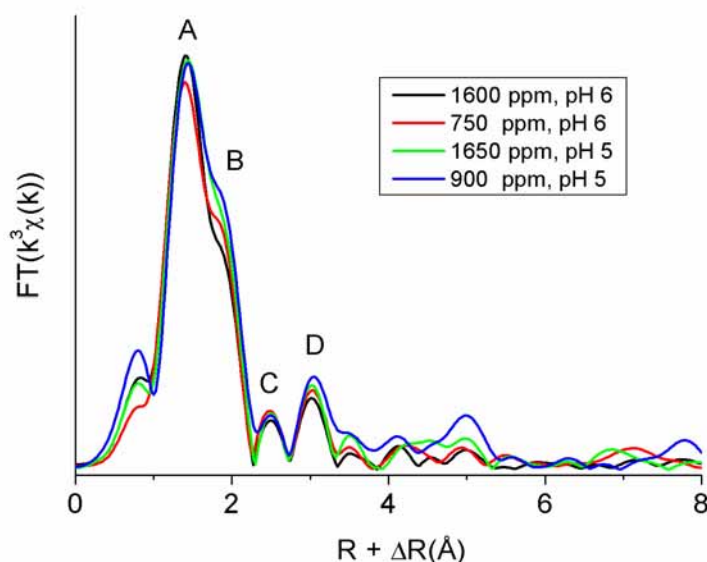


Fig. 4.4: RSFs of k^3 -weighted U L_{III} -edge EXAFS spectra for U sorbed onto illite at pH 5 and 6 and various U concentrations.

Data analysis reveals that the uranium atoms in all samples are coordinated by 2 axial oxygen atoms (O_{ax} , peak A) at a distance of ~ 1.78 Å. The multiple-scattering (MS) path of the uranyl moiety was linked during data analysis to the U- O_{ax} scattering parameters without introducing additional variable fit parameters (HUDSON et al., 1996). The distances between the uranium and the equatorial oxygen atoms (O_{eq} , peak B) vary slightly between 2.27 Å and 2.29 Å and the coordination numbers N (U- O_{eq}) are in the range of 4.9 to 5.7. These U- O_{eq} distances are far from values for mononuclear outer-sphere uranyl aquo-complexes with U- O_{eq} distances of 2.41 Å–2.43 Å obtained at lower pH values (see for example DENT et al., 1992).

The short U- O_{eq} distances indicate that an inner-sphere complexation process dominates the sorption under the used experimental conditions. This finding is supported by analyzing the structural origin of peak D. Data analysis indicates that peak D is caused by U-Al/Si backscattering pairs (1-2 U-Al/Si pairs at 3.35-3.38 Å). The origin of peak C is not yet completely resolved. It is possible to fit this peak with a Si atom at ~ 3.1 Å. Such short U-Si distances are common in U and Si bearing minerals like e.g. soddyite and coffinite. It should be noted that peak C could be fitted similar well with an oxygen shell (2.9 Å) or a carbon shell (2.9 Å). The uranium-carbon distance is typical for bidentate coordinated carbonate as in ternary uranium-(VI)-carbonato surface complexes (BARGAR et al., 2000), the experimental conditions, i.e., N_2 atmosphere,

pH = 5, and 0.1 M NaClO₄, make however the formation of uranium(VI)-carbonato surface species unlikely. It is foreseen in the upcoming ROBL beam time to verify this hypothesis by preparing samples under atmospheric conditions. It is unlikely that peak C is caused by a long oxygen shell (2.9 Å), since to the best of our knowledge such long O distances have never been observed in U(VI) sorption experiments. Typical long U-O distances observed in the literature normally vary from 2.45 to 2.49 Å (e.g. THOMPSON et al., 1997; BARGAR et al., 2000; SYLWESTER et al., 2000).

4.3.2 Montmorillonite

The majority of the work performed on montmorillonite was done within the 5th EU programme FEBEX II.

4.3.2.1 Porewater chemistry in compacted FEBEX bentonite

The porewater composition of compacted re-saturated Febex bentonite for the Spanish reference dry density of 1650 kg m⁻³ has been modelled. A key parameter in the geochemical modelling was a knowledge of the chloride accessible porosity which was obtained from Cl⁻ through diffusion experiments. The initial porewater after re-saturation under constant volume conditions was calculated to be a Na-Ca-Mg chloride type with a high ionic strength, 0.9 M and a pH of ~7.4. Porewater chemistries at other initial dry densities could readily be calculated if the corresponding Cl⁻ accessible porosity values are available. This work has been written up and the paper has been accepted for publication (FERNANDEZ et al., 2003).

4.3.2.2 Modelling radionuclide sorption on Na-montmorillonite

Cs sorption edges and isotherms were measured on purified and conditioned Na- and Ca-montmorillonites (SWy-1). The isotherms indicated a non-linear sorption behaviour. There is mineralogical evidence that the SWy-1 montmorillonite contains ~1 wt. % illite and the hypothesis was that this illite was the cause of the non-linear behaviour. At low Cs concentrations the uptake on illite is particularly effective due to the presence of high affinity sites, frayed edge sites (SAHWNEY, 1972). Such sites are not generally associated with montmorillonite. The Cs sorption isotherms on Na- and Ca-montmorillonites were calculated with the site capacity values and selectivity coefficients for montmorillonite, together with those for illite obtained in this study. The site capacity values for illite were scaled according to the 1 wt. % fraction of illite in the SWy-1 system. The predicted isotherms corresponded very well to those measured for the montmorillonites for both Na- and Ca-SWy-1. Fig. 4.5a shows the highly non-linear Cs sorption data obtained for Ca-montmorillonite together with the modelled curve.

The Cs sorption model was successfully applied to the Cs sorption isotherm measured on MX-80 bentonite in a complex porewater chemistry. For MX-80 bentonite a 1 wt.% illite content was assumed in the modelling. The result is shown in Fig. 4.5b. The difference between MX-80 and Ca-SWy-1 is that in the former case Na is the dominating cation, and, due to its high concentration, the non-linear behaviour is less pronounced.

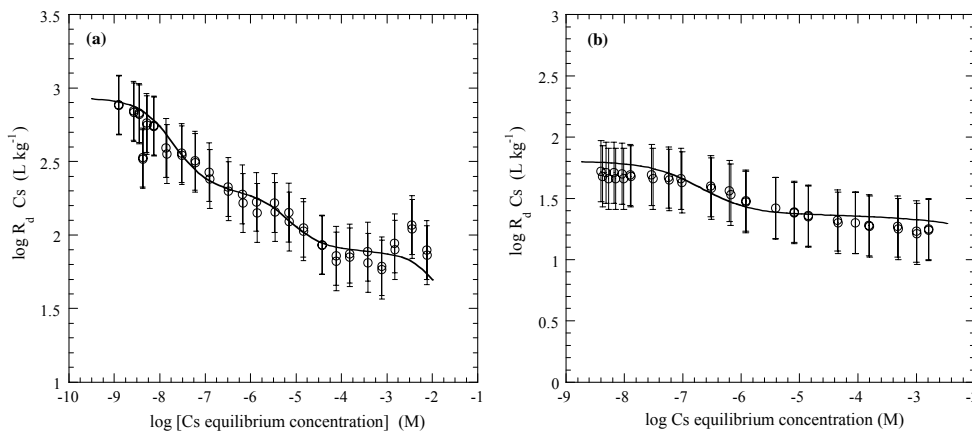


Fig. 4.5: Cs sorption on (a) conditioned Ca-montmorillonite (SWy-1) at 0.005 M $\text{Ca}(\text{NO}_3)_2$ and (b) on MX-80 montmorillonite in a high NaCl type porewater (I.S. = 0.7 M).

The Cs sorption model could not be applied to the Cs sorption data measured on Febex bentonite. The reason is that the mineralogical analysis of Febex bentonite indicated that no illite was present but instead ~ 15 wt.% illite/smectite mixed layers. The site capacities and selectivities for illite/smectite mixed layers are different from those of illite.

Sorption measurements of U(VI) were carried out on purified and conditioned Na-montmorillonite (SWy-1). Sorption edge measurements were carried out at 0.1 and 0.01 M NaClO_4 . The data indicated that there is a clear influence of pH which is indicative for a surface complexation mechanism. An effect of the Na background electrolyte concentration was observed at $\text{pH} < 5$. This uptake behaviour is characteristic of cation exchange. For the sorption isotherm determination, a series of $\text{UO}_2(\text{NO}_3)_2$ solutions covering a large concentration range was made up at $\text{pH} = 5$ in a buffered 0.1 M NaClO_4 background electrolyte and labelled with ^{233}U . The sorption isotherm was linear in the U(VI) equilibrium concentration range between 10^{-5} and 10^{-8} M. At higher equilibrium concentrations the U(VI) sorption became non-linear. The data have not yet been analysed but as before the aim is to develop a sorption model for the uptake of uranyl on Na-montmorillonite.

4.4 Determination of aqueous Ni-carbonate and Ni-oxalate complexation constants

An ion exchange method was used to determine complexation constants for the Ni-oxalate and Ni-carbonate systems in a NaClO₄ background electrolyte. The Ni-oxalate data were interpreted in terms of a single NiOx(aq) complex having log K_1 values for Ni²⁺ + ox²⁻ ⇌ NiOx(aq) of 3.9 ± 0.1 (I.S. = 0.5 M, p[H] = 8.6) and 4.4 ± 0.1 (I.S. = 0.1 M, p[H] = 7.1) at 22 ± 1°C. Specific ion interaction theory (SIT) was used to obtain log K_1° = 5.17 ± 0.05 (95% confidence level and Δε = -0.23 ± 0.15) at I.S. = 0. The Ni-carbonate studies were carried out at p[H] values of 7.5, 8.5 and 9.6 in 0.5 M NaClO₄/NaHCO₃ solutions. The NiCO₃(aq) species was the dominant complex in the [CO₃²⁻] concentration ranges studied at all three p[H] values. A log K_1 value for Ni²⁺ + CO₃²⁻ ⇌ NiCO₃(aq) of 2.9 ± 0.3 was deduced at I.S. = 0.5 M. Extrapolating this value to zero ionic strength using the SIT approach yielded log K_1° = 4.2 ± 0.3 (95% confidence level and Δε = -0.26 ± 0.04). The data allowed upper bound values for the complexation constants for NiHCO₃⁺ and Ni(CO₃)₂²⁻ to be estimated, i.e. log K° < 1.4 for Ni²⁺ + HCO₃⁻ ⇌ NiHCO₃⁺, and log K_2° < 2 for NiCO₃(aq) + CO₃²⁻ ⇌ Ni(CO₃)₂²⁻, respectively. This study has been recently published (BAEYENS et al., 2003).

4.5 Highlights, lowlights and future activities

Sorption data base reports for OPA and MX-80 have been published (BRADBURY & BAEYENS, 2003a,b). A SDB for a disturbed/altered OPA is in preparation (BRADBURY & BAEYENS, 2003c). Further, a study has been published comparing sorption values obtained from batch type measurements and “in diffusion” data revealed that to a first approximation they do not differ significantly from one another (BRADBURY & BAEYENS, 2003d).

MX-80 porewater chemistry modelling presented at the Migration 2001 conference has been published (BRADBURY & BAEYENS, 2003f).

The Ni-carbonate and Ni-oxalate complexation studies (BAEYENS et al., 2003) have been published. The results will be included in the NEA TDB (GAMSJÄGER, pers. comm.).

The activities within the two 5th EU framework projects, ACTAF and FEBEX II, are coming to a conclusion. The major experimental and modelling tasks have been successfully completed and much of the work has been written up and is either accepted for publication (FERNANDEZ et al., 2003) or is in a draft form (BRADBURY & BAEYENS,

2003e) Mechanistic sorption studies on clay minerals will be continued within the 6th EU framework projects NF-PRO (bentonite), and FUNMIG (illite).

The U(VI)/illite measurement campaign at ROBL was very successful and good data were collected in the framework of the ACTAF project.

First micro-XAS experiments on the metal uptake onto heterogeneous OPA clay samples took place at the beamline 10.3.2 of the Advanced Light Source (ALS) in Berkeley. These kick-off experiments showed the unique potential of this new technique for the investigation of uptake processes on the micro-scale.

Future experimental work will focus on sorption experiments where other competitive metals are present. This is not only important for the validation of the existing mechanistic sorption models but can also have an important impact on PA.

The influence of the inorganic carbonate on the sorption of important radionuclides is a new topic which is proposed within the NF-PRO project.

Another future new activity is sorption studies on clay systems using redox sensitive elements.

A new proposal for U(VI) uptake onto clay minerals for ROBL was submitted and accepted by the ESRF review panel. The measurement campaign is scheduled in 2003.

Because of difficulties experienced at the GILDA beamline (ESRF) with the Eu/montmorillonite EXAFS measurements, a proposal to apply for beamtime at the Hamburger Synchrotron Strahlungslabor (HASYLAB) is foreseen. HASYLAB has developed an energy dispersive detector which allows measurements at the Eu L_{III}-edge on Fe containing samples such as montmorillonite.

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5 CEMENT SYSTEMS

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5.1 Overview

In Switzerland cement is used to solidify and surround low- and intermediate-level (L/ILW, or SMA in Swiss terminology) and long-lived intermediate level (ILW, or LMA in Swiss terminology) radioactive waste. Furthermore, cement is an important component of the engineered barrier system (lining and backfill materials). The immobilisation of safety-relevant radionuclides by hardened cement paste (HCP) is taken into account in performance assessment (PA) studies where solubility and the interaction of radionuclides with the cement matrix determine the source term for radionuclide migration from the cementitious near field into the host rock. The long-term aims of the sub-programme *Cement Systems* are i) to deduce well established sorption data to be used in sorption databases required in PA studies for nuclear waste repositories, and ii) to gain a mechanistic understanding of the interaction of safety-relevant radionuclides with HCP, cement minerals and cementitious backfill materials under conditions prevailing in the near field and the disturbed far field (pH plume) of a repository for radioactive waste.

In the time period between September 2002 and September 2003 wet chemistry studies were carried out for safety-relevant radioelements or their appropriate analogues, i.e., Na(I), Sr(II), Ni(II), Eu(III), Th(IV), Sn(IV) and U(VI). Complementary time-resolved laser fluorescence spectroscopy (TRLFS) studies using Cm(III) as chemical analogue for Eu(III) and X-ray absorption fine structure (XAFS) measurements on U(VI) enabled us to gain molecular-scale information on uptake processes. Macroscopic and spectroscopic studies were conducted on a sulphate-resisting Portland cement (Haute Teneur en Silice (HTS) cement) and calcium silicate hydrates (CSH phases). CSH phases are the most important constituents in both “freshly” hydrated and degraded HCP and are important secondary alteration products in the disturbed far-field resulting from the interaction of highly alkaline fluids (pH plume) with argillaceous host rocks. Due to their long-term stability in an evolving near-field environment, which is caused by the interaction of cementitious materials with infiltrating groundwater, CSH phases may control the release of several radionuclides from the near field into the far field.

TRLFS and XAFS studies on cement systems are carried out complementary to wet chemistry studies with a view to gain a sufficiently complete understanding of the

chemical processes on a molecular scale. The results from spectroscopic studies provide structural information on uptake mechanisms and enable us to identify the uptake-controlling cement phase. Clearly, a mechanistic understanding of uptake processes will strengthen the credibility of the sorption values recommended for use in PA studies and provide essential information required for the development of thermodynamic models.

The investigations carried out in the last year and the results from these activities can be summarised as follows:

The cement sorption database for performance assessment of an ILW repository in Opalinus clay has been published (WIELAND & VAN LOON 2002).

The importance of isotopic exchange as retention process in HCP has been confirmed for Na(I), Sr(II) and Ni(II).

Uptake studies of Eu(III), Sn(IV) and U(VI) on HCP have been conducted to critically assess the high sorption values determined in earlier studies.

A new series of sorption and co-precipitation studies on CSH phases using Sr(II), Eu(III), Th(IV) and U(VI) as tracers have been conducted within the frameworks of the ECOCLAY II project (5th EU framework programme) and a joint research project with CRIEPI.

TRLFS studies on Cm(III) uptake by CSH phases and HCP have been brought to a close. The Cm/CSH study has been published (TITS et al. 2003a). These studies were performed in collaboration with Dr. T. Stumpf of the Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, Germany.

The XAFS investigations on Sn(IV) uptake by HCP and CSH phases have been published (BONHOURE et al. 2003a), and a paper on the immobilisation of Se(IV/VI) in cementitious systems studied by XAFS has been submitted (BONHOURE et al. 2003b). A new series of XAFS measurements have been carried out on U(VI) loaded CSH phases at the European Synchrotron Radiation Facility (ESRF) in Grenoble.

A series of colloid concentration measurements have been performed on samples collected from the hyper-alkaline plume in fractured rocks (HPF experiment at the Grimsel Test Site).

5.2 Sorption database

The cement sorption database for performance assessment of an ILW repository in Opalinus clay has been published and issued simultaneously as a PSI Bericht and a Nagra Technical Report (WIELAND & VAN LOON 2002). In the compilation of the ILW

cement SDB the basic principles outlined and recommended in previous SDBs were applied to ensure continuity in the methodology and transparency concerning the selection of the sorption values (BRADBURY & SAROTT 1995; BRADBURY & VAN LOON 1998). Sorption values were revised if new information and/or data were available which allowed changes to, or re-appraisals of, the data to be made. The sorption values recommended in this report were either selected on the basis of data from in-house experimental studies or from literature data. For some key radioelements, i.e., Cs(I), Sr(II), Ni(II), Eu(III), Th(IV) and Sn(IV), new data were available from in-house measurements. Additional aspects including assessment of the uptake processes, error estimates for the recommended sorption values and the potential effects of degradation products of bitumen and cellulose, concrete admixtures and cement-derived near-field colloids on sorption processes were taken into account. A summary of the SDB was published in the open literature (WIELAND et al. 2003a).

5.3 Cement studies

In this project it is intended to elucidate the role of isotopic exchange as a retention process in HCP for the weakly and moderately sorbing radionuclides which have high inventories of stable isotopes in the cement matrix, and to investigate the uptake of strongly sorbing metal cations such as actinides and lanthanides (or appropriate chemical analogues).

5.3.1 Isotopic exchange in HCP

Isotopic exchange, i.e., the replacement of stable isotopes in the HCP by radioisotopes released from the waste matrix, is considered to be a potentially important immobilisation process of radionuclides in cementitious materials. The inventories of stable isotopes arise from impurities associated with the cement matrix (intrinsic impurities).

The uptake of ^{85}Sr by HCP can be described in terms of isotopic exchange (WIELAND & VAN LOON 2002). In the last year sorption/desorption experiments were carried out to test the reversibility of ^{85}Sr uptake by HCP and the immobilisation of stable Sr in HCP. For this, ^{85}Sr uptake experiments were carried out on HCP (particle size $\leq 70 \mu\text{m}$) in contact with artificial cement pore water (ACW). ACW is a (Na,K)OH solution (pH = 13.3) saturated with respect to portlandite and calcite. The ^{85}Sr concentration added in the tracer experiments was $1.15 \cdot 10^{-8}$ M. Note that the concentration of stable Sr is about 1290 ppm in HCP and about 10^{-4} M in ACW. Desorption of ^{85}Sr and stable Sr was studied by sequential replacement of ACW, i.e. is centrifugation of the suspensions and

replacement of the supernatant by fresh ACW. Stable Sr (intrinsic impurity) as well as ^{85}Sr was found to be reversibly bound in HCP as indicated by the good agreement of predicted and measured Sr concentrations in solution (Fig. 5.1). Predictions were made assuming the R_d values as determined in the batch-type sorption experiments using the ^{85}Sr tracer ($R_d = 0.08 - 0.1 \text{ m}^3 \text{ kg}^{-1}$). The results indicate that the total inventory of stable Sr is accessible to exchange, and further, Sr is reversibly bound in the cement matrix.

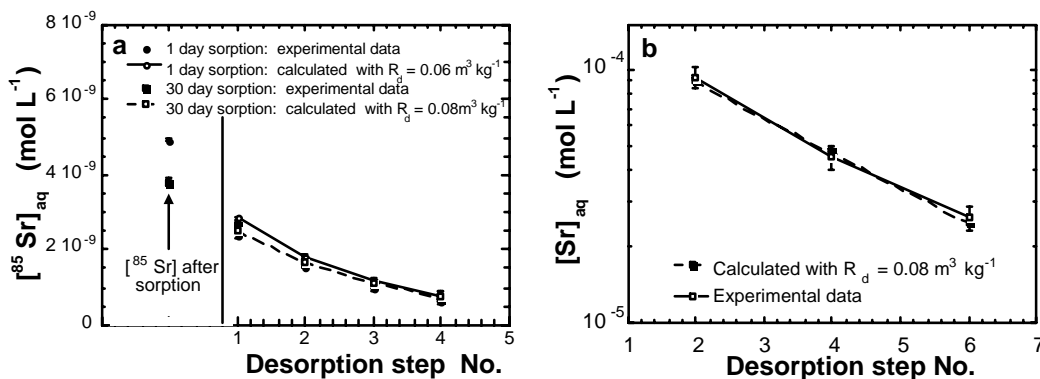


Fig. 5.1: Desorption of a) ^{85}Sr and b) stable Sr from HCP.

Recently, TITS et al. (2003b) suggested that ^{22}Na immobilisation in HCP can be explained in terms of isotopic exchange. Based on this assumption the authors estimated the R_d value for ^{22}Na uptake using the initial inventories of stable Na in the HCP and ACW for the calculation ($R_d = 2 \cdot 10^{-4} \text{ m}^3 \text{ kg}^{-1}$). However, this value was found to be a factor of about 2 to 3 less than the value obtained from batch sorption studies using ^{22}Na ($R_d = (5 \pm 1) \cdot 10^{-4} \text{ m}^3 \text{ kg}^{-1}$). A possible explanation for this discrepancy can be given by taking into account that, in the above approach, TITS et al. (2003b) assumed that the initial Na concentrations in HCP and ACW also correspond to the respective concentrations in HCP and ACW after equilibration.

This assumption had to be tested and, for this, batch-type studies were performed to determine the equilibrium concentrations of stable Na. HCP suspensions were prepared according to the conditions used in the study of TITS et al. (2003b) and equilibrated for 7 days maximum. Supernatant solutions were analysed for Na using inductively coupled plasma-optical emission spectrometry (ICP-OES), whereas the stable Na concentration in HCP was determined after total dissolution of the solid material in HF and analysing the solution by means of ICP-OES. The R_d value was then calculated based on the measured equilibrium concentrations of stable Na in HCP and ACW. The value was

determined to be $(5.5 \pm 2.0) \cdot 10^{-4} \text{ m}^3 \text{ kg}^{-1}$. Thus, excellent agreement was found between the batch R_d from tracer experiments with ^{22}Na and the value deduced from the mass balance of stable Na. This finding shows that R_d values have to be based on equilibrium concentrations rather than initial concentrations. The study further shows that, in the case of Na, isotopic exchange is indeed an important process of radionuclide immobilisation in cementitious systems.

Isotopic exchange is also considered to be a possible uptake process for ^{63}Ni . Investigations of stable Ni concentrations in cement systems showed that the Ni concentration in ACW appears to be controlled by a solubility-limiting process (WIELAND & VAN LOON 2002). Further, the partitioning of ^{63}Ni was modelled assuming isotopic exchange with stable Ni of HCP (WIELAND & VAN LOON 2002). At the present time, however, the fraction of the stable Ni inventory accessible to isotopic exchange is unknown. Thus, more detailed information on the processes affecting the partitioning of stable Ni and ^{63}Ni between HCP and ACW is required to assess whether or not isotopic exchange may be a relevant process and to develop a mechanistic model of ^{63}Ni uptake by HCP.

In the last year the R_d values of ^{63}Ni partitioning were determined at different inventories of stable Ni added to the HCP system. Note that the initial Ni concentration is 19.9 ppm in HCP and about $5 \cdot 10^{-8} \text{ M}$ in ACW. The results show that the aqueous concentration of stable Ni is constant within experimental uncertainties if the Ni inventory added to the cement system is low (added $[\text{Ni}] < 10^{-4} \text{ M}$). However, the aqueous Ni concentration was found to increase with increasing Ni inventory added to the cement system above 10^{-4} M . This finding suggests that the aqueous Ni concentration in ACW depends on the added Ni inventory. ^{63}Ni tracer experiments carried out in these systems further reveal that the total inventory of stable Ni is only accessible for isotopic exchange at low Ni inventories. The above findings are based on a first series of experiments, and further research is required to confirm the results.

5.3.2 Uptake of strongly sorbing radionuclides by HCP

During the last year, uptake studies of strongly sorbing radioelements, i.e. Eu(III), Sn(IV) and U(VI), have been conducted to complete data sets obtained from a series of preliminary sorption studies which were carried out before the refurbishment of the Hot Lab.

A large body of experimental data on Eu(III) uptake by HCP is available and has already been published (WIELAND et al. 1998; WIELAND & VAN LOON 2002). In all of

these experiments (with the exception of those carried out at high isosaccharinic (ISA) concentrations) strong uptake of Eu by HCP was observed. Furthermore, the formation of ternary Eu-ISA surface complexes is indicated from the wet chemistry data. However, a conclusive data interpretation requires precise measurements of the R_d values at very low cement to pore water (S/L) ratios (WIELAND et al. 2002). Recent sorption kinetics and sorption isotherm measurements corroborate the strong uptake of Eu by HCP reported in previous studies. Investigations on the effects of ISA and the S/L ratio of the suspensions on uptake processes are ongoing.

Kinetic studies of Sn(IV) uptake by HCP have been conducted to critically assess the results from a first series of measurements. These studies were carried out using initial Sn concentrations of $9.4 \cdot 10^{-8}$ M (Progress report 1999/2000). XAFS studies have shown that Ca-stannate is formed in cement systems at high initial Sn concentrations (BONHORE et al. 2003a), and hence the possibility of precipitation at high Sn inventories cannot be excluded. Therefore, a new series of sorption experiments was performed using trace concentrations of Sn ($[Sn] = 1.7 - 2.6 \cdot 10^{-9}$ M). The results from both experimental series were found to be consistent.

In the case of U(VI), sorption kinetics on HCP and a sorption isotherm were determined. The kinetic data agree with results from earlier measurements (Progress report 2000/2001). U sorption was found to be linear in the concentration range $[U]_{aq} < 6 \cdot 10^{-6}$ M. Above this concentration, however, the formation of a precipitate is indicated from the wet chemistry data. XAFS investigations suggest the formation of a Ca-uranate compound.

5.3.3 TRLFS investigations

In the last year TRLFS investigations on the Cm(III)/HCP system have been conducted. The results reveal the existence of three sorbed Cm species on HCP. Detailed spectroscopic investigations finally showed that one species corresponds to Cm sorbed on the portlandite fraction of HCP. The two other species have structural properties that are similar to those previously found on CSH. The first species has one water molecule left in the first coordination sphere, which is interpreted as Cm being sorbed as polynuclear species on the surface of the bulk material. The second species has no water molecules left in the first coordination sphere and is consistent with Cm being incorporated into the CSH structure. To the best of our knowledge, this is the first direct evidence that CSH are the uptake-controlling cement phases in HCP for Cm and presumably other trivalent lanthanides. A paper on this topic is in preparation (STUMPF et al. 2003).

5.4 Calcium silicate hydrate (CSH) studies

This project aims at determining adsorption onto and co-precipitation processes with CSH phases as possible immobilisation mechanisms for radionuclides in the near field and in the alkaline disturbed zone (pH plume). The studies are performed in a pH range between 11.5 and 13.3, simulating the chemical conditions prevailing during the first and second stage of the cement degradation.

The project is carried out within the framework of a co-operation with and partially funded by CRIEPI and contributes to the ECOCLAY II project, partially funded through the 5th EU framework programme. The project comprises experimental studies with Sr(II) and Eu(III) for the ECOCLAY II project, as well as investigations with Th(IV) and U(VI) for the joint CRIEPI-PSI project.

5.4.1 CSH synthesis and characterisation

In the last year CSH phases (C:S mol ratios of 1.07, 1.29, 1.5 and 1.82) synthesized in MilliQ water were characterised by chemical analysis of the bulk composition and the equilibrium solutions as well as by quantitative XRD. The XRD measurements were carried out in collaboration with the Laboratory of Environmental Geotechnics and Clay Mineralogy (Swiss Federal Institute of Technology, Zürich). The well-characterized materials were then used in the sorption and co-precipitation studies.

The synthesis of CSH phases was conducted in water because it was demonstrated that, under ACW conditions, CSH phases with target C:S mol ratios above 1.29 cannot be prepared in a pure form. The CSH phases are always contaminated with Ca(OH)_2 , and thus, have effective C:S ratios significantly below the target C:S ratios. The results from the characterisation studies show that the Ca solubility of the CSH phases synthesized in MilliQ water is a factor of 10 higher than the Ca solubility of the same phases synthesized in ACW. By contrast, the Si solubility is a factor of 5 to 10 lower. The XRD measurements confirm that in all cases a CSH phase is formed. Furthermore, all samples are free of Ca(OH)_2 except the sample with the highest C:S ratio, which contains 7.7 wt% of Ca(OH)_2 . Based on this finding, the corresponding effective C:S mol ratio of this CSH phase was estimated to be 1.6.

Table 5.1: Characterisation of CSH phases synthesized in MilliQ water (pH = 12-12.5).

Target C:S [mol/mol]	Bulk C:S [mol/mol]	Portlandite (XRD) [%]	Effective C:S calculated [mol/mol]	Ca conc in the eq. sol. [M]	Si conc. in the eq. sol. [M]
1.07	1.02±0.1	-	1.07	5.9·10 ⁻³	4.4·10 ⁻⁵
1.29	1.29±0.1	-	1.29	1.0·10 ⁻²	9.9·10 ⁻⁶
1.5	1.44±0.1	-	1.5	1.8·10 ⁻²	5.6·10 ⁻⁶
1.82	1.67±0.1	7.7	1.6	2.0·10 ⁻²	4.3·10 ⁻⁶

5.4.2 Studies of the sorption and co-precipitation of Sr(II) and Eu(III)

Investigations on the Sr(II) sorption kinetics and measurements of the sorption isotherms as well as desorption tests have been brought to a close. These experiments were conducted on CSH phases with different C:S ratios under ACW conditions. In addition, a series of sorption and co-precipitation experiments were performed using CSH phases synthesized in MilliQ water (pH = 12 - 12.5).

The results corroborated previous findings that, under ACW conditions, the sorption and co-precipitation processes are fast, and give rise to constant R_d values after equilibration for approximately three days. Sorption and co-precipitation isotherms are linear over the entire concentration range, and the R_d values deduced are similar. Slightly increasing R_d values with increasing number of ACW replacements were obtained from sequential desorption tests. Nevertheless, uncertainty on the data also increases with decreasing Sr inventories in these systems, and thus, the significance of the increase in the R_d value might be in question. In the case of the sorption and co-precipitation experiments at lower pH value, the isotherms are also linear, and the R_d values obtained are similar. In this case, however, sequential desorption tests result in R_d values similar in value to those determined from the sorption or co-precipitation experiments, indicating reversibility of the uptake process.

Furthermore, it was observed that the R_d values of Sr decrease with increasing C:S ratio in both sorption and co-precipitation experiments (Figure 5.2a). This decrease in the R_d value further coincides with an increase in the Ca concentration in the equilibrium solution (Figure 5.2b). This finding implies a competition between Ca and Sr for

sorption sites on the CSH phases. An attempt will be made to further assess the effect of the Ca concentration in connection with the high Na and K concentrations under ACW conditions on Sr uptake by modelling the data with the GEMS code.

Part of the above work was presented at the MRS meeting in Kalmar, Sweden, and will be published in the MRS proceedings (TITS et al. 2003b).

Sorption studies of Eu indicate strong uptake by CSH phases ($R_d = 5 \cdot 10^5 \text{ L kg}^{-1}$ to $5 \cdot 10^6 \text{ L kg}^{-1}$). In the last year the sorption studies were complemented by some desorption tests. The R_d values obtained from these tests were found to be similar in value to those determined in the sorption experiments. Nevertheless, any detailed interpretation is limited since the measured activities are extremely low after desorption.

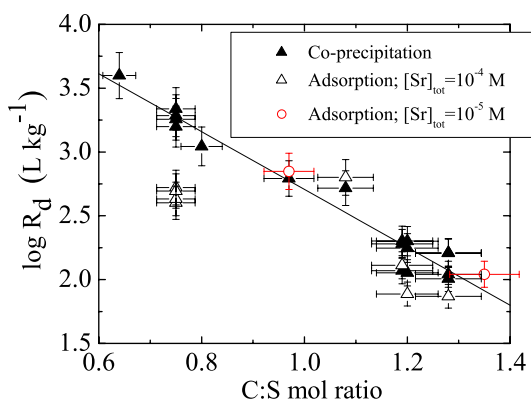


Fig. 5.2a: Dependence of the R_d values of Sr on the C:S ratio of CSH phases from sorption and co-precipitation experiments in ACW. The solid line is added to guide the eye.

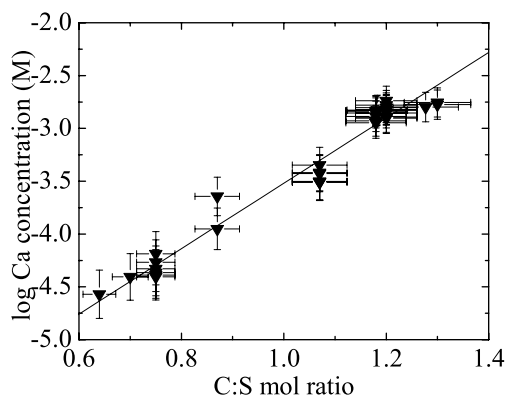


Fig. 5.2b: Dependence of the aqueous Ca equilibrium concentration on the C:S ratio of CSH phases. The solid line is added to guide the eye.

5.4.3 Studies of the sorption and co-precipitation of Th(IV) and U(VI)

Sorption and co-precipitation studies of Th(IV) and U(VI) on CSH phases prepared using the CRIEPI method for CSH synthesis have been conducted. Synthesis of the CSH phases is described in FUJITA et al. (2003). The CSH phases were prepared and the experiments started during a stay of T. Fujita at PSI in July and August 2002. PSI staff carried out the follow-up of the experiments (sampling, activity measurements, data compilation) and finished the experimental work.

The experimental studies consisted of a series of sorption kinetic tests and co-precipitation tests of Th and U on CSH phases having different C:S ratios. The CSH phases were synthesized in ACW and in water. Fig. 5.3 shows selected results from U uptake studies carried out at pH ~12 (CSH phases synthesized in water).

Fast kinetics was observed for both processes, i.e., co-precipitation and adsorption, and equilibrium conditions were established within a few days. It is worth mentioning that both processes lead to similar R_d values, indicating that the same process controls U immobilisation. It is to be noted that these conclusions also hold for the Th/CSH system. The same type of experiment is currently being performed on CSH phases which were prepared using the PSI method for CSH synthesis. A direct comparison of the two data sets will enable us to assess the influence of CSH preparation and differences in the C:S ratios of CSH phases on sorption and co-precipitation processes. Furthermore, XAFS measurements on the U/CSH systems have been carried out at the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, complementing the above wet chemistry studies. The CSH phases were prepared using the CRIEPI method for CSH synthesis and loaded with U. Data analysis is ongoing.

5.5 Colloid studies

A paper on the impact of near-field colloids on radionuclide mobilisation has been submitted to Applied Geochemistry (WIELAND et al. 2003b). As it was decided to reduce the work on near-field colloids, no major project has been started during the last year.

A minor activity concerned colloid analysis on samples collected from the hyper-alkaline plume experiments in fractured rocks (HPF experiment at the Grimsel Test Site). The HPF plume provides a unique opportunity to determine colloid concentrations in high pH water which is in contact with fractured rock. These data can then be compared with colloid concentration measurements previously performed in cementitious systems (WIELAND & SPIELER 2001). Preliminary data analysis shows that the colloid concentrations are similar in value to those previously found in cement pore waters, but slightly lower than the concentrations in the Grimsel groundwater.

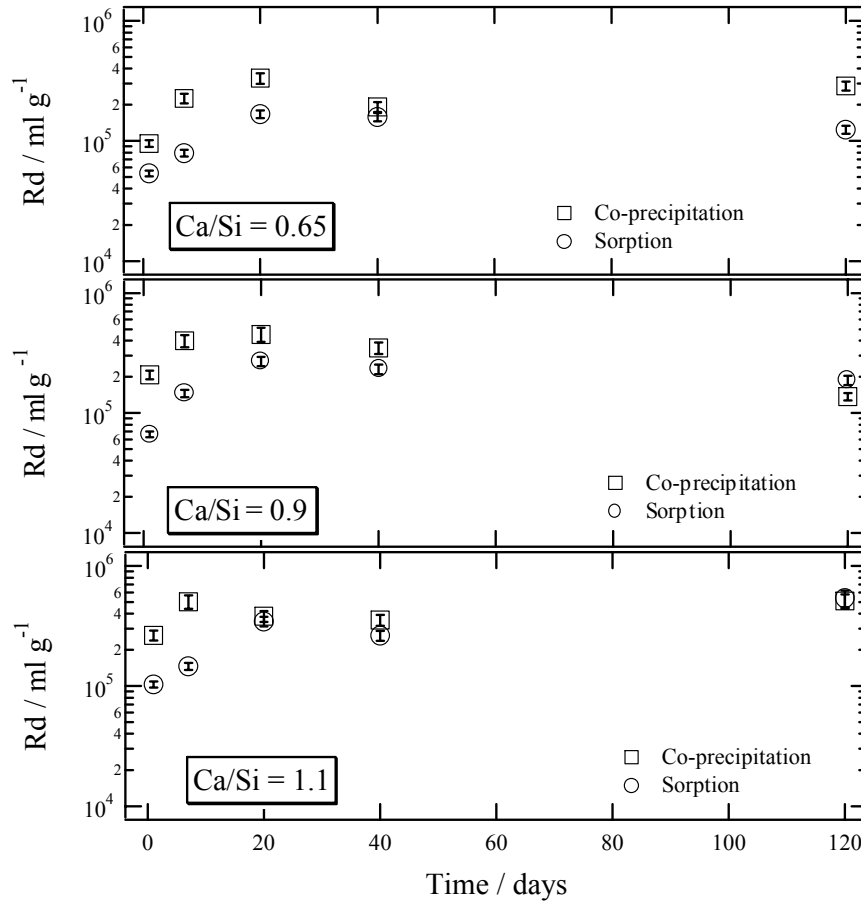


Fig. 5.3: U(VI) sorption and co-precipitation kinetics on CSH phases synthesized by precipitation from a mixture of calcium hydroxide solution and sodium metasilicate solution ($\text{pH} = 11.8 - 12.2$). Target C:S mol ratios were 0.65, 0.9 and 1.1 (FUJITA, personal communication).

5.6 EU framework programme and joint project

The sorption and co-precipitation studies of Sr and Eu on CSH phases are included in, and partially financed by, the 5th EU framework project ECOCLAY II. The investigations carried out within the framework of ECOCLAY II are summarized in Section 5.4. This project will end in September 2003.

The contract with CRIEPI concerning the joint research project on “Radionuclide uptake by calcium silicate hydrates” ended in March 2003. The investigations carried out within the framework of the joint project are summarized in Section 5.4. Nevertheless, as the time schedule of the project was influenced by the refurbishment of the Hot Lab it was agreed between CRIEPI and PSI that some remaining tasks were still

to be addressed. The remaining tasks and preparation of the final report are to be finished by the end of 2003.

5.7 Personnel

At the beginning of June 2003 M. Vespa joined LES as a Ph.D. student. The objective of the Ph.D project is to investigate the influence of the inherent heterogeneity of cementitious systems on the uptake mechanisms of radionuclides using microspectroscopic techniques. R. Rossé joined the sub-programme *Cement Systems* on September 1, 2002, for a period of one year.

5.8 References

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- BONHOURE, I., BAUR, I., WIELAND, E., JOHNSON, C.A. & SCHEIDEGGER, A.M. (2003b) Se(IV/VI) oxyanion immobilization by cementitious systems: An X-ray absorption study. *Environ. Sci. Technol.* (submitted).
- TITS, J., STUMPF, T., RABUNG, T., WIELAND, E. & FANGHÄNEL, T. (2003a) Uptake of trivalent actinides (Cm(III)) and lanthanides (Eu(III)) by calcium silicate hydrates: A wet chemistry and time-resolved laser fluorescence spectroscopy (TRLFS) Study. *Environ. Sci. Technol.* 37, 3568-3573.
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- WIELAND, E. & VAN LOON, L.R. (2002) Cementitious near-field sorption data base for performance assessment of an ILW repository in Opalinus clay, PSI Bericht Nr. 03-06, Paul Scherrer Institut, Villigen, Switzerland, 2003, and Nagra Technical Report NTB 02-20, Wetingen, Switzerland 2002.
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- WIELAND, E., TITS, J. & BRADBURY, M.H. (2003b) The potential effect of cement-derived colloids on radionuclide mobilisation in a repository for radioactive waste. *Appl. Geochem.* (in press).

5.9.2 Conferences/Workshops/Presentations

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- TITS, J., WIELAND, E., DOBLER, J.-P. & KUNZ, D. Uptake of strontium by calcium silicate hydrates under high pH conditions: An experimental approach to distinguish adsorption from co-precipitation processes. MRS 2003 (Scientific basis for radioactive waste management XXVII), Kalmar, Sweden, 15-18 June, 2003.
- WIELAND, E., ROSSÉ, R. & MOOR, C.¹ Immobilization of radiotracers and stable isotopes in cement systems. MRS 2003 (Scientific basis for radioactive waste management XXVII), Kalmar, Sweden, 15-18 June, 2003.

¹ Swiss Federal Laboratories for Materials Testing and Research (EMPA), CH-8600 Dübendorf, Switzerland

5.9.3 Internal reports

EIKENBERG, J., TITS, J., WIELAND, E., KUNZ, D., SCHAIBLE, A. & RÜTHI, M. (2003) Results of the batch sorption stability experiments with ^{58}Co , ^{60}Co and ^{152}Eu in high pH solutions. PSI Technical Report TM-96-03-14, Paul Scherrer Institut, Villigen, Switzerland.

WIELAND, E., TITS, J. & DÄHN, R. (2003) Radionuclide uptake by calcium silicate hydrates (CSH phases): CRIEPI-PSI joint research project – 3rd Annual Report. PSI Internal Report AN-44-03-02, Paul Scherrer Institut, Villigen, Switzerland.

6 COLLOID CHEMISTRY

C. Degueldre

6.1 Introduction

The colloid sub-programme is investigating the potential role of groundwater colloids on the migration of radionuclides in the geosphere. The groundwater colloids are characterised with emphasis on properties such as their nature, concentration and size distribution in the considered aquifers. Their association properties with relevant nuclides and their stability and mobility in the subsurface environment is also studied.

This report summarises the co-operation work in the frame of the Grimsel Colloid and Radionuclide Retardation Project. Activities also included colloid studies such as the analytical tests on single particle analysis by ICP-MS. During the reporting period, the proceedings of the symposium Colloid 2002 organised by the author in June 02 as an EMRS symposium held in Strasbourg were published as a special issue in Colloids and Surfaces A, in April 2003.

6.2 Activities for the Grimsel Colloid and Radionuclide Retardation Project

The Colloid and Radionuclide Retardation CRR experiment is dedicated to the study of the in situ migration behaviour of selected actinides and fission products in the absence and presence of bentonite colloids in a water-conducting feature (shear zone) in the Grimsel Test Site (GTS). The technical scenario considers the bentonite backfill/host rock interface as a potential source for colloids. The experiment investigates the migration behaviour of U, Th, Pu, Am, Np, Sr, Cs, I and Tc and the influence of smectitic bentonite colloids by two in situ tracer injections in a well-characterised dipole. The field experiments are supported by an extended laboratory and modelling programme. Colloid breakthrough is determined on-line by a mobile, laser-induced breakdown detection apparatus (LIBD), a mobile photon correlation spectrometer (PCS) and, afterwards in the laboratory, by a single particle counting method (SPC) using a laser light scattering technique.

Bentonite colloids were found to be stable in the experimental groundwater and the influence of pH and salinity on colloid stability was investigated. The in situ monitored breakthrough of I and of the tri- and tetravalent actinides Am and Pu followed the colloid breakthrough indicating some degree of colloid-mediated migration of the actinide radionuclides in the experimental shear zone (see Fig. 6.1). But even when no

montmorillonite colloids had been added to the tracer cocktail, part of Am(III) and Pu(IV) appeared to migrate not as dissolved species, but as colloids. The different colloid detection techniques revealed a colloid recovery between 80 and 90% of the injected bentonite colloids.

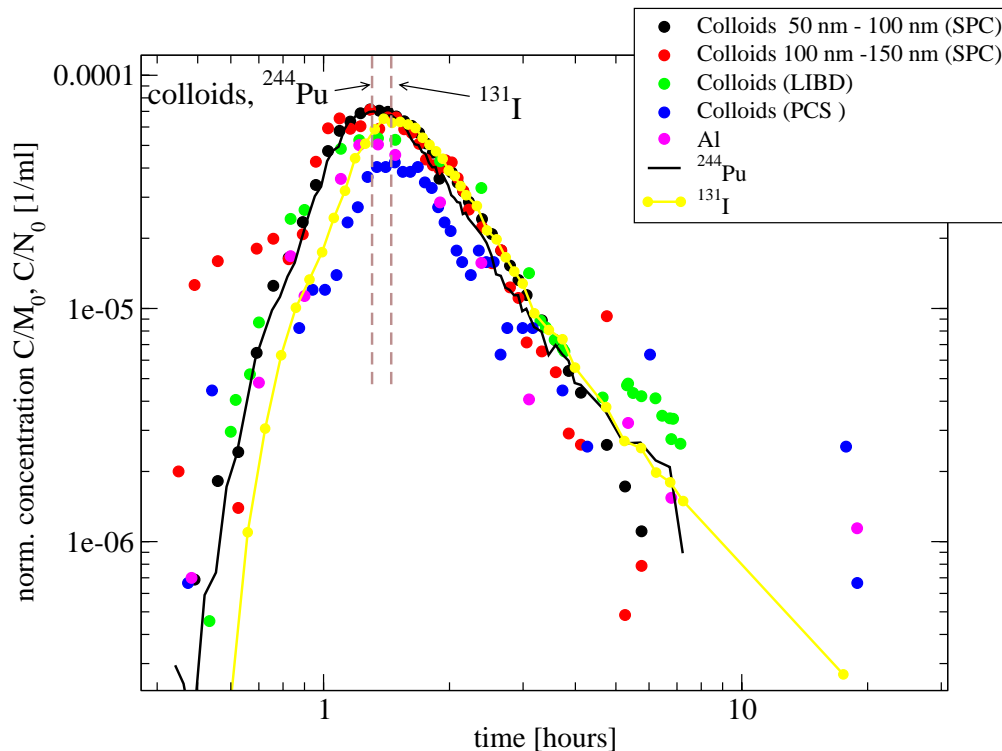


Fig. 6.1: Colloid breakthrough curves detected by LIBD, PCS, SPC and ICP-MS compared with the breakthrough of ^{131}I and ^{244}Pu ; in case of ICP-MS detection, Al is measured as, being representative of the bentonite colloids.

The CRR experimental results should be considered from the perspective of understanding the likely long-term behaviour of a deep geological repository for radioactive waste and as indicators of the way forward to the next generation of in situ experiments. Our results for the CRR project were presented at Colloid 2002 and published in Colloids and Surfaces A (MOERI et al. 2003).

6.3 Other colloid activities

6.3.1 Colloid analytics

Single particle analysis of zirconia colloids in water has been performed by inductively coupled plasma-mass spectroscopy (ICP-MS). The transient signal induced by the flash of ions due to the ionisation of a zirconia colloidal particle in the plasma torch can be detected and measured for selected zirconium ion masses by the mass spectrometer (see Fig. 6.2.a). The intensity of the MS signal is recorded in a time scan. The peaks recorded are analysed as a function of the particle size, and the fraction of the studied element or isotope in the colloid phase (Fig. 6.2.b). The frequency of the flashes is directly proportional to the concentration of particles in the colloidal suspension (see DEGUELDRE & FAVARGER, 2003). After developing the theoretical aspects on detection, composition and intensity of ion flashes generated by colloid ionisation in the plasma torch, tests were performed on model zirconia colloids and on silica colloids coated with zirconia. This feasibility study also describes the experimental conditions and the choice of isotopes to detect zirconia colloids in a single particle analysis mode. A manuscript was submitted for publication.

Similar tests were also performed with thorium colloids and a study was submitted for publication.

6.3.2 Proceedings of Colloid 2002

The symposium Colloid 2002 was held at the European Materials Research Society (EMRS) meeting in Strasbourg on 18-20 June 2002. It was the first symposium on colloid science to be held at an EMRS meeting, and marks the increasing importance of soft condensed matter and environmental and biological colloids. The symposium attracted 60 contributing presentations (40 oral and 20 posters) presented by delegates from ten different countries representing a wide range of modern colloid science. From these papers, 25 publications were accepted in the proceedings.

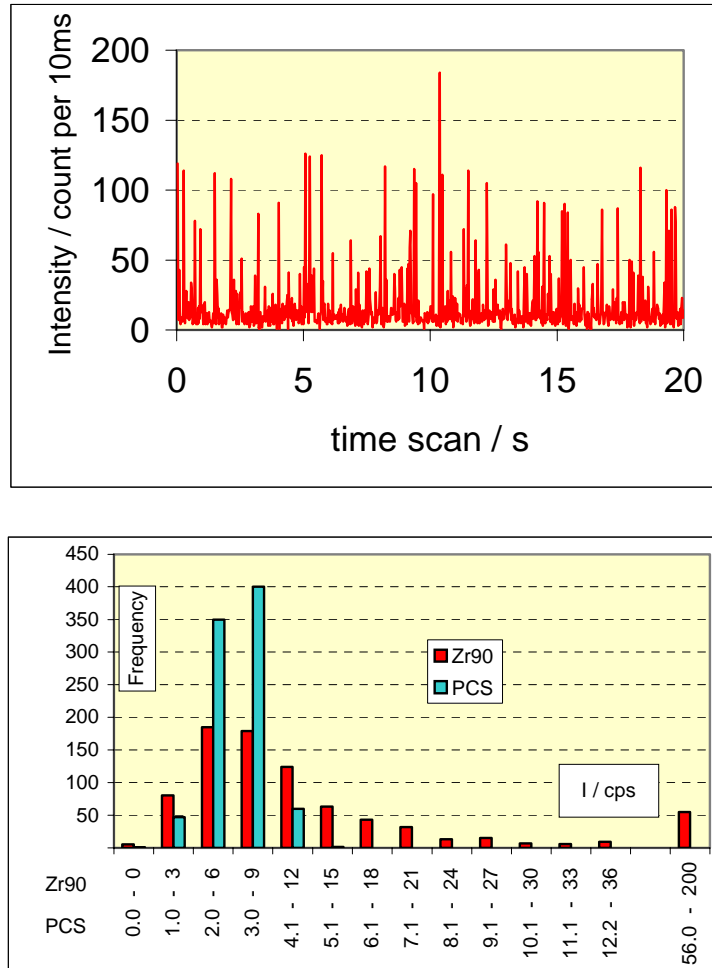


Fig. 6.2: Analysis of zirconia colloids by ICP-MS in a single particle mode.
a: Signal for $^{90}\text{Zr}^+$ recorded in time scan, particle sample recorded during 20 seconds
b: Comparison of the ICP-MS signal distribution with the colloid volume distribution derived from the assumed gaussian distribution estimated from PCS measurements.

Conditions: colloidal suspension of ZrO_2 , 10 ms detection time for $^{90}\text{Zr}^+$ ion detection, colloidal solution injection rate $2 \times 10^{-5} \text{ cm}^3 \text{ s}^{-1}$ within the pure water at injection rate $5 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ for nebulising in argon flow $19 \text{ cm}^3 \text{ s}^{-1}$ through plasma torch prior to mass analysis.

6.3.3 Wellenberg SB6 groundwater colloids

Since early 1999, the free artesian flow at bore hole SB6 has been stopped for technical reasons. The results on the groundwater colloid characterisation and on the sorption of Am(III) on the colloids were reported earlier (DEGUELDRE et al. 2001).

The sorption of americium on Wellenberg groundwater colloids was studied in the 2×10^{-2} M sodium bicarbonate groundwater and 2×10^{-2} M sodium chloride bicarbonate-free solutions. In the in-situ groundwater (pH of 8.6), the americium was strongly sorbed onto the colloids. XAFS analyses were performed on these sorbed Am species to establish the near-neighbour bonding. The work was performed in co-operation with scientists at the Advanced Photon Source (APS), Argonne National Laboratory. Am was sorbed onto colloid samples in bicarbonate and carbonate free solutions, and wet colloid cakes were examined by EXAFS after microfiltration. The XANES part confirms the presence of Am(III) with the Am(III) L_3 -edge at $E^o = 18505$ eV. The spectra recorded were further analysed by normalisation and Fourier Transformation. Distances (R) and number of next neighbour (N) for Am sorbed under bicarbonate and carbonate free conditions were compared with other data. The average distance to the nearest neighbour is 2.50 ± 0.02 Å in both cases with 10 to 11 nearest neighbour atoms. In the surface complex e.g. $>Al-O-Am(OH)_2 \cdot 7H_2O$ (see Fig. 6.3) the distances Am-O would be comparable (somewhat larger than 2.37 for Am_2O_3) and the number of next neighbour (N) of Am would be around 10 (larger than 6 for Am_2O_3). It was also noted that hydrated surface complexes are formed with the colloids without surface precipitation. This conclusion is based on the absence of Am-Am interaction in the third shell.

The results of this XAS study were partially presented at Migration'01, and the work is submitted for publication.

6.3.4 Mont Terri groundwater sampling study

The work on groundwater samplings from the short borehole in the Lower Dogger Limestone, the boreholes A1, A2, A3 and A6 in the Opalinus Clay and from a spring from the underlying Jurensis Marls, was completed and published (DEGUELDRE et al. 2003).

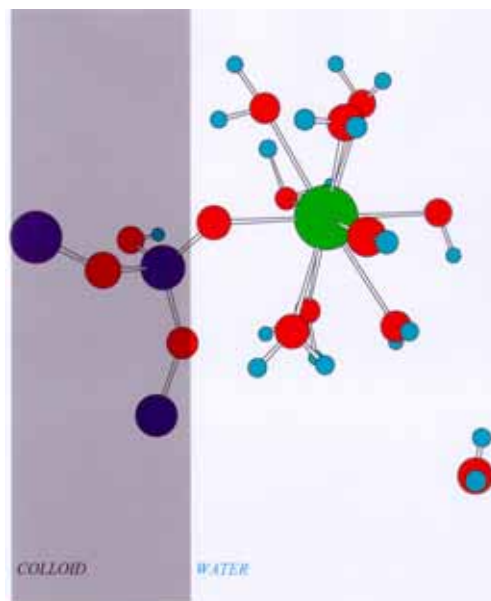


Fig. 6.3: Americium atomic environment after sorption on a groundwater colloid. The picture was obtained by using the experimental distances and coordination numbers from this study and applying the code ChemDraw for the hydrated Am(III) (●) dihydroxo-complex (hydrogen: ●) sorbed on a Al/Si (●)-oxygen (●) site on a colloid ■.

6.4 Future work

The work at Mont Terri in the Opalinus clay is now published and will not be continued since new boreholes are not foreseen at the moment in the OPA formation.

At PSI, interest is placed on using the large facilities (SLS). This motivated us to perform the XAS Am sorption work on Wellenberg colloids. We have also planned candidate studies for the micro-EXAFS beam line.

The participation in the Colloid and Radionuclide Retardation program at Grimsel has been fruitful. This program will be completed by the end of 2003. However, we will participate in the subsequent project: Colloid Formation and Migration (CFM), where the emphasis will be on understanding the generation of colloids at a bentonite block/groundwater flow interface.

Analytical tests on single colloids by ICP-MS will continue (in collaboration with University of Geneva) with tests on uranium colloids as oxides and sorbed on clay particles.

Other collaborative work will also continue in order to complete the global picture on the colloid properties in aquifers.

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¹ Institute of Nuclear Chemistry, Warsaw, Poland

² Institut Forel, Université de Genève, Switzerland

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¹ Amt für Umwelt, Kanton Turgau, 8500 Frauenfeld, Switzerland

² CIEMAT, Av. Complutense, 28040 Madrid, Spain

³ Institut Forel, University of Geneva, 1290 Versoix, Switzerland

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¹ Geotechnisches Institut, Bern, Switzerland

² NAGRA, Wettingen, Switzerland

³ INE, Forschungszentrum Karlsruhe,

⁴ Solexperts, Schwerzenbach, Switzerland

⁵ CIEMAT, Madrid, Spain

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¹ Institut Forel, University of Geneva, Versoix, Switzerland

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¹ University Duhram, UK

² CEA, Saclay, France

DEGUELDRE C., P.-Y. FAVARGER¹ P.-Y., BITEA² C., Zirconia Colloid Analysis by Single Particle Inductively Coupled Plasma - Mass Spectroscopy, *Anal. Chim.* (submitted)

¹ Institut Forel, University of Geneva, 1290 Versoix, Switzerland

² Institut für Nukleare Entsorgung, Forschungszentrum Karlsruhe, 76021 Karlsruhe, Germany

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¹ Institut Forel, University of Geneva, Versoix, Switzerland

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¹ Geotechnisches Institut, Bern, Switzerland

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¹ CMT, Argonne National Laboratory, IL, USA

7 DIFFUSION PROCESSES

L.R. Van Loon, A. Jakob, W. Müller, A. Laube, M. Glaus, Th. Gimmi, M.H. Bradbury

7.1 General

In the reporting period the main effort in the group “Diffusion Processes” was involved in diffusion experiments on Opalinus Clay samples. The following experiments (measurements) were performed:

- Diffusion coefficients and rock capacity factors for diffusion perpendicular to bedding for $^{22}\text{Na}^+$ and $^{85}\text{Sr}^{2+}$ were measured by through-diffusion and out-diffusion.
- Diffusion of $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ parallel to bedding was measured using the radial through-diffusion technique. These measurements were performed within the framework of the in-situ diffusion experiment (DI-A) in the Mont Terri Underground Rock Laboratory.
- The effect of temperature on the diffusion of HTO, $^{22}\text{Na}^+$ and $^{36}\text{Cl}^-$ using a continuous through-diffusion method developed at PSI.
- A first series of measurements using time-of-flight neutron spectroscopy were performed on Opalinus Clay, sandstone and compacted bentonite. Using appropriate models, the microscopic (local) diffusion coefficients could be derived from the observed peak-broadening.

The activities in the field of organic ligands were restricted to experiments on the degradation of cellulose at elevated temperature (60 °C). This work is a joint research project between PSI, NAGRA, SKB and NIREX.

A Ph.D. project on the “Structure and Dynamics of Confined Water in Compacted Clay Systems (CCS)” was submitted to, and accepted by, the PSI Research Committee.

The group “Diffusion Processes” will take part in the EU Integrated Project on key-processes in the near-field (NF-PRO). A proposal on diffusion in compacted bentonite was prepared and submitted to the European Commission as a part of the NF-PRO Project.

7.2 Diffusion

Opalinus Clay is a potential host rock for a repository for spent fuel, high-level vitrified waste and long-lived intermediate-level waste in Switzerland. It is a highly compacted argillaceous rock ($\rho = 2500 \text{ kg m}^{-3}$) with a very low hydraulic conductivity ($K_h = 10^{-14} \text{ m s}^{-1}$). In such a highly compacted formation, diffusion is the main transport process for radionuclides. Diffusion in OPA is currently under investigation at PSI. The main objectives of these diffusion studies are:

- Measuring site specific diffusion coefficients and diffusion accessible porosities in Opalinus clay. These data are necessary for performance assessment studies.
- Assessing the effect of overburden pressure, temperature and layer orientation on diffusion.
- Comparison of Mont Terri samples with Benken samples.

The through-diffusion techniques used have been described in VAN LOON et al. (2003a, 2003b).

7.2.1 Diffusion perpendicular to bedding

Effective diffusion coefficients (D_e) and rock capacity factors (α) for the weakly sorbing tracers $^{22}\text{Na}^+$ and $^{85}\text{Sr}^{2+}$ were measured using through- and out-diffusion. Figure 7.1 gives a typical through-diffusion and out-diffusion curve (Flux vs. time) for $^{22}\text{Na}^+$.

The rock capacity factor is defined by

$$\alpha = \varepsilon + \rho \cdot K_d \quad 7.1$$

where ε is the diffusion accessible porosity, ρ the bulk dry density ($\text{kg}\cdot\text{m}^{-3}$) and K_d the sorption value ($\text{m}^3\cdot\text{kg}^{-1}$). The out-diffusion data showed that the sorption of $^{22}\text{Na}^+$ and $^{85}\text{Sr}^{2+}$ is linear and reversible. The effective diffusion coefficients measured for $^{22}\text{Na}^+$ and $^{85}\text{Sr}^{2+}$ are identical to those for HTO in the case of Mont Terri OPA. In the case of Benken OPA, D_e is a factor of 2 higher than for HTO (Table 7.1). The reason for this phenomenon is still unclear.

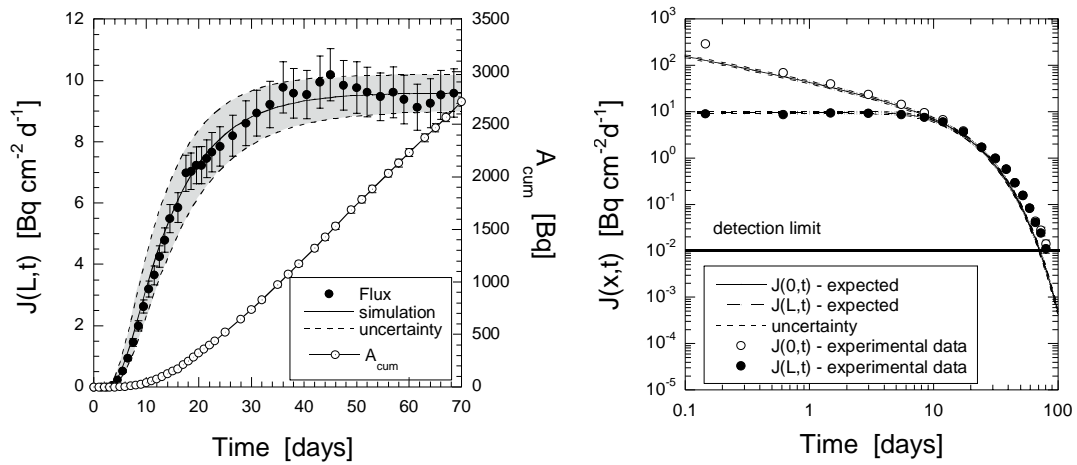


Fig. 7.1: Through-diffusion (a) and out-diffusion (b) of $^{22}\text{Na}^+$ in Benken Opalinus clay of (15 MPa).

Table 7.1: Values of the effective diffusion coefficient (D_e^\perp) and rock capacity factors (α) of HTO, $^{22}\text{Na}^+$ and $^{85}\text{Sr}^{2+}$ measured by through-diffusion at different confining pressures.

Sample	HTO		$^{22}\text{Na}^+$		$^{85}\text{Sr}^{2+}$	
	D_e^\perp ($\text{m}^2 \cdot \text{s}^{-1}$)	α	D_e^\perp ($\text{m}^2 \cdot \text{s}^{-1}$)	α	D_e^\perp ($\text{m}^2 \cdot \text{s}^{-1}$)	α
MT-1a	$(1.5 \pm 0.1) \times 10^{-11}$	0.10 ± 0.01	$(1.6 \pm 0.1) \times 10^{-11}$	0.33 ± 0.03	$(1.7 \pm 0.1) \times 10^{-11}$	1.99 ± 0.18
MT-3a	$(1.2 \pm 0.1) \times 10^{-11}$	0.10 ± 0.01	$(1.4 \pm 0.1) \times 10^{-11}$	0.34 ± 0.02	$(1.4 \pm 0.1) \times 10^{-11}$	1.93 ± 0.16
BE-2a	$(6.7 \pm 0.4) \times 10^{-12}$	0.15 ± 0.01	$(1.5 \pm 0.1) \times 10^{-11}$	0.87 ± 0.07	ongoing	
BE-3a	$(5.9 \pm 0.4) \times 10^{-12}$	0.14 ± 0.01	$(1.3 \pm 0.1) \times 10^{-11}$	0.83 ± 0.06	ongoing	
BE-4a	$(5.6 \pm 0.3) \times 10^{-12}$	0.13 ± 0.01	$(1.2 \pm 0.1) \times 10^{-11}$	0.82 ± 0.06	ongoing	

MT: Mont Terri samples; BE: Benken samples

MT-1a: 1 MPa; MT-3a: 5 MPa; BE-2a: 4 MPa; BE-3a: 8 MPa; BE-4a: 14 MPa

7.2.2 Diffusion parallel to bedding

Through- and out-diffusion of $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ was measured using the radial through-diffusion technique (VAN LOON et al 2003c). The results of the through-diffusion studies are summarised in Table 7.2. Compared to diffusion perpendicular to bedding, diffusion parallel to bedding is larger by a factor of 4-6. This is explained by the smaller tortuosity in the case of diffusion parallel to bedding. The rock capacity factors are independent of the direction of diffusion.

Table 7.2: Values for the effective diffusion coefficients and rock capacity factors for the diffusion of HTO, $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ in Opalinus clay parallel and perpendicular to the bedding (measured by the through-diffusion technique).

Sample	Isotope	D_e (parallel) ($\text{m}^2\cdot\text{s}^{-1}$)	α (parallel)	D_e (perpend.) ($\text{m}^2\cdot\text{s}^{-1}$)	α (perpend.)
BE/1	HTO	$(3.1\pm 0.3)\times 10^{-11}$	0.15 ± 0.02	$(5.4\pm 0.4)\times 10^{-12}$	0.14 ± 0.02
BE/2	HTO	$(3.2\pm 0.2)\times 10^{-11}$	0.13 ± 0.02	$(5.4\pm 0.4)\times 10^{-12}$	0.13 ± 0.02
MT/1	HTO	$(5.4\pm 0.4)\times 10^{-11}$	0.15 ± 0.03	$(1.4\pm 0.1)\times 10^{-11}$	0.17 ± 0.02
MT/2	HTO	$(5.4\pm 0.4)\times 10^{-11}$	0.17 ± 0.02	$(1.4\pm 0.1)\times 10^{-11}$	0.14 ± 0.02
¹ MT	HDO	$(5.1-8.4)\times 10^{-11}$	0.17 - 0.24	n.m	n.m
¹ MT	H_2O^{18}	$(5.6-10)\times 10^{-11}$	0.19 - 0.25	n.m	n.m
BE/1	$^{36}\text{Cl}^-$	$(3.4\pm 0.3)\times 10^{-12}$	0.05 ± 0.01	$(6.7\pm 0.4)\times 10^{-13}$	0.04 ± 0.01
MT/1	$^{36}\text{Cl}^-$	$(1.6\pm 0.1)\times 10^{-11}$	0.08 ± 0.01	$(4.1\pm 0.3)\times 10^{-12}$	0.08 ± 0.01
¹ MT	Cl^-	$(1.8-5.6)\times 10^{-11}$	0.10 - 0.15	n.m	n.m
¹ MT	Br^-	$(1.7-4.5)\times 10^{-11}$	0.10 - 0.15	n.m	n.m
BE/1	$^{22}\text{Na}^+$	$(7.8\pm 0.6)\times 10^{-11}$	0.89 ± 0.08	$(1.3\pm 0.1)\times 10^{-11}$	1.11 ± 0.11
MT/1	$^{22}\text{Na}^+$	$(7.2\pm 0.5)\times 10^{-11}$	0.62 ± 0.05	$(1.5\pm 0.1)\times 10^{-11}$	0.48 ± 0.04

n.m: not measured; BE: sample from Benken(14 MPa); MT: sample from Mont Terri (7 MPa); 1: series 1; 2: series 2

¹data from van der Kamp and Van Stempvoort (1998)

As was discussed in the previous annual report (LES 2002), the out-diffusion data of HTO showed two different diffusion pathways: a fast and a slow one. In the through-diffusion measurements, however, these two processes were not observed because the fast process dominates the transport.

The out-diffusion of $^{36}\text{Cl}^-$ showed only one diffusion pathway in the case of Benken OPA and two for Mont Terri. The out-diffusion of $^{22}\text{Na}^+$ again showed two diffusion pathways for both OPA from Benken and Mont Terri. So far, the observed phenomena cannot yet be explained.

7.2.3 Effect of temperature on diffusion

The effect of temperature on the diffusion of HTO, $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ was investigated. For all three radionuclides, the temperature dependence showed an Arrhenius behaviour. The activation energies for the diffusion of HTO, $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ were slightly higher (2-4 kJ/mol higher) than those measured in bulk liquid water in the case of OPA from Benken. In the case of Mont Terri OPA, HTO showed a slightly higher activation energy (2 kJ/mol higher) whereas $^{36}\text{Cl}^-$ and $^{22}\text{Na}^+$ have similar values to bulk liquid water.

7.2.4 Time of flight neutron spectroscopy

Quasi-elastic neutron scattering (QENS) is a unique tool for probing the microscopic mechanism of self-diffusion of water in the pores of porous materials and obtaining a more detailed insight into the environment of water confined between solid particles. First measurements, aiming to explore the microscopic mechanism of the water diffusion in different porous media, were carried out at the PSI time-of-flight neutron spectrometer, FOCUS at SINQ. They allow microscopic diffusion coefficients in the pore water to be estimated. Unlike through- and out-diffusion on the macroscopic scale, these measurements are not influenced by the larger scale geometry of the rock samples and provide direct information on the average state of the water. Preliminary results aimed at demonstrating the feasibility of the proposed method are shown in Figure 7.2.

The spectrum (Figure 7.2a) was fitted assuming an elastic part (matrix and water; delta function), a quasi-elastic part (water; Lorentz function) and a constant background. The limited instrument resolution was taken into account by convolution of the model spectrum with the Gauss peak of a vanadium sample. The obtained half-width at half-maximum (hwhm) of the Lorentzian was plotted against the momentum transfer, Q (Figure 7.2b), and fitted to a jump diffusion model:

$$\text{hwhm} = \frac{D \cdot Q^2}{1 + D \cdot Q^2 \cdot \tau} \quad 7.2$$

where D is the microscopic diffusion coefficient and τ the time between jumps. The main difficulty for data interpretation is the choice of a proper model for the microscopic diffusion of water. It is therefore a challenging task to vary the experimental conditions in such a way that a discrimination between different models can be achieved. This is part of a PhD project that will be started by the end of 2003.

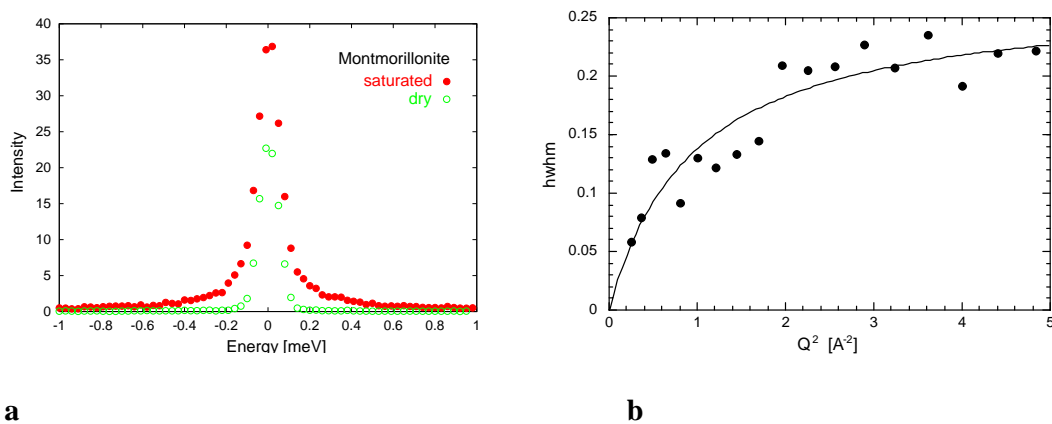


Fig. 7.2: Quasi-elastic neutron scattering from wet and dry compacted Montmorillonite (a), and obtained linewidths (hwhm) of the quasielastic spectra as a function of the momentum transfer (Q) for wet Montmorillonite (b), from which microscopic diffusion coefficients can be estimated with suitable models.

7.2.5 Diffusion in pure compacted clay systems

The long-term aim of these experiments is a better understanding of the transport behaviour of sorbing and non-sorbing cations and anions in the buffer material of a repository for HLW. Diffusion processes dominate the dispersion of these ions – similar will be to the situation in Opalinus clay. As a first step in this direction, experiments will be carried out using pure compacted clay systems in which the effects of dry density and anion exclusion phenomena on the diffusion behaviour of selected ions will be investigated. The project is thus strongly linked to the questions of the physico-chemical state of water in compacted clay systems and the question of possible effects of ion exclusion and degree of compaction on the speciation and sorption of radionuclides. Presently, suitable diffusion cells, in which the diffusion length of the sample can be varied, are under construction. First experiments are planned to be started in October of this year. In these experiments the minimum diffusion length of a

compacted clay sample will be evaluated using HTO as a conservative tracer. A minimisation of this sample length is desirable for the study of through-diffusion for sorbing radiotracers.

7.3 Organic Ligands

The experimental activities of LES in the field of organic ligands have been more or less restricted to answering remaining key-questions in the field of cellulose degradation. The purpose of the experiments is to establish a reliable relationship between the reaction rate constant for the alkaline hydrolysis of cellulose (mid-chain scission), which is a slow reaction, and temperature. Substantial efforts were made for purchasing and testing a new device for measuring concentrations of carbon and a new device for high performance ion chromatography. Minor activities were measurements of α -ISA from sorption experiments on Boom Clay carried out for SCK-CEN (Belgium).

The experiments for cellulose degradation at 60 °C, carried out within a collaboration between PSI, Nagra, Nirex and SKB, have been terminated in February of this year. For Aldrich cellulose, the reaction has levelled-off at a degradation degree of ~60 % and for cotton cellulose at ~40% (cf. Fig. 7.3).

7.3.1 Cellulose

The degradation of cellulose as a function of time can be divided in three reaction phases observed in the experiments: (i) an initial fast reaction phase interpreted as being dominated by the peeling-off process, (ii) a further slow reaction, interpreted in a working hypothesis as alkaline hydrolysis and (iii) a complete stopping of cellulose degradation. The experimental findings are unexpected in several respects: (i) the degree of cellulose degradation as a function of time is almost identical for the experiments carried out at 60 °C and 90 °C, and (ii) the degree of cellulose degradation as a function of time is almost identical for both pure cellulose and cotton cellulose. It can be concluded that the reaction behaviour of the materials tested cannot be explained within the classical frame of a combination of the peeling-off process and alkaline hydrolysis at the temperatures tested here. It may be hypothesised that the alkaline hydrolysis has not even been observed in the experiments. However, if this is true, cellulose degradation proceeds via another unknown type of reaction. Mass balances for carbon show that the large majority of reaction products found in solution can be explained by formation of isosaccharinic acids and other low-molecular weight carboxylic acids. The results obtained so far were discussed on the occasion of the final

meeting of the ‘Cellulose degradation project technical group’, and the conclusions were accepted by the contract partners. A draft version of a PSI report (GLAUS et al., 2003a) summarising the results and conclusions drawn from the experiments at 60 °C and 90 °C has been completed and undergone external review.

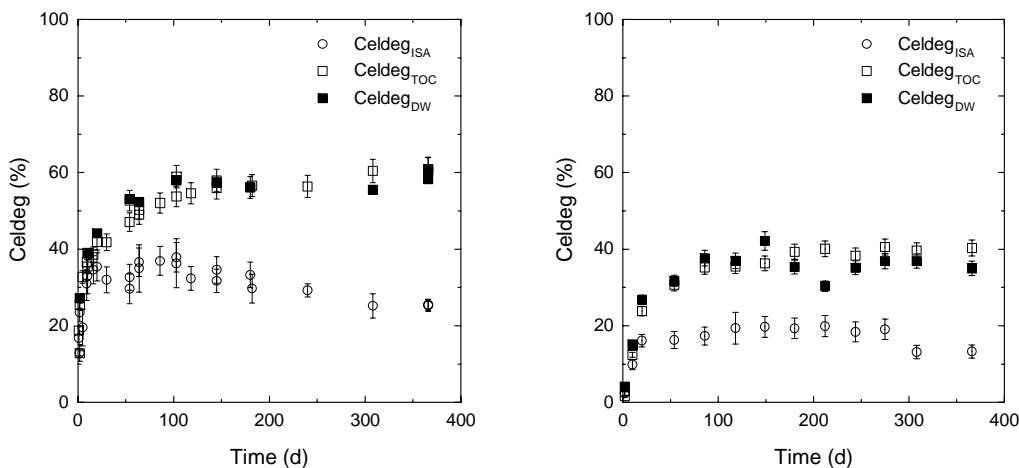


Fig. 7.3: Plot of the degree of cellulose degradation (*Celdeg*) as a function of reaction time for the degradation of Aldrich cellulose in the presence of $\text{Ca}(\text{OH})_2$ at pH 13.3 (left) and for cotton cellulose (right) at 60 °C. The subscripts of indicate that *Celdeg* has been determined either by measurement of the sum of α - and β -isosaccharinic acid (ISA), total organic carbon (TOC) or dry weight of the remaining cellulose (DW).

As already discussed at the interim meeting of the ‘Cellulose degradation project technical group’ (Feb. 2002), the focus of the future work will be on experiments addressing the reactivity of α -isosaccharinic acid (α -ISA) under the conditions of an artificial cement pore water. A series of preliminary experiments has shown that α -ISA is not stable in the presence of $\text{Ca}(\text{OH})_2$. Analysis of the transformation products suggests that a fragmentation of α -ISA leads to the formation of short-chain aliphatic carbonic acids. A contract between PSI, Nagra, Nirex and SKB defining future experiments has been signed this summer. The contract comprises of a work programme for experiments aiming at an understanding of the processes involved, at an assessment of the relevant parameters and at using this knowledge for possible applications in the safety analysis. Within the frame of this work programme, first experiments using $\text{Ca}(\text{OH})_2$ as the solid phase have been started, and an evaluation of methods to analyse the reaction products of the conversion of α -ISA, i.e. low-molecular carboxylic acids, using high performance ion exclusion chromatography was carried out.

7.3.2 Cement additives

The PSI report (GLAUS et al., 2003b) on concrete admixtures has been released as a draft version, which has undergone external review and is currently in internal review at Nagra.

7.4 References

GLAUS, M.A. & VAN LOON, L.R. (2003a) Cellulose degradation at alkaline conditions: Long-term experiments at elevated temperatures. PSI Bericht and Nagra Technical Report, in preparation.

GLAUS, M.A. & VAN LOON, L.R. (2003b) A generic procedure for the assessment of the effect of concrete admixtures on the retention behaviour of cement for radionuclides: Concept and case studies. PSI Bericht and Nagra Technical Report, in preparation.

LES (2002) Waste Management Laboratory Progress Report September 2001 to August 2002. AN-44-02-14, Paul Scherrer Institut, Villigen, Switzerland.

VAN DER KAMP, G. & VAN STEMPVOORT, D.R. (1999) Water sampling (laboratory) experiment (WS-B). Laboratory measurement of porosity, pore water isotopic composition and effective diffusivities of Opalinus Clay core samples. Mont Terri Project, Technical Note 98-38.

VAN LOON, L.R., J. SOLER¹, J. & BRADBURY, M.H. (2003a) Diffusion of HTO, ³⁶Cl⁻ and ¹²⁵I⁻ in Opalinus Clay from Mont Terri: Effect of confining pressure. J. Contam. Hydrol 61, 73-83.

¹ Inst. Ciències de la Terra, CSIC, Barcelona, Spain

VAN LOON, L.R., SOLER, J.M., JAKOB, A. & BRADBURY, M.H. (2003b) Effect of Confining Pressure on the Diffusion of HTO, ³⁶Cl⁻ and ¹²⁵I⁻ in a layered Argillaceous Rock (Opalinus Clay): Diffusion Perpendicular to the Fabric. Applied Geochemistry 18, 1653-1662.

VAN LOON, L.R., SOLER, J., MÜLLER, W. & BRADBURY, M.H. (2003c) Anisotropic Diffusion in layered argillaceous rocks: a Case Study with Opalinus Clay. PSI Scientific Report 2002/Volume IV, Paul Scherrer Institut, Villigen, Switzerland, 97-104.

7.5 Publications

7.5.1 Peer reviewed journals and reports

GERAEDTS¹, K., BRUGGEMAN¹, C., MAES¹, A., VAN LOON, L.R., ROSSBERG², A. & REICH, T². (2002): Evidence for the existence of Tc(IV)-humic substances species by X-ray Absorption Near - Edge Spectroscopy. Radiochimica Acta 90, 879 - 884.

¹ Laboratory for Colloid Chemistry, University of Louvain, Leuven, Belgium

² Institute for Radiochemistry, FZR, Rossendorf, Germany

VAN LOON, L.R., J. SOLER¹, J. & BRADBURY, M.H. (2003a) Diffusion of HTO, ³⁶Cl⁻ and ¹²⁵I⁻ in Opalinus Clay from Mont Terri: Effect of confining pressure. J. Contam. Hydrol 61, 73 - 83.

¹ CSIC-IJA, Barcelona, Spain

VAN LOON, L.R., SOLER¹, J.M., JAKOB, A. & BRADBURY, M.H. (2003b) Effect of Confining Pressure on the Diffusion of HTO, ³⁶Cl⁻ and ¹²⁵I⁻ in a layered Argillaceous Rock (Opalinus Clay): Diffusion Perpendicular to the Fabric. *Applied Geochemistry* 18, 1653 -1662.

¹ CSIC-IJA, Barcelona, Spain

WIELAND, E., BRADBURY, M.H. & VAN LOON, L.R. (2003) Development of a Sorption Data Base for the cementitious near-field of a repository for radioactive waste. *Cz. J. Phys* 53, A629 - A638.

7.5.2 Conferences/Workshops/Presentations

GLAUS, M.A., LAUBE, A. & VAN LOON, L.R. A Generic Procedure of the Assessment of the Effect of Concrete Admixtures on the Sorption of Radionuclides on Cement: Concept and selected Results. MRS Conference, 16–19 June, 2003, Kalmar, Sweden.

VAN LOON, L.R. Anisotropic diffusion in argillaceous rocks: A case study with Opalinus Clay. International Workshop on “Clay microstructure and its importance to soil behaviour“, Lund, Sweden, 15–17 Octobre, 2002.

VAN LOON, L.R., MÜLLER, W., GIMMI, TH. & IJIMA, K. Activation Energy of the Self-Diffusion of Water in Compacted Clay Systems: A Case Study with Opalinus Clay. International Symposium on “Clays in natural and engineered barriers for radioactive waste confinement”. Reims, France, 9-12 Decembre, 2002.

VAN LOON, L.R., GIMMI, TH., JANSSEN, S. & JURANYI, F. (2003) A time-of-flight neutron spectroscopic study on the dynamics of confined water in compacted geological materials. SINQ user meeting, PSI, Villigen, 18 January, 2003.

¹ Laboratory for Neutron Scattering, PSI, Villigen, Switzerland

² Laboratory for Physical Chemistry, Universität des Saarlandes, Saarbrücken, Germany

VAN LOON, L.R., GIMMI, TH., JANSSEN, S.¹ & JURANYI, F.² (2003) A time-of-flight neutron spectroscopic study on the dynamics of confined water in compacted geological materials. International Workshop on “Dynamics in Confinement”, Grenoble, France, 22-25 January, 2003.

¹ Laboratory for Neutron Scattering, PSI, Villigen, Switzerland

² Laboratory for Physical Chemistry, Universität des Saarlandes, Saarbrücken, Germany

WERSIN, P.¹, VAN LOON, L.R., SOLER, J.², YLLERA, A.³, EIKENBERG, J., GIMMI, TH., HERNAN, P.⁴ & BOISSON, J.-Y.⁵ (2002) Long-term diffusion experiment at Mont Terri (DI-A): First results from field and laboratory data. International Symposium on “Clays in natural and engineered barriers for radioactive waste confinement”. Reims, France, 9-12 Decembre, 2002.

¹ Nagra, Wettingen, Switzerland

² CSIC-IJA, Barcelona, Spain

³ CIEMAT, Madrid, Spain

⁴ ENRESA, Madrid, Spain

⁵ IRSN, Fontenay-aux-Roses, France

7.5.3 Internal reports

VAN LOON, L.R., SOLER, J.M.¹ & BRADBURY, M.H. (2003) Through-diffusion experiments with Opalinus Clay samples. Results for Na-22 (Na⁺). PSI Technical Report TM-44-03-01, Paul Scherrer Institut, Villigen, Switzerland.

¹ CSIC-IJA, Barcelona, Spain

VAN LOON, L.R., MÜLLER, W., SOLER, J.M.¹ & BRADBURY, M.H. (2003) Anisotropic diffusion of HTO and ³⁶Cl⁻ in Opalinus Clay. PSI Technical Report TM-44-03-02, Paul Scherrer Institut, Villigen, Switzerland.

¹ CSIC-IJA, Barcelona, Spain

VAN LOON, L.R. & MÜLLER, W. (2003) Effect of temperature on the diffusion of HTO in Opalinus Clay: Activation energy of diffusion. PSI Technical Report TM-44-03-03, Paul Scherrer Institut, Villigen, Switzerland.

7.6 Proposal

A Ph.D proposal was submitted to, and accepted by, the PSI Research Committee. The project focusses on the “Dynamics and Structure of Confined Water in Compacted Clay Systems.” The main technique to be used is the time-of-flight neutron spectroscopy and through-diffusion. The project is a co-operation between the following persons (groups):

L.R. Van Loon: Diffusion processes, LES

Th. Gimmi, L. Diamond: Rock/water interaction group, University of Bern

S. Janssen, F. Juranyi: Laboratory for Neutron Scattering

N. Skipper: Laboratory for Astrophysics, University College London

7.7 Personnel

A. Laube left the group on June, 1st. He will be replaced by R. Rossé who joined the group on September 1st.

8 STATUS OF THE MICRO-XAS BEAMLINE PROJECT

A.M. Scheidegger, D. Grolimund, B. Meyer, M. Willimann

8.1 Overview

The microXAS beamline will focus on X-ray absorption spectroscopy (XAS) and X-ray fluorescence (XRF) experiments requiring high spatial resolution (SCHEIDEGGER et al. 2000). Furthermore, the beamline will host the *FEMTO* project that will allow investigations of time-dependent phenomena in the femtosecond time regime (INGOLD et al. 2002, 2003). The design of the micro XAS beamline is conceptualized to yield monochromatic X-ray beams (5-20 keV) with high energy resolution combined with dynamic microfocusing capabilities (GROLIMUND et al. 2002, SCHEIDEGGER et al. 2003). In this chapter a description of the key optical layout is provided and a status report of the microXAS beamline project is presented.

8.2 Beamline layout

Front end

The microXAS beamline will be located at the long straight section X05L hosting the radiator and the modulator. A minigap in-vacuum undulator (U19) serves as radiation source and will provide high brightness X-rays in the energy range ~ 5 - ~ 20 keV (SCHMIDT et al., 2001). A schematic drawing of the front end components is given in Fig. 8.1 (side view). Briefly, the front-end includes

- power management components
 - a moveable diaphragm (A19)
 - a water-cooled CVD-diamond filter unit that can be moved in the vertical direction by means of a pneumatic manipulator (A25). Although the filter unit is physically in the optics hutch, it belongs from a conceptual point of view to the front end.
- diagnostic components
 - 2 Photon Beam Position Monitors (A3, A15)
- safety components
 - photon shutter (A7)
 - fast valve (A10)
 - beam stopper (A12)

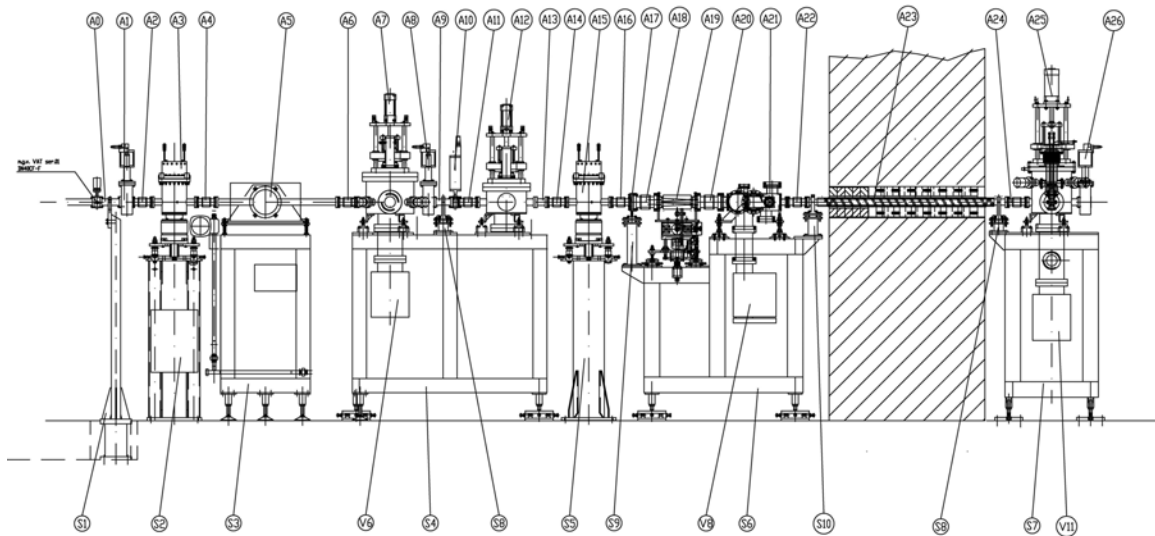


Fig. 8.1: Side view of micro-XAS Front end.

All components described above are Ultra High Vacuum (UHV) components. Two beams, (i) the undisturbed U19 beam and (ii) the sliced FEMTO beam, will pass through all front end components (except the moveable diaphragm) without change any in position of components in both operation modes.

Optics Hutch

A side view of the optics hutch is shown in Figure 8.2. Again, the components in the optics hutch can be divided into sub-groups according to their function.

- components for spatial and spectral refinement of the X-ray beam
 - filter unit for pink beam and flux reduction (A10)
 - double slits assembly (A6)
 - toroidal mirror (A10)
 - double crystal monochromator (A24)
- safety components
 - fast valves (A14, A30)
 - bremsstrahlungstopper (A26)
 - shutter-stopper assembly (A34)
- diagnostic components
 - diagnostic chamber (A12) hosting a photon beam position monitor
 - fluorescence screen (A17)
 - photon beam position monitor (A32)

The beamline will be operated windowless up to the experimental hutch (minimization of scattering effects). The vacuum scheme in the optics hutch will be divided into 5 sections each separated by UHV-gate valves (A8, A12, A21, A28, A40). The vacuum within these sections will vary between 10^{-10} and 10^{-9} mbar (section 1) and 10^{-7} mbar (section 5). In order to guarantee the proposed vacuum scheme, a differential pumping unit (A19) and several ion pumps are foreseen along the X-ray path within the optics hutch.

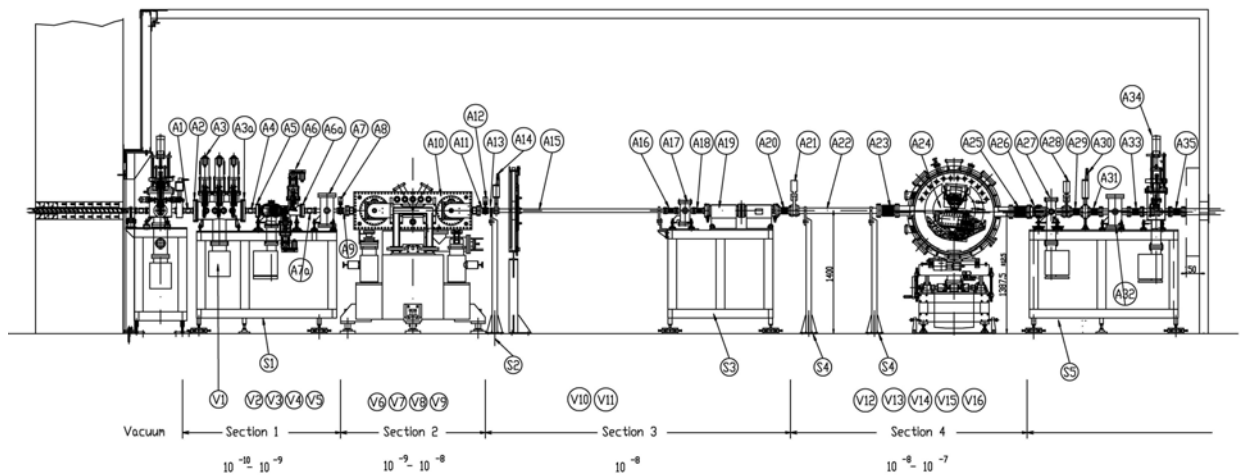


Fig. 8.2: Side view of micro-XAS optics hutch.

8.3 Key optical components

In the following two key optical components, the mirror (A10) and the monochromator (A24), are described in more details.

Mirror

The mirror corresponds to the first key optical component within the beamline design. The mirror unit serves three main purposes:

- to collimate the beam in the vertical dimension
- to produce a 1.4:1 image in the horizontal dimension,
- to act as a low-pass filter with an energy cut-off of ~ 22 keV.

The microXAS beamline is designed to deliver a micro-focused X-ray beam with high energy resolution ($\Delta E/E < 10^{-4}$). Applying a focusing scheme using vertical collimation, the transmitted energy bandwidth can be narrowed down to the Darwin width of the monochromator crystal cuts used. The horizontal focusing corresponds to the first part of a two-step focusing strategy. Such a step-wise reduction in x-ray spot size offers two

main advantages: First, the capability of dynamical focusing and second, optimizing the overall acceptance of the optical system. By using just one mirror, the required focusing characteristic can be achieved by means of a toroidal mirror shape. The toroidal figure will be produced by bending a cylindrical mirror into the shape of a toroid.

Concerning low-pass filter characteristics, the upper energy cut-off will be determined by the grazing angle of incidence in combination with the mirror coating employed. For the microXAS mirror system, an angle of incidence of 3.1 mrad and a Rh coating is foreseen. This combination yields a reduced transmission for x-rays with energies higher than approximately 22 keV.

As a specialty, the mirror will deflect sideward. Although more demanding from an engineering point of view, such a mirror orientation results in an important suppression of the spot size broadening due to figure errors (GROLIMUND et al. 2002, HOWELLS et al. 2000).

The current design foresees that the same mirror is also used for the redirection of the X-rays in the *FEMTO* project. This requests for the possibility of a relatively fast change between two well-defined positions of operation. Due to the high restrictions concerning spatial beam stability the mechanical stability and the request for maintaining tight mechanical tolerances are critical.

At present, the mirror system (with a total unit weight of more than 3 tons!) is being installed at the microXAS beamline (Fig. 8.3).



Fig. 8.3: Installation of microXAS mirror tank.

Monochromator

The source size at SLS is small and the double crystal monochromator (DCM) is located at quite a distance (~10 m) from the intermediate focus point in the experimental hutch. These facts put very drastic constraints on the stability of the DCM (A24). To maintain a fixed height offset and a fixed angle with respect to the incident white beam during an energy scan the monochromator needs to operate with a fixed vertical offset. For the second crystal fine-tuning the angular offsets with respect to the first crystal is required and thus, every design consideration for the DCM should be given to maintaining the angular stability. Furthermore, for maintaining a fixed offset in height relative to the incident beam during energy scanning, the second crystal also needs to be translated in the direction normal to the crystal plane.

In order to meet the stringent requirements on the relative accuracies between the two crystals we have chosen a double cam design from *Kohzu Co.* that offers a good parallelism and stability when scanning over a large angular range as required for microbeam XAS. In a double cam system the first and second crystal holders are mounted on the same rotating table of the Bragg axis goniometer. Crystal translations, which are necessary in order to keep the beam hitting the center of each crystal and beam offset fixed, are provided through mechanical link to rotation of the main Bragg axis by two cams. Therefore, any change of energy or Bragg angle can be performed by actuating just one motor (placed outside of the vacuum chamber), while the exit beam runs parallel with the incident beam with constant offset independently on the Bragg angle.

The fixed-exit monochromator will be equipped with two sets of monochromator crystals, namely Si(111) and Si(311), allowing to optimize the experiments with respect to photon flux or energy resolution. Due to the power density impinging on the first monochromator crystal, liquid nitrogen cooling is required. The LN₂ cooling will be performed by a closed loop system from *Messer Co.* The experience with an identical cooling system at SLS has shown that the flow of liquid nitrogen does not introduce any noticeable vibrations.

8.4 Experimental infrastructure

Figure 8.4 shows a schematic illustration of the microXAS beamline. Besides the Pb shielded hutches (optical (A) and experimental hutch (B)) the drawing shows the outline of the control hutch (C-E) and the *FEMTO* laboratory (F). The experimental hutch (B) will be equipped with two optical benches. The first bench will host measurements which do not necessarily require a micro-beam (e.g., *FEMTO* and *in-situ* studies). The

second optical bench is hosting the KB mirror pair and is dedicated to micro beam applications. The beamline will be equipped with precise motorized sample stages (translations: x , y , z ; rotations: γ , θ , ω), which should allow – in addition to microXAS and XRF-mapping – for techniques such as Gracing-Incidence X-ray Absorption Fine Structure (GI-XAFS), x-ray reflectivity, and (rudimentary) micro-diffraction. It is foreseen that a motorized optical microscope and a CCD camera will be available for beam monitoring and sample alignment. Detector systems available in a first phase are photodiodes or ion-chambers for transmission experiments and a multi-element Ge solid-state detector and a Stern-Heald detector system for measurements in fluorescence and electron-yield mode, respectively.

The control hutch consists of a control room (C), a small laboratory for sample preparation procedures and the preparation of *in-situ* experiments (D), and a small room offering working space for users (E). As far as possible, the surveillance and operation of the entire microXAS station is to be done from the control room. There will be a series of computers and screens that will display information on the beamline status (e.g., positions of motors, valves, gauges) and real time camera images from components in the optical and experimental hutch. The *FEMTO* laboratory (F) is built adjacent to the control room. It is equipped with optical tables hosting lasers, amplifiers, oscillators and diagnostic tools. Because the lab is supposed to act as a main future laser lab at PSI, the lab should be available anytime for laser experiments from different PSI departments.

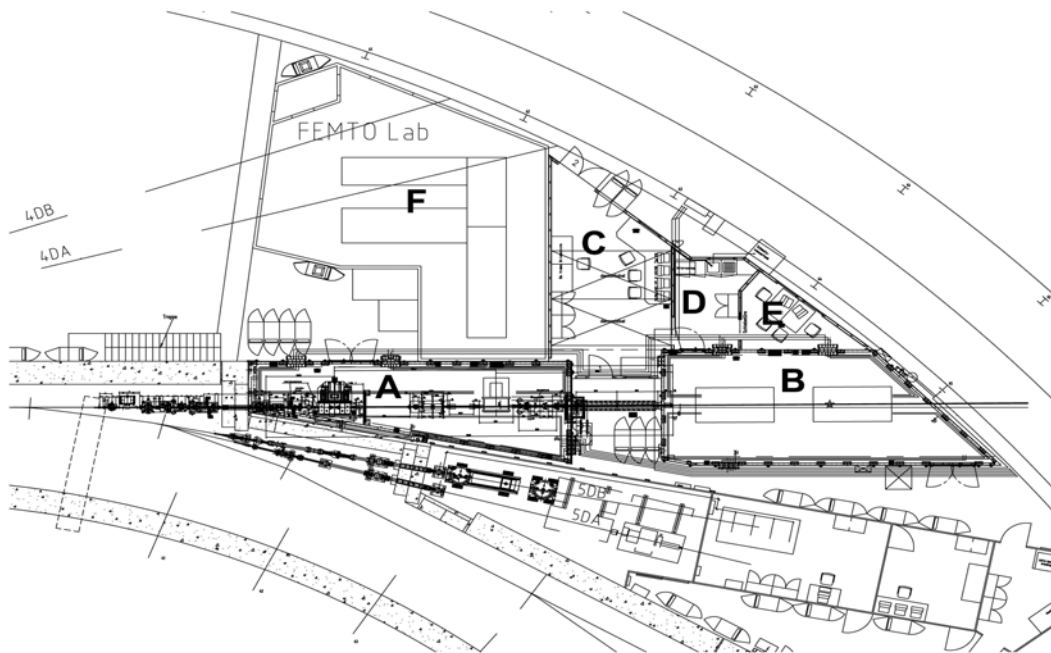


Fig. 8.4: Schematic illustration of the microXAS beamline layout.

8.5 Bright, micro, and ultraFAST!

Only over the past few years, ultra-fast chemistry ('femto-chemistry') has developed into a vital and promising scientific discipline. The largest part of the recent advancement is based on new developments in the area of femto-second spectroscopic techniques.

In 'classical' chemistry, a chemical reaction describes the transition from reactants to products by specifying both the end members. However, the outcome of a chemical reaction is the result of a complex interference of different possible molecular pathways. A detailed description of each reaction sequence corresponds to an important prerequisite in order to improve our understanding of natural or man-made chemical processes. In addition, knowing reaction pathways would allow to induce distinct perturbations forcing the system along a well-defined reaction channel, resulting in a *designed outcome* of a chemical reaction.

Concerning the identification of reaction pathways, x-ray spectroscopy could provide essential structural information revealing the nature of activated and transient species. X-ray Absorption Near Edge Structure (XANES) Spectroscopy is an ideal tool for studying the electronic structure of excited and ground state species while Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy has unique capabilities to elucidate the local chemical environment (geometrical structure). However, the different sequences building up a reaction follow each other extremely rapidly, occurring on the very short timescale of femtoseconds to picoseconds. Most recently, different schemes involving ultra-short X-ray pulses have been proposed (SCHOENLEIN et al. 2000). Sub-picosecond, high brilliant X-rays would enable *time-resolved laser/X-ray pump-probe experiments* to study on a short timescale structural dynamics and order-disorder phenomena in condensed matter and biological systems as well as ultra-fast photochemical reactions.

Without doubt, ultrafast, time-resolved x-ray experiments are on the frontier of synchrotron radiation science. The availability of a tunable femto-second x-ray source will open new and unique research opportunities in chemistry, biology, and materials science. Most recently, a team researcher lead by the University of Lausanne demonstrated successfully the feasibility of such ultrafast XAS experiments using

XANES and EXAFS to identify changes in oxidation state as well as structural coordination of activated organo-metallic complexes (BRESSLER et al., 2003; Fig. 8.5).

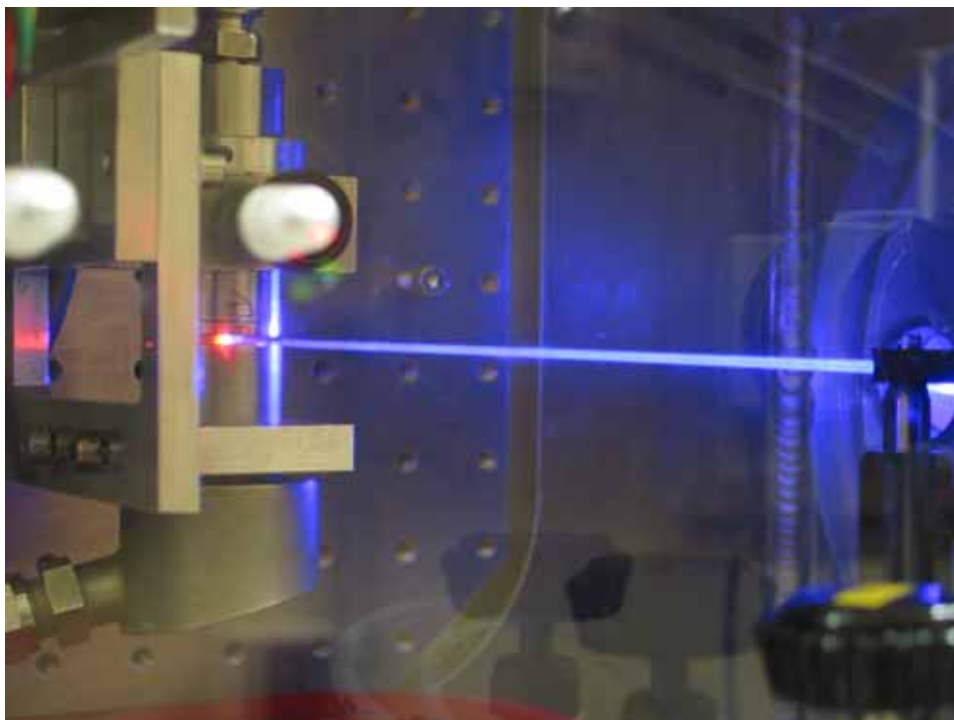


Fig. 8.5: A titanium-sapphire femtosecond laser served as the pump for the 'laser pump - x-ray probe' measurements. For details see ALS Science Highlights, (http://www.als.lbl.gov/als/science/sci_archive/65photochemical.html) (BRESSLER et al.).

At present, a source for ultra-short X-ray pulses is at an advanced design stage at the Swiss Light Source (SLS). To generate sub-ps hard X-ray pulses at the SLS storage ring, the laser/e-beam 'slicing' method will be used. From a research and development point of view, the 'slicing' source corresponds to an intermediate step towards laser-seeded high-gain Free Electron Lasers (FEL's). The SLS 'FEMTO source' is designed to deliver 100 fs X-ray pulses in the energy range of 5-20keV. The 'FEMTO source' will be providing ps- and sub-ps X-ray pulses for the microXAS beamline.

8.6 Measurements of Active Samples

As described in more details in the LES Progress Report 2002, a concept for working with active samples at the microXAS beamline has been worked out. Meanwhile remaining open questions have been solved and the concept has been approved by the

safety department at PSI (RESTANI et al. 2003). Nevertheless there are important items to be mentioned:

- The dose rate will be limited to 20 $\mu\text{Sv}/\text{week}$ outside the hutch.
- PSI has the approval to transport small amounts of spent fuel from the 'Hotlab' to the SLS (requires information of 'Bundesamt für Gesundheit' (BAG) and HSK).
- The SLS hall is a non-controlled area (zone 0) in which no contamination is allowed. In case a contamination occurs that can not be cleaned up within one day, the authorities must be informed ('meldepflichtiges Ereignis').

As next steps, the construction of the sample holder and the loading box at the 'Hotlab' can be initiated. Furthermore, a detailed description of the loading and measurement procedures is required. The safety department at PSI will inform the BAG about the project (including time schedule) and organize a common meeting in which the concept will be presented and potential unclear issues from the side of the authority can be addressed.

8.7 Personnel and time scale for realization

In July of 2003 Markus Willimann joined the beamline project. He is an electrical engineer and has an in-depth experience in developing soft- and hardware related to the controlling of motors (robotics). Markus Willimann will be responsible for the implementation of the control electronics of various hardware components. Furthermore, he acts as a link to the SLS control group and will work on the beamline control software. During the beamline commissioning phase (see below) additional man-power from LES personnel is mandatory (R. Dähn and M. Harfouche (new Postdoc starting in September 2003)). With respect to the design of the sample holder and the loading box for active samples at the 'Hotlab', we anticipate man-power support (G. Kuri) from side of the Laboratory for Materials Behaviour (LWV) at PSI.

In 2002/2003 the work focused on the specification and evaluation of key beamline components (call for tenders, WTO). Furthermore, the design of the beamline layout with respect to the FEMTO project has been finalized. A major milestone was the installation of the shielded optical and experimental Pb hutches by *Caratelli Co.* After

the construction of the control hut, the work currently focuses on the installation of the beamline infrastructure (cooling and electric media, air-conditioning, network) and the layout of the Equipment Protection System (EPS) and the Local Access Control (LAC). As the first component in the optical hut, the mirror tank (*Instrument Design Technology Ltd.*) was installed in August 2003. The monochromator will be delivered in October 2003 and the X05L beamline front end will be installed during the October/November shutdown. The beamline assembly, up to the experimental hut, will be completed in December 2003. The mirror (*Seiso*) and the insertion device (U19; *Sumitomo, Spring-8*) will be installed in February 2004. Thereafter (spring 2004) we plan to have the first synchrotron light in the experimental hut. The delivery of sophisticated equipment such as the multi-element solid state Ge detector (*call for tender is running*) and the Kirkpatrick-Baez (KB) mirror system (*in evaluation*) will be expected in the summer of 2004. The remaining part of 2004 will be dedicated to the beamline commissioning. We anticipate that the beamline will be open for users in 2005.

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SCHEIDEGGER, A.M., GROLIMUND, D., CHEESEMAN¹, C.R. (2002) A microspectroscopic study on the influence of the inherent heterogeneity of waste repository materials on contaminant uptake. *Geochim. Cosmochim. Acta.* **66(15A):A676-Suppl.1.**

¹ Department of Civil and Environmental Engineering, Imperial College of Science Technology and Medicine, London, England

SCHEIDEGGER, A.M., GROLIMUND, D., DÄHN, R., BONHOUR., I., WIELAND, E., CUI¹, D. (2003) The use of XAFS in Nuclear Waste Management, Invited talk at the International XAFS XII Conference, Malmö, Sweden.

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SCHEIDEGGER, A.M., GROLIMUND, D., DÄHN, R., BONHOUR, I., CUI¹, D. Use of X-ray absorption spectroscopy (XAS) to study radionuclide uptake on nuclear waste repository materials. Invited talk at the 225th American Chemical Society Meeting, New Orleans, USA, March 2003.

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8.9.2 Others, Teaching

GROLIMUND, D. Honorary Lecturer, Department of Civil & Environmental Engineering, Imperial College of Science, Technology and Medicine, London, UK.

SCHEIDEGGER, A.M. Privatdozent at the Swiss Federal Institute of Technology (ETH), lecture entitled 'Introduction and Applications of Synchrotron Radiation in Environmental Science, Chemistry, Physics, and Biology', WS 02/03.