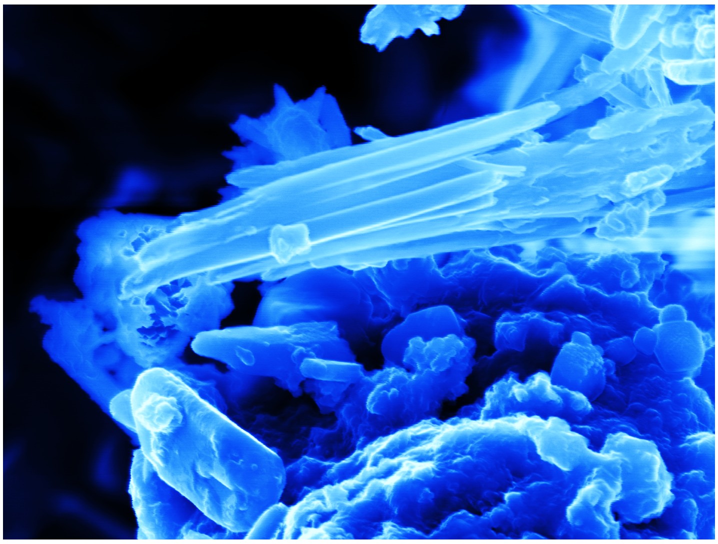
5th International Workshop on

# "Mechanisms and Modelling of Waste / Cement Interactions"



Karlsruhe, Germany, March, 25th – 27th, 2019

Karlsruhe Institute of Technology

# Book of Abstracts

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## *Scope and Background*

The workshop “Mechanisms and Modelling of Waste/ Cement Interactions” focuses on the chemical understanding and the thermodynamic modelling of the processes responsible for the stabilization of hazardous and radioactive wastes in cementitious systems. Like the very successful earlier meetings in this series of workshops (Meiringen, 2005; Le Croisic, 2008; Ghent 2013; Murten, 2016), the 5th workshop intends to bring together world-leading and junior scientists from the different branches of the research communities.

Although many research activities related to cement chemistry take place in the waste management field, there is an ongoing need for close scientific contact to fundamental research on cement chemistry to assure state-of-the-art research and to continue to promote national and international collaboration.

## Topics

The workshop aims at exchanging state-of-the-art knowledge on chemical and physical processes of waste/cement interactions.

- **Cement Chemistry & Microstructure (CEM/STRUC)**
  Modelling, multiscale-approaches, alternative cements
- **Cement/Rock/Soil Interfaces and Transport (CEM/ROCK)**
  Cement / host rock, transport processes and modelling
- **Interaction of Cement with Waste Constituents (CEM/WASTE)**
  Radioactive waste, toxic waste, metal binding mechanisms, organic compounds
- **Nanoscale Characterization & Molecular Dynamics (NANO/MD)**
  Methods at large scale facilities, advanced methods
- **Deterioration and Leaching (LEACH)**
  Alkali-aggregate reaction, carbonation, sulfate interaction, ageing process, natural analogues

## Key Dates

| | |
|---|---|
| February 15, 2019: | Deadline for registration |
| March 25-27, 2019: | Workshop in Karlsruhe |
| April 1, 2019: | Start of full paper submission |
| July 1, 2019: | Deadline for submission of full paper for special issue in Appl. Geochem. |

## Call for Papers

Submission of full papers will be appreciated after the workshop until July 1, 2019. Submitted papers will be subjected to a scientific review process and, if accepted, published in a special issue of Applied Geochemistry. The format of manuscripts follows the rules of Applied Geochemistry. Further details regarding the manuscripts will be given by the managing editor of the special issue during the workshop.

## Location

The workshop will be held at the ACHAT Plaza Hotel in the city of Karlsruhe, Germany. (http://www.achat-hotels.com/de/hotel/karlsruhe-city).

Karlsruhe is located less than two hours from the international airports of Frankfurt, Baden, Basel, Strasbourg or Stuttgart and can be easily reached by car or via train connections from all major German cities.

## Accommodation

The participants are kindly asked to arrange their own accommodation. In the ACHAT Plaza Hotel, an allotment of rooms is arranged (until February 28) for a special offer to workshop participants.

## Registration

The registration fee is 350 EUR. Registration includes admission to the workshop, coffee breaks, lunches, poster-buffet dinner, a workshop dinner at the Karlsruhe Palace and a booklet of abstracts.

# Program

**Monday 25th March 2019**

12:00 Registration – Conference office opens

13:45 Welcome address and practical information

## SESSION 1 CEM/WASTE 1

| *Chairs:* | *M. Altmaier (Germany) and B. Grambow (France)* | *page* |
|---|---|---|
| 14:00 | A GEOCHEMICAL MODELLING APPROACH FOR PREDICTING LONG-TERM WASTE-CEMENT INTERACTIONS<br>*Wieland, E., Kosakowski, G., Lothenbach, B., Kulik, D.A. (Switzerland)* | **106** |
| 14:20 | REACTIVE TRANSPORT AND TRITIUM TRANSPORT MODELS IN CONCRETE CELLS FOR STORING RADIOACTIVE WASTE<br>*Chaparro, M.C., Saaltink, M.W. (Germany)* | **19** |
| 14:40 | SURFACE COMPLEXATION MODELING OF NICKEL SORPTION UNDER VARYING GEOCHEMICAL CONDITIONS<br>*Um, W., Park, J. (South Korea)* | **99** |
| 15:00 | MECHANISMS OF ANION EXCHANGE IN HYDRATED CALCIUM ALUMINATES<br>*Grangeon, S., Marty, N., Claret F. (France)* | **41** |
| 15:20 | THERMODYNAMIC MODELLING OF An & FP UPTAKE IN C-S-H<br>*Kulik, D.A., Miron, G.-D., Lothenbach, B. (Switzerland)* | **62** |
| 15.40 | **COFFEE BREAK** | |

## SESSION 2 CEM/ROCK 1

*Chairs:* *J. Cama (Spain) and V. Metz (Germany)* *page*

## SESSION 3 POSTER SESSION (19:00 – 22:00)

Incl. Dinner buffet

**Tuesday 26th March 2019**

## SESSION 4 CHEM/STRUC 1

| *Chairs:* | *B. Lothenbach (Switzerland) and F. Claret (France)* | *page* |
|---|---|---|
| 08:30 | THERMODYNAMIC DATA FOR MAGNESIUM PHOSPHATE CEMENTS<br>*Lothenbach, B., Xu, B., Winnefeld, F. (Switzerland)* | **69** |
| 08:50 | HTO AND CHLORIDE-36 DIFFUSION ON PORTLAND-TYPE AND LOW PH CEMENTITIOUS MATERIALS<br>*Rosendorf, T., Červinka R., Vopálka D., Večerník P. (Czech Republic)* | **84** |
| 09:10 | LOW-PH CEMENTS BASED ON BLENDS OF MGO AND HYDROMAGNESITE<br>*Winnefeld, F., Epifania, E., Montagnaro, F., Gartner, E.M. (Switzerland)* | **107** |
| 09.30 | PERFORMANCE EVALUATION OF NEW HYDRAULIC BINDERS IN INFRASTRUCTURES WITH A SULFATE SOURCE: INSIGHT FROM MODELING AND EXPERIMENTS<br>*Tapsoba, N., Serclerat, I. Sabio, S., Meulenyzer, M., Huet, B., Brouard, E., Barbarulo, R., Albert B. (France)* | **2** |
| 09.50 | BORON AND HEAVY METAL BINDING POTENTIAL OF BELITE YE'ELIMITE FERRITE (BYF) CEMENTS<br>*Bullerjahn, F., Zajac, M., Skocek, J., Ben Haha, M. (Germany)* | **11** |
| 10.10 | **COFFEE BREAK** | |

## SESSION 5 CHEM/STRUC 2

## SESSION 6 CEM/WASTE 2

*Chairs:* *X. Gaona (Germany) and E. Wieland (Switzerland)* *page*

## SESSION 7 CEM/ROCK 2

**Wednesday 27th March 2019**

## SESSION 8 CEM/WASTE 3

| *Chairs:* | *C. Cau Dit Coumes (France) and C. Landesman (France)* | *page* |
|---|---|---|
| 08:30 | EXPERIMENTAL AND MODELING EFFORTS TO PREDICT LONG-TERM INTERFACIAL GEOCHEMISTRY OF SALT WASTE WITH CONCRETE VAULTS AT U.S. DOE DISPOSAL SITES<br>*Garrabrants, A.C., Zhang, P., Van der Sloot, H.A., Kosson, D.S., Brown, K.G. (USA)* | **39** |
| 08.50 | $UO_2$ DOPED DISOLUTION STUDIES UNDER CEMENTITIOUS STORAGE CONDITIONS<br>*Rodríguez-Villagra, N., Fernández, S., Anta, L., Durán, S., Cobos, J. (Spain)* | **83** |
| 09.10 | ON THE VERY LOW SOLUBILITY OF Np(V) HYDROXIDE SOLID PHASES IN ALKALINE SOLUTIONS CONTAINING (SUB)MILLIMOLAR CONCENTRATIONS OF $Ca^{2+}$<br>*Fellhauer, D., Gaona, X., Altmaier, M., Geckeis, H. (Germany)* | **29** |
| 09.30 | SORPTION BEHAVIOR OF SMALL ORGANIC COMPOUNDS ONTO CEMENTITIOUS MATERIALS: INTERACTIONS AND COMPETITION EFFECTS WITH THORIUM<br>*Olmeda, J., García, D., Henocq, P., Robinet, J.-C., Grivé, M. (Spain)* | **37** |
| 09.50 | INVESTIGATION OF THE UPTAKE OF Th, U, Np, Pu AND Am BY CALCIUM-SILICATE-HYDRATE PHASES<br>*Häußler, V., Amayri, S., Beck, A., Platte, T., Prieur, D., Roßberg, A., Stern, T.A., Vitova, T., Reich, T. (Germany)* | **48** |
| 10.10 | **COFFEE BREAK** | |
| 10.40 | SOLUBILITY AND SORPTION OF Be(II) IN CEMENTITIOUS SYSTEMS<br>*Cevirim-Papaioannou, N., Gaona, X., Han, S., Ait Mouheb, N., Böttle, M., Gaboreau, S., Claret, F., Um, W., Altmaier, M. (Germany)* | **17** |
| 11.00 | MOLYBDENUM ADSORPTION ONTO CEMENT HYDRATES. THE ROLE OF C-S-H AND AFM PHASES<br>*López-García, M., Olmeda, J., Grivé, M., Henoqc, P. (France)* | **65** |

## SESSION 9 LEACH

| Chairs: | *H. van der Sloot (The Netherlands) and D. Jacques (Belgium)* | *page* |
|---|---|---|
| 11:20 | ESTIMATES OF MINERAL STABILITY CONSTANTS DERIVED FROM PH DEPENDENCE LEACHING TEST DATA FOR GEOCHEMICAL MODELLING OF CEMENT-BASED WASTE SYSTEMS<br>*van der Sloot, H. A., Kosson, D.S. (The Netherlands)* | **101** |
| 11:40 | THE INTERACTION OF ACID MINE DRAINAGE WITH PORTLAND CEMENT AND ROCK<br>*Cama, J., Soler, J.M., Gutiérrez-Leon J., Fernández-Rojo L., Pérez-Hueros P. (Spain)* | **13** |
| 12:00 | STABILIZATION OF SOILS CONTAINING SULFATES BY USING HYDRAULIC BINDERS<br>*Diaz Caselles, L., Hot, J., Cyr, M. (France)* | **28** |
| 12:20 | **LUNCH BREAK** | |
| 14:00 | CHEMICAL AND MICROSTRUCTURAL EVOLUTION OF LOW-PH CEMENTITIOUS MATERIALS EXPOSED TO CALCAREOUS WATER: LAB EXPERIMENTS AND MODELLING<br>*Dauzères, A., Grellier, A., De Windt, L., L'Hôpital, E., Neji, M. (France)* | **76** |
| 14.20 | MODELING OF STRONTIUM LEACHING FROM CARBONATED PORTLAND CEMENT PASTES USING A SIMPLIFIED DIFFUSION-KINETIC ANALYTICAL MODEL<br>*Boukobza, E., Bar-Nes, G., Klein Ben-David, O., Carmeli, B. (Israel)* | **9** |
| 14.40 | UNDERSTANDING CEMENTITIOUS BACKFILL INTERACTIONS WITH GROUNDWATER COMPONENTS<br>*Heath, T., Schofield, J., Shelton, A. (UK)* | **49** |
| 15.00 | A CONTINUUM MODEL COUPLED DIFFUSION, MICROSTRUCTURE AND GEOCHEMICAL TO DESCRIBE COMBINED CARBONATION-LEACHING OF CEMENT PASTES IN A CLAY ENVIRONMENT<br>*Phung, Q.T., Jacques, D., Maes, N. (Belgium)* | **81** |
| 15.20 | COMPARISON OF EXPERIMENTAL AND MODELLED LEACHING OF CEMENTITIOUS MATERIALS IN NUCLEAR WASTE REPOSITORY ENVIRONMENT<br>*Vehmas, T., Leivo, M., Holt, E. (Finland)* | **104** |
| 15.40 | **COFFEE BREAK** | |
| 16.10 | ALTERATION OF CHEMICO-PHYSICAL PROPERTIES OF ORDINARY CEMENT PASTE USED IN NUCLEAR WASTE DISPOSAL SUBJECTED TO COMBINED CARBONATION AND LEACHING DEGRADATION<br>*Hoder, G., Ye, G., Maes, N. (Belgium)* | **54** |

## SESSION 10 NANO/MD

*Chairs:* *P. Stemmermann (Germany) and V. Metz (Germany)* *page*

17:50 END OF WORKSHOP

## **Poster Presentations** (in alphabetical order of presenting author)

# DIFFUSION OF TRITIATED WATER THROUGH LOW pH CEMENTS

Ait Mouheb, N.[a]; Montoya, V.[a]; Joseph, C.[a]; Schäfer, T.[a,b]; Geckeis, H[a].

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Low pH cement is investigated as potential barrier material in deep geological repositories for nuclear waste. During the relatively long period of disposal, this material will undergo alterations, changing its chemical and physical properties affecting the migration of radionuclides. In order to determine its effectiveness as barrier, solute transport parameters in porous media, such as the effective diffusion coefficient, $D_e$, the accessible porosity, $\varepsilon$ and the correlation between them are needed to be implemented in complex coupled models. In this work an experimental and numerical methodology have been used to determine these required parameters.

First of all, a cylindrical diffusion cell has been designed, optimized, and constructed for performing through-diffusion experiments with tritiated water (HTO). The set-up consists of a thin cement sample of 10 mm thickness sealed with PMMA or araldite, mounted between two compartments, called high and low reservoir, with total volumes of 50 mL and 3.8 mL, respectively. The high reservoir is filled with water in equilibrium with each low pH cements (*pH* ~ 11 and *ionic strength* ~ $7.5\cdot10^{-2}$ M) and doped by HTO with an initial concentration of $1.86\cdot10^{-9}$ M. The low reservoir is filled with the same aqueous solution without HTO. The experiments were conducted during 60 days, inside a glove box under controlled Ar atmosphere in order to avoid carbonation of the alkaline waters. Three low pH cement pastes with different composition (MIX A, MIX B, and IRP) have been selected to perform the experiments. All the samples were mainly composed of C-S-H and C-A-S-H phases with Ca:Si ratios between 0.6 - 1.1 and Al:Si ratio of ~0.05. Unreacted silica fume is also present in all the samples. Ettringite is identified as a minor hydrated solid phase while limestone filler is present in MIX B, only, where it has been added initially for its manufacturing. Unreacted clinker (alite and belite) blast furnace slag, and quartz filler have been identified in IRP where low water/binder ratio was used. No portlandite or Friedel's salt are present in any of the samples.

Transport parameters were obtained by inverse modelling considering Fickian diffusion and using the finite element code Comsol Multiphysics 5.3 to solve the partial differential equations.

First approach used for fitting the experimental data was carried out by using a modified Archie's law $D_e = a\, D_w\, \varepsilon^{\,n}$ (with $n$ [-] as empirical constant depending on the pore geometry of the porous medium, $a$ as a fitting parameter, $D_w$ [m$^2$/s] as the diffusion coefficient of the ions being considered in free water, and $\varepsilon_c$ as the accessible porosity [-]. However, the transport parameters obtained were unrealistic without any physical meaning.

Therefore, a second approach developed in the National Institute of Standards and Technology "NIST", was used to fit the diffusion data. In this case, the correlation porosity-effective diffusivity used takes into account the percolating and non-percolating fraction of the capillary pores and the contribution of the C-S-H phase. Additionally, differences between low-density (LD) and high-density (HD) C-S-H content is considered. Finally, a good fit of the HTO diffusion data of MIX A and MIX B have been obtained by using the correlation developed in NIST.

**Acknowledgements:**

The research leading to these results has received funding from the European Union's European Atomic Energy Community's (Euratom) Horizon 2020 Program (NFRP-2014/2015) under grant agreement, 662147 – Cebama.

# PERFORMANCE EVALUATION OF NEW HYDRAULIC BINDERS IN INFRASTRUCTURES WITH ASULFATE SOURCE: INSIGHT FROM MODELINGAND EXPERIMENTS

Tapsoba, N.; Serclerat, I.; Sabio, S.; Meulenyzer, M.; Huet, B.; Brouard, E.; Barbarulo, R.; Albert,B.

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Hydraulic binders are ubiquitous to modern infrastructure. Very often they become in contact with sulfate rich system, as early as the curing or slowly over the life of concrete structure. If not properly chosen, cement paste structure may suffer from contact with sulfate as it is the case for internal or external sulfate attacks (ISA, ESA). However, if properly chosen, cementitious materials may show excellent performance. Performance criteria vary from one application to another and may include dimensional stability over time, sulfate retention in solids or leaching and always include mechanical property integrity. In this work, we present three applications of new hydraulic binder solutions: sulfate retention and soil stabilization, precast concrete for waste water and minimization of expansion due to ESA. All these applications include similar methods to analyze performance: phase assemblage, water composition, expansion or leaching tests and thermodynamic calculation or coupled reactive transport simulations.

Soil remediation and decontamination is a growing demand and comes with high stakes in terms of public health and environmental protection. Landfill of excavated soil from civil engineering construction, contaminated with sulfate and or heavy metals, obeys to strict regulation. The landfill classes range from Class I (hazardous waste) to Class III (inert waste). The more the soil is considered dangerous, the more landfill constraints and regulations are stringent and therefore costly. The inertization and immobilization of the contaminants with hydraulic binders is an interesting path of valorization, in terms of economical and environmental considerations. For this application, lab results according to the standard EN 12457-2, with innovative binders are presented. The treatment allows for trapping rapidly, durably and extensively anions such as sulfate and heavy metal ions and thereby for treating soils contaminated with such pollutants, limiting further their leaching and reducing their environmental impact. Trapping mechanisms and retention stability over time are confirmed by reactive transport tools.

In high sulfates medium, it is well known that concretes can be subject to deleterious swellings if they are not designed in a particular way (OPC with vey C3A content, limitation of water to cement ratio, use of addition like slag among other formulation parameters). We show that calcium sulfoaluminate cements, more or less belitic, make it possible to manufacture mortars with performing dimensional and mechanical stability. Expansion and mineralogical transformations occurring during the long-term tests (>2 y.) are discussed, on the basis of experimental results and modeling.

In sewer networks precast concrete are exposed to H2SO4 leading to cement paste leaching and expansive reactions (gypsum and/or ettringite). Both chemical and biological resistance should be combined. Mainly ordinary binders (OPC, OPC with/without slag) and CAC have been tested in these conditions. The better resistance of CAC is not very well understood but it is generally assigned to the stability of AH3. However, the origin of its biological resistance – often related to the inhibitory potential of aluminum on bacterial activity – is still not known. Reactive transport models calibrated against laboratory results are used to characterize phase assemblage and aqueous species profiles for both OPC and CAC in presence of sulfuric acid. We highlight the impact of the sulfate concentration and pH of the aggressive solution and binder type on secondary phase nature and location over time.

# GROUND WATERS INTERACTION WITH EBS FOR HLW: FROM LABORATORY TO IN-SITU SPATIAL AND TIME SCALE UP

Turrero, M.J.[2]; Cuevas[3], J.; Alonso[1], M.C.; Fernandez, A.[1]; González-Santamaría, D.E.[3]; Fernández, R.[3]; Garcia-Calvo-J.L.[1]; Ruiz, A.I.[3]; Torres, E.[2]

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Simulated experiments in laboratory of the real site conditions of a DGR are used for the models of the long term performance of the EBSs. However, the scale up differences in time and space of the laboratory experiments respect to real-site is not an easy task to validate and contrast the information. This article analyses the knowledge acquired from the characterization of the FEBEX concrete plug which has been operating for 13 years in the Grimsel Test Site. During this time the concrete has interacted with granite groundwater and also with the bentonite porewater. In parallel, laboratory experiments of different sizes and age have been carried out. The spatial and temporal differences and parallelism are analysed and compared.

From the real site FEBEX 13 years experiment main alterations are characterized by low mineralogical alteration impact in bentonite that is only affected by a few millimetres. Accumulation of Mg at the bentonite side of the interface, precipitating as silicates in various forms, and heterogeneous carbonation at the interface, but mostly affecting the concrete side, have been determined at the different scales. Transport of aqueous species, being the most relevant the diffusion of chloride and sulfate from bentonite to concrete, are better observed in large scales in concrete materials. Processes determined at long term and large scale at the concrete interface are: (1) leaching of concrete with subsequent portlandite dissolution, and secondary ettringite formation, (2) progressive dissolution of C-S-H gels with incorporation of Al, and Mg and (3) friedel salt formation.

Three types of laboratory experiments were simulated. Type 1 experiments include concrete cores taken from the FEBEX plug, far from the altered zones (granite and bentonite). The cores were contacted with simulated FEBEX bentonite porewater, ponding transport tests were carried out during 6, 9 and 12 months and interaction processes were analysed. The transport of Cl, sulfates, alkalis and Mg is demonstrated. From the initial stages of interaction, the formation of new solid phases similar to those found in the Grimsel experiment, ettringite, friedel salt and calcite that extend up to 1 cm in the concrete is detected. CaO and $SiO_2$ from the CSH are also altered. Type 2 experiments consist of long-term (10y) concrete (CEM-I)-bentonite interaction under heat gradient (hot bentonite to cold concrete). Secondary ettringite in concrete and 1-2 mm thickness Mg accumulation was observed in bentonite, in which soluble salt migration was observed towards the heated bentonite, coupled with redistribution of exchangeable cations ($Na^+$ and $Ca^{2+}$ concentrated at the concrete and $Mg^{2+}$ and $K^+$ towards the hottest parts. Type 3 experiments are made of new mortar samples prepared with CEM-I and CEM-II (high pH) cement in contact with FEBEX bentonite, that have run for 4, 6 and 18 months. Their micrometric chemical profiles reproduced, in 100 µm to 1mm thickness, the characteristic elemental gradients of Mg-perturbation in the bentonite and carbonation towards the cement materials were followed. These processes of mineralogical alteration are clearly developed in 10 to 13year time scale experiments within < 5mm distance from interface.

- *Alonso et al. 2017.* Interaction processes at the concrete-bentonite interface after 13 years of FEBEX-Plug operation. Part I: Concrete alteration. Phys. Chem. of the Earth, 99: 38-48.
- *Fernández et al. 2017*. Interaction processes at the concrete-bentonite interface after 13 years of FEBEX-Plug operation. Part II: Bentonite contact, Phys. Chem. of the Earth, 99: 49-63.

Acknowledgements: This work was financially supported by the European Union's Horizon 2020 grant agreement n° 662147 (www.cebama.eu).

# SORPTION AND SPECIATION OF Pu ON HARDENED CEMENT PASTE (HCP)

Amayri[1], S.; Häußler[1], V.; Hagenlocher[1], D.; Meyer[1], C.-Ch.; Prieur[2], D.; Roßberg[2], A.; Scholze[1], R.; Stern[1], T.; Reich[1], T.

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Cement-based materials are considered as construction material in the engineered barrier system of high-level nuclear waste repositories [1]. Cement has well-known mechanical properties, low permeability and a significant affinity for radionuclides (RN). Long-lived plutonium ($t_{1/2}(^{239}Pu) = 2.44 \times 10^4$ a) and minor actinides such as americium ($^{241}Am$) contribute significantly to the long-term radiotoxicity of nuclear waste. For performance assessments, an understanding of the immobilization of RN in cement is required. Therefore, we investigated the uptake of redox sensitive $^{239}Pu(III)$ and redox-stable analogues $^{234}Th(IV)$ and $^{241}Am(III)$ by ordinary Portland cement. Batch sorption experiments were performed in dependence of the pH (9 – 13) and the solid-to-liquid ratio (S/L: 0.5 – 15 g/L) with a contact time of 72 h under Ar atmosphere. For obtaining a molecular-level understanding of the interaction between Pu and crushed hardened cement paste (HCP), X-ray absorption fine structure (XAFS) spectroscopy was applied to determine the near-neighbor environment of Pu and its oxidation state after the uptake of Pu(III) by HCP. Samples were prepared in different background electrolytes (diluted cap rock solution (ger. verdünnte Gipshutlösung, abbr. VGL) as a reference pore water for clay formations in Northern Germany and artificial cement pore water obtained by leaching of HCP (W/C = 0.5) in VGL for one week (abbr. VGL-ACW)) at pH values of 10.4 and 12.7. Radionuclide concentrations in batch experiments were $1 \times 10^{-7}$ mol/L ($^{234}Th$) and $1 \times 10^{-8}$ mol/L ($^{241}Am$ and $^{239}Pu$) and $5 \times 10^{-6}$ mol/L in the samples for the spectroscopic investigations.

Our results obtained from batch experiments in VGL show high affinities of RN for Portland cement (quantitative uptake > 93%). At pH values > 9 the average logarithmic distribution coefficients (log $R_d$ in L/kg) were between 3.5 and 5.6 for all investigated RN, independent of the S/L ratio. Our results are in a good agreement with available literature data for Th(IV) and Am(III) with log $R_d = 5$ [2].

Pu $L_{III}$-edge XANES spectra confirmed that in all investigated samples Pu(IV) is the dominating oxidation state after uptake of Pu(III) on HCP. At pH 12.7 the background electrolyte does not influence the coordination environment of sorbed Pu on HCP. Furthermore, our results indicate that Pu is mainly incorporated in the calcium silicate hydrate phases (C-S-H) of HCP. Under nuclear repository conditions, cement-based materials have a high immobilization potential for Pu and other RN.

This work was financially supported by the Federal Ministry for Economic Affairs and Energy (BMWi) under contract No. 02E11415A.

## References

1. Jobmann, M., Lommerzheim, A., 2015. Projekt ANSICHT, DBE Technology GmbH TEC-26-2015-TB.
2. Wieland, E., 2014, Nagra Technical Report NTB 14-08, Nagra, Wettingen, Switzerland.

# MOLECULAR DYNAMICS MODELLING OF THE INTERACTION OF URANIUM (VI) WITH C-S-H PHASES IN THE PRESENCE OF ORGANIC ADDITIVES

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Cementitious materials are extensively used in the design and construction of geological radioactive waste repositories in the argillaceous rock (Callovo-Oxfordian geological formation) in the East of the Parisian basin. They can be both part of the packaging for some intermediate level waste or part of the sealing material for storage cells, and also a construction material for the galleries and access shafts of the waste storage facilities. During cement paste production, organic additives (e.g., superplasticisers) are often used to enhance mechanical properties of the final cement material. The presence of potentially reactive chemicals may affect the mobility of radionuclides and cause additional safety concerns. So, even though the amount of organic additives is usually quite small, the mechanisms of their interactions with all components of the waste storage system should be systematically studied, described and understood.

To study molecular interactions in a generalized ternary system cement – radionuclides – organic additives we have developed several representative models consisting of three principal components: pure calcium silicate hydrate (C-S-H) phases corresponding to different Ca/Si ratios; gluconate, a simple well-described molecule, as a representative of organic additives; U(VI), as one of the most studied radionuclides in actinide series. Structural, energetic, and dynamic aspects of the sorption processes on the surface of cement of uranyl, gluconate, and their mutual correlations were quantitatively modeled by molecular dynamics (MD) technique. This study has provided an insight of what are the preferential sorption sites on the surface. Adsorption free energy profiles (potentials of mean force) for various solution species as functions of their distance from the surface were then calculated using the “umbrella sampling” algorithm to probe site-specific surface adsorption (Fig.1.).

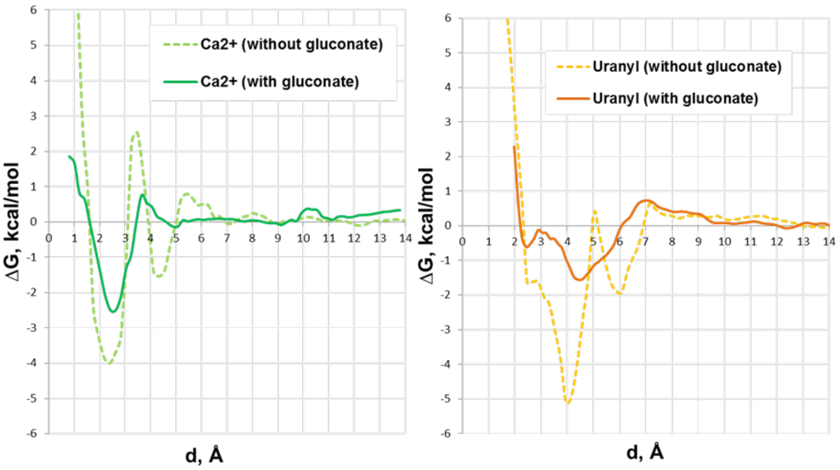

**Figure 1:** Potentials of mean force calculated as functions of distance between the interfacial $Ca^{2+}$ and $UO_2^{2+}$ ions and a deprotonated silanol group of the bridging Si-tetrahedron on the C-S-H surface with and without a gluconate ion in the nearest solution environment.

It is known that pH of the solution has an important influence on the speciation and behavior of ions on the interfaces. A separate study is designed to understand how the presence of negatively charged hydroxyl ions in the first coordination sphere of cations ($Ca^{2+}$ and $UO_2^{2+}$) affects their adsorption behavior and potential formation of multinuclear surface complexes that include organic ligands. It has been confirmed that hydroxyl complexes of uranyl cations can form relatively stable and strong bridging complexes with $Ca^{2+}$ in aqueous solution and near the C-S-H surfaces.

# ANALYSIS AND RESULTS OF CLAYSTONE / CEMENT PASTE INTERFACES BY SEM/EDS, µ-XRD, AND FTIR MAPS FOR PROCESS UNDERSTANDING

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The safety of a geological repository designed for deep storage of nuclear waste rests on the long-lived isolation properties of the geological environment and the anthropogenic underground facility. To study the chemical and physical behaviors of cementitious/clayey interfaces, such interfaces had been collected during repeat sampling campaigns of the CI Experiment (Cement-Clay Interaction Experiment) at the Mont Terri rock laboratory (St. Ursanne, Switzerland, www.mont-terri.ch) over the last decade.

Mäder et al.[1] summarized and compared the main findings regarding mineralogy and porosity alterations. Studies [2-5] involving SEM/EDS, TEM/EDS, EPMA, EDAX, Raman, FTIR, XRD helped to understand the processes. The high pH (Portland) and low pH cement pastes feature a de-calcification zone at the interface associated with an opening of the porosity along with a carbonation. While the Portland concrete showed a distinct sulphate enrichment zone, indicating an ingress from Opalinus Clay, the low pH concrete displayed a wide magnesium enriched zone. However, some processes have still to be explained.

This present study focuses on advanced analysis as µ-XRD and FTIR maps to locate and identify the mineral phases on each side of the interface. The identification of mineral phases involved in reactions facilitates the understanding of the processes, thus, will help to improve the reactive transport models used to simulate the evolutions over long times.

Additionally, the reactive transport properties of the same type of interface were investigated by a percolation experiment to also constrain hydraulic properties: a cylindrical container including the interface sample under confining pressure with independent infiltration driven by a hydraulic gradient. Similar SEM/EDS and FTIR map analysis were performed post mortem.

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# MODELING OF STRONTIUM LEACHING FROM CARBONATED PORTLAND CEMENT PASTES USING A SIMPLIFIED DIFFUSION-KINETIC ANALYTICAL MODEL

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One of the main challenges in nuclear waste management is to predict release of radionuclides during their long-term disposal within an intact matrix in the repository. One way to tackle this challenge is to conduct leaching experiments which emulate radionuclide release under extreme conditions in a relatively short time. In this work we present a simple analytical diffusion-kinetic model for strontium leaching from cylindrical samples of Portland cement paste [1]. The model accounts explicitly for both strontium diffusion and strontium carbonate precipitation. We compare this model with a standard diffusion model, and demonstrate that it better fits experimental strontium leaching data from samples that showed minor carbonation, as well as samples that showed atmospheric carbonation. This diffusion-kinetic model gives rise to narrower prediction bounds and substantially smaller errors. Furthermore, it provides experimentalists conducting leaching tests an easily implementable tool to analyze their data in systems where precipitation is expected to occur. The approach presented here may serve as an alternative to a plain diffusion analysis often found in standardized leaching protocols, and to more intricate thermodynamic numerical software.

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# MIGRATON PROCESSES ON CEMENTITIOUS MATERIALS USED IN WASTE MANAGEMENT IN THE CZECH REPUBLIC WITH FOCUS ON $^{125}$I UPTAKE

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Cementitious materials are widely used in low level waste (LLW) and intermediate level waste (ILW) management in the Czech Republic, particularly as solidification material. Nowadays, cementitious materials are in focus also for disposal of high level waste (HLW) in deep geology repository (DGR), being considered both for waste solidification and construction of concrete containers. Using for such a purpose, cementitious materials are supposed to contribute to overall DGR safety function. A research program has been started with focus on migration of concerned radionuclides in order to evaluate all the chemical processes that the materials can undergo.

According to these presumptions, samples for experiments were chosen from the list of materials used in different stages of the Czech waste management program. In ÚJV Řež, Radioactive Waste and Decommissioning Division, CEM II type Ordinary Portland Cement (OPC) is used as a fixation matrix of radioactive wastes in the internal 100L steel drums. Concrete with CEM I type OPC is used as a sealing, reinforcement and first migration barrier surrounding the inner drum with fixed waste in the 200L steel container. Another studied material was a concrete mixture with CEM III type Ordinary Portland Cement which is used for fixation and closure of storage niches in the Richard LLW/ILW repository operated by SÚRAO (Radioactive Waste Repository Authority in the Czech Republic).

Studies of the contaminants migration processes consists mainly of diffusion and sorption experiments. First results from diffusion studies of $^{3}$H and $^{125}$I focused our attention on $^{125}$I uptake to the cement matrix. Tritiated water (HTO, $^{3}$H) was used as a representative non-interacting tracer. Radioisotope $^{125}$I was used as a short-lived alternative ($T½ = 59.4y$) for $^{129}$I isotope which is a significant long-lived fission product ($T½ = 1.6\times10^{7}y$).

Diffusion processes were studied using through diffusion method on the hardened cement paste and concrete samples (50mm in diameter, 10mm in length) in simulated ground water (SGW) saturated with portlandite $Ca(OH)_2$. Sorption batch experiments were performed to evaluate retention coefficients of tested contaminant ($^{125}$I) in saturated solution of portlandite. Tested materials were crushed and sieved to 0.25–1.0mm fraction.

Results from diffusion experiments showed relatively fast HTO diffusion through hardened cement past samples, on the other hand diffusion of $^{125}$I was not observed. Sorption experiments confirmed strong uptake of $^{125}$I from solution by cementitious materials.

All the results and obtained data should contribute to improvement of the performance and safety assessment of operating repositories. Moreover, they could be also used as an input for the DGR planning and performance and safety assessment of the DGR part, where cementitious materials will be used for waste fixation and disposal.

## Acknowledgement:

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# BORON AND HEAVY METAL BINDING POTENTIAL OF BELITE YE'ELIMITE FERRITE (BYF) CEMENTS

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Calcium sulphoaluminate cements (CSA) are a class of non-Portland cements where the main phase is ye'elimite ($C_4A_3\bar{S}$). CSA are considered as promising low-$CO_2$ binders [1]. Lately, a subclass of belite-rich CSAs, referred sometimes as belite ye'elimite ferrite (BYF) cements, are gaining increasing interest [2] [3]. The hydration of the cements based on these clinkers depends on the clinker composition [4] [5], the amount and reactivity of calcium sulfate [6]. In comparison to ordinary Portland type cements, CSA cements react faster, and most of the hydration heat evolution occurs between 2 and 12 h of hydration [7]. The hydration kinetics can be controlled by e.g. the use of retarders, whereby borates present a very promising solution [8] [9]. Additionally, studies on the treatment of boron-rich solutions from the storage of radioactive waste demonstrated an excellent boron immobilization potential of CSA type cements [10] [11]. Another interesting feature is the excellent heavy metal binding potential [11] [12] [13]. Especially, as there is increasing interest in the use of industrial by-products and wastes as main raw material sources for the production of CSA and BYF [4] [14]. Those materials often contain high contents of heavy metals. Consequently, the amount of those will rise in the clinkers produced from those materials and the heavy metal binding potential becomes of high importance.

The purpose of this study is to determine the effect of boron during the early hydration of BYF cement and its binding potential in the hardened cement matrix. Furthermore, the heavy metal binding potential of two chosen cements was investigated. Several borates, their impact on the hydration kinetics and on the properties of fresh mortar were investigated. Those experiments were supplemented with the analyses of the solution composition, focusing on the boron concentration, over the first seconds to hours of hydration. The determination of the leaching behavior and heavy metal binding potential was carried out in accordance to the procedure from the draft standard "Generic horizontal dynamic surface leaching test (DSLT) for determination of surface dependent release of substances from construction products". The leaching of Pb, Cd, Cr, Cu, Ni, V and B was followed, as well as of the main elements such as Ca, Al, S, etc. for the two reference cements. A second set of experiments were done, adding soluble salts of Pb, Cd, Cr, Cu, Ni, Tl and V to the mixing water to reach 1000 ppm of the respective heavy metal.

Boron effectively retards the hydration BYF type cements, independently of the type of borate used. The tested borates dissolved rapidly providing boron to solution. However, also the depletion of boron from solution occurs rapidly, within seconds to minutes after the mixing with water. Boron seems to be initially adsorbed on the formed amorphous hydrate(s). At later hydration times it is permanently bound in the cement matrix by ettringite and monosulfate. BYF cements demonstrated high heavy metals binding potential for all elements tested, even for mortars with 1000 ppm of heavy metals added as soluble salts.

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# THE INTERACTION OF ACID MINE DRAINAGE WITH PORTLAND CEMENT AND ROCK

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## Introduction

The main objective of this work is to better understand the interaction between Acid Mine Drainage (AMD) and concrete in AMD treatment plants and host rocks. The AMD-treatment plant at the Esperanza mine in the Iberian Pyrite Belt (Huelva, south Spain) is used as case study. Materials and methods

To this end, the following approach has been applied. First, concrete cores (2 - 6 cm long and 2.5 cm in diameter) were sampled at the 9-year-old Esperanza mine AMD treatment plant and were examined by SEM-EDS to characterize the degree of concrete alteration and by XRD-Rietveld analysis to identify the mineralogical content. Second, in the laboratory, column experiments (6 cm long and 2.5 cm in diameter) filled with alternating layers of Portland cement and siliceous limestone (composed of calcite, quartz, microcline, illite and ankerite), reacting with synthetic pH-2 AMD waters, were performed to identify the occurring reactions and consequent mineralogical changes (optical microscopy, SEM-EDS and XRD). Third, 1D reactive transport modelling was performed to reproduce the experimental variation in aqueous chemistry over time and to quantify processes. This allows us to compare the mineralogical alteration observed in the treatment-plant core samples with resulting mineral changes in the laboratory column experiments.

## Results and discussion

SEM-EDS inspection of thin sections along the concrete core samples showed that alteration mainly occurred at the concrete-AMD interface (top 2-3 mm), revealing dissolution features in the cement matrix. Alteration was not observed further into the cores. This suggests that for 9 years of treatment-plant operation the interaction between AMD and concrete mostly affected the upper contact area.

In the column experiments, the aqueous chemistry variation at the outlet showed an excess of calcium concentration, a deficit of sulphate concentration and an increase in solution pH up to about 12 initially and to about 6 later. SEM-EDS observations revealed an absence of portlandite in the cement matrix and the presence of newly formed gypsum, aragonite, brucite, and aluminum- and iron-hydroxides, which was confirmed by XRD-Rietveld analyses.

1D reactive transport simulations reproduced the variation of the aqueous chemistry over time, indicating that portlandite exhaustion was responsible for the initial high pH (about 12), that calcite dissolution later buffered the output pH at about 6, and that their dissolution released Ca for aragonite to precipitate at the cement layers. Sulphate deficit was caused by gypsum precipitation.

## Summary and conclusions

In the concrete core samples, mineralogical alteration occurred at the AMD-concrete interface, and it was characterized by dissolution features of the matrix-cement and by the presence of iron-rich phases. In the column experiments, dissolution of calcite (rock) and portlandite (cement) and precipitation of gypsum and aragonite were the main reactions during AMD circulation through layers of siliceous limestone and Portland cement. The high pH caused by portlandite dissolution led to precipitation of brucite and metal-hydroxides.

## Acknowledgements

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# ENCAPSULATION OF CATIONIC EXCHANGE RESINS USING PORTLAND CEMENT: WHY IS IT INTERESTING TO PRE-TREAT THE RESINS WITH A CALCIUM SALT?

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Ion exchange resins (IERs) are widely used by the nuclear industry to decontaminate radioactive effluents. Spent IERs have to be stabilized and solidified, that is placed under a solid, stable, monolithic and confining form. Calcium silicate cements offer many advantages for resins encapsulation: easy supply, simple process, good mechanical strength, compatibility with aqueous wastes, good self-shielding, and high alkalinity which makes it possible to precipitate and thus confine many radionuclides. However, several specificities of IERs must be taken into account to design a robust cement formula: *(i)* their ability to exchange ions with the cementitious medium, which may influence cement hydration, *(ii)* their low mechanical strength, which strongly weakens the strength of the solidified waste forms, and *(iii)* their strong dimensional variations which can, under severe conditions, induce swelling and cracking of the matrix. It is well known that the volume of IER beads in a saturated medium depends on their ionic form and on the osmotic pressure of the external solution. The first objective of this work is to quantify the volume change of IERs induced by a variation in these two parameters. Observations of IER beads using optical microscopy show that the resins tend to swell when the osmotic pressure decreases, with a higher volume change for resins in the sodium or potassium form than in the calcium form. Significant swelling also results from a change from the potassium or calcium to the sodium form (+6.1% and +5.6% respectively). The affinity of IERs for $Ca^{2+}$, $Na^+$ and $K^+$ cations is then compared by measuring the exchange constant between these cations. As expected, the higher the charge density of the cation, the higher the affinity of the resin for this cation ($Ca^{2+} > K^+ > Na^+$). The second objective of this work is to explain why a rapid expansion is observed at an early age when Portland cement is used to solidify cationic IERs saturated with sodium ($Na^+$-IERs), whereas no swelling is observed when the resins are initially in the calcium form. The mineralogy, interstitial solution composition and microstructure of Portland cement pastes containing resins initially saturated with $Na^+$ or $Ca^{2+}$ ions are characterized with ongoing hydration and compared to that of a reference without any resins. When the paste contains $Na^+$-IERs, ionic exchanges are observed with $Ca^{2+}$ and $K^+$ ions released by the dissolution of cement. These exchanges accelerate the dissolution process, leading to an accumulation of sulfate ions in solution, and to a rapid increase in the osmotic pressure of the pore solution. As a consequence, the resins shrink. Then, in a second stage, the osmotic pressure decreases for two reasons:

- the consumption of sulfate ions from the interstitial solution due to the precipitation of ettringite,
- a decrease in its sodium concentration due to the precipitation of sodium-bearing C-S-H.

Under these conditions, the IERs swell, and thus can damage the hardened matrix which is still poorly consolidated.

When the IERs are in the $Ca^{2+}$ form, only limited variations of the osmotic pressure occur. Some exchanges with $Na^+$ and $K^+$ ions released by the cement dissolution are evidenced, but they induce opposite volumetric changes, with a net variation close to zero, which explains the good stability of the matrix.

# REDOX CHEMISTRY AND SOLUBILITY OF URANIUM IN ALKALINE SYSTEMS

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The prediction of the possible mobilization of radionuclides from the repository to the biosphere is of high importance for the long-term safety assessment of nuclear waste repositories. Uranium is an important element in the nuclear fuel cycle that contributes with a large inventory to the radioactive waste. U(VI) is the most stable oxidation state of uranium under anoxic and oxidizing conditions, whereas U(IV) prevails in strongly reducing environments. U(VI) precipitates as $UO_3{\cdot}2H_2O$(cr) and M–U(VI)–OH(s) with M = Na, K, Ca under acidic and alkaline conditions, respectively. U(IV) forms sparingly soluble $UO_2$(am,hyd), which defines [U] < $10^{-8}$ M above pH ≈ 5. $U(OH)_4$(aq) is expected to control the aqueous speciation of uranium under hyperalkaline reducing conditions. However, the known stabilization of higher oxidation states and the proposed formation of $U(OH)_5^-$ and $U(OH)_6^{2-}$ at pH > 12 [1] pose relevant uncertainties on the solubility and redox behavior of uranium in these conditions. In contrast to Ca- and Na-uranates, little is known on the solubility of K–U(VI)–OH phases.

All experiments were performed in Ar gloveboxes at $T$ = (22 ± 2) °C. The redox chemistry of uranium was investigated in 0.1–5.0 M NaCl–NaOH solutions with $8 \leq pH_m \leq 14.5$ ($pH_m = -\log [H^+]$). Strongly reducing conditions ($pH_m$ + pe < 4) were chemically set for each independent redox sample in the presence of individual ($Na_2S_2O_4$ and Sn(II)) and mixed (Sn(II) + Fe(0), $Fe_3O_4$, $TiO_2$) reducing systems. Uranium was added to independent batch samples as U(VI), and [U], $pH_m$ and $E_h$ were monitored for $t \leq 635$ days. A slow decrease in [U] below the solubility limit of U(VI) is observed in all redox systems indicating the reduction of U(VI) to $UO_2$(am,hyd). The predominance of U(IV) in the aqueous and solid phases of selected samples was further confirmed by XANES and solvent extraction. A $pH_m$-independent behavior of the solubility is observed up to $pH_m$ = 14.5, in agreement with the predominance of $U(OH)_4$(aq) in solution and thus disregarding the formation of anionic U(IV) hydrolysis species. These results provide relevant insights on the redox chemistry of U in hyperalkaline conditions, and highlight the need of a strict exclusion of $O_2$ and sufficiently long equilibration times for a correct evaluation of U behavior under these conditions.

The solubility of U(VI) was investigated from undersaturation conditions in 0.1 – 4.0 M KCl–KOH solutions at $pH_m$= 7.5–14.6. XRD, quantitative chemical analysis, SEM–EDS and TG–DTA confirm that $K_2U_2O_7{\cdot}1.5H_2O$(cr) is the solid phase controlling the solubility in all evaluated systems at $pH_m \geq 9.5$. Below this $pH_m$ and with decreasing KCl concentration, the formation of sub-stoichiometric phases with K:U < 1 is hinted by XRD and solubility data. Uranium concentration in equilibrium with $K_2U_2O_7{\cdot}1.5H_2O$(cr) shows a pH-independent behavior up to $pH_m \approx 11$ regardless of ionic strength, whereas an increase of the solubility with a well–defined slope of +1 (log [U] *vs.* $pH_m$) is observed at $pH_m \geq 11$. These results are consistent with the predominance of $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$ species as previously reported. The combination of solubility data obtained in the present study with $K_2U_2O_7{\cdot}1.5H_2O$(cr) and the U(VI) hydrolysis scheme reported in [2] allows the determination of $\log {}^*K^{\circ}_{s,0}\{0.5K_2U_2O_7{\cdot}1.5H_2O(cr)\}$. This work extends the thermodynamic database available for U(VI) and allows more accurate source term calculations under boundary conditions relevant for nuclear waste disposal. The solid phase $K_2U_2O_7{\cdot}1.5H_2O$(cr) should be considered as likely candidate to control the solubility of U(VI) in the degradation phase I of cement and cementitious materials.

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# SOLUBILITY AND SORPTION OF Be(II) IN CEMENTITIOUS SYSTEMS

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Beryllium is a chemotoxic element expected in specific waste forms to be disposed of in repositories for radioactive waste. The amphoteric behavior of Be(II) is widely accepted in the literature, although the number of experimental studies reporting the formation of anionic hydrolysis species ($Be(OH)_3^-$ and $Be(OH)_4^{2-}$) under alkaline to hyperalkaline pH conditions is very limited. In spite of the lack of dedicated studies assessing the uptake of Be(II) by cementitious materials, a weak sorption is predicted based on the formation of negatively charged hydrolysis species of Be(II) in the pH conditions relevant in cement systems. In this context, this study focuses on the solubility and hydrolysis of Be(II) under alkaline to hyperalkaline pH conditions, further extending to its sorption behavior in cementitious systems. The main objectives are the development of comprehensive thermodynamic and activity models for the system $Be^{2+}$–$Na^+$–$K^+$–$Ca^{2+}$–$H^+$–$Cl^-$–$OH^-$–$H_2O(l)$, as well as the quantitative evaluation of the uptake of Be(II) by different cementitious materials and C-S-H phases.

Sample preparation and handling were performed in an Ar-glove box at $T$ = (22 ± 2) °C. Solubility experiments were conducted with $Be(OH)_2(s)$ obtained by precipitating a ≈ 0.35 M $BeSO_4$ stock solution at $pH_m \approx 10.5$ (with $pH_m = -\log [H^+]$). Solubility samples were prepared by contacting 0.5–5 mg of solid phase (per sample) with the following systems: (i) 0.1–5.0 M NaCl–NaOH ($5 \leq pH_m \leq 14.5$); (ii) 0.1–4.0 M KCl–KOH ($9 \leq pH_m \leq 14.3$); (iii) 0.05–3.5 M $CaCl_2$ ($9 \leq pH_m \leq 12$); (iv) 0.01–4.0 M NaOH; v. 0.01–4.0 M KOH. The uptake of Be(II) by ordinary Portland cement, low pH cement and C-S-H phases with Ca:Si ratio 0.6, 1.0 and 1.6 was investigated at $10 \leq pH_m \leq 13$, as imposed by the equilibrium with portlandite, C-S-H phases and Na/K hydroxides. Batch sorption samples were prepared with solid-to-liquid ratios of 0.2-10 g/L and $10^{-6}$ M $\leq [Be(II)]_0 \leq 10^{-3.5}$ M, considering the solubility limit of $\beta$-$Be(OH)_2(cr)$ at the investigated pH conditions. In both studies, total concentration of Be(II) in the aqueous phase was quantified by ICP–MS after ultrafiltration with 10 kD filters. Solid and aqueous phases in selected solubility/sorption experiments were characterized by XRD, TG-DTA, BET, SEM-EDX, XPS, quantitative chemical analysis and $^9$Be NMR.

Solubility data obtained with $Be(OH)_2(s)$ confirm the amphoteric character of Be(II), with a solubility minimum at $pH_m \approx 9$. At this $pH_m$ value, [Be(II)] in equilibrium with $\beta$-$Be(OH)_2(cr)$ is ≈ $10^{-7}$ M. No transformation of this solid phase was observed under alkaline conditions within $t \leq$ 437 days. Slope analysis of the solubility data in alkaline to hyperalkaline conditions supports the predominance of the species $Be(OH)_3^-$ and $Be(OH)_4^{2-}$ within the $pH_m$-region relevant in cementitious systems. The combination of solubility data, solid phase characterization and the hydrolysis scheme reported in the literature for Be(II) cationic species forming in acidic conditions allows deriving chemical, thermodynamic and (SIT) activity models for the system $Be^{2+}$–$Na^+$–$K^+$–$Ca^{2+}$–$H^+$–$Cl^-$–$OH^-$–$H_2O(l)$. These models can be implemented in thermodynamic databases and geochemical calculations, thus representing an accurate and robust tool for the evaluation of Be(II) solubility in a diversity of geochemical conditions, including source term estimations in the context of repositories for nuclear waste disposal. Experimental results from the on-going sorption studies with different cementitious materials and C-S-H phases will be extensively discussed in this contribution.

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# REACTIVE TRANSPORT AND TRITIUM TRANSPORT MODELS IN CONCRETE CELLS FOR STORING RADIOACTIVE WASTE

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Water with high concentrations of tritium is leaking from drains situated inside 'El Cabril', Spain's disposal facility for low and intermediate level radioactive waste. This indicates flow of water into the concrete cells that store the waste. 2D numerical models together with temperature and humidity measurements suggest that this leak of water is caused by a combination of thermo-hydraulic processes occurring in the unsaturated concrete, such as capillary rise from the groundwater, evaporation and condensation due to temperature gradients caused by seasonal temperature fluctuations outside (1). To study the effect of these processes of condensation and evaporation on the mineralogy of the concrete, a 1D reactive transport model was developed following the 2D thermo-hydraulic conceptual model. It included several mineral phases such as portlandite, ettringite, calcite, C-S-H and C-A-S-H. Model results showed that especially portlandite, but also other minerals, precipitate and dissolve following clearly the yearly fluctuations of condensation and evaporation. The model suggest that precipitation-dissolution can be particularly important near gaps of air in the concrete, where water condenses and evaporates more easily.

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# DECIPHERING CEMENT PASTE MINERALOGY USING DIFFRACTION TOMOGRAPHY

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Large amounts of nuclear waste await final disposal worldwide. A combination of waste matrix and overpacks (*e.g.* metal canisters, concrete), engineered barriers, and natural barriers such as clay rocks, constitutes the elements of the so-called "multiple-barrier system" between the radioactive waste and the biosphere. The number, types and assigned functions of these various barriers depend on the chosen repository concept, the waste form and their chemical behavior, the radionuclide inventory in the waste, the selected host rock, the hydrogeological and geochemical settings of the disposal site, etc. [1, 2]. These barrier properties will evolve with time in response to the physical and chemical interactions between the various constituents of the barriers and the surrounding environment. Consequently, predicting how these properties evolve is of prime importance as input data for performance and safety evaluations of the repository concepts. As a prerequisite, initial properties of the materials used in the disposal have to be understood, to better predict their long-term behavior. Although micro imaging techniques are more and more sophisticated and powerful [3], few techniques allow *in-situ* characterization of both the evolution of the different phases's mineralogy and their 3D spatial arrangement. To tackle this issue, X-Ray diffraction computed tomography (XRD-CT) that allows to record in each voxel of the recorded volume an X-ray diffraction pattern, has been successfully applied to investigate hydration and microstructural development in cements [4]. Here we present results obtained by synchrotron XRD-CT on a cement paste formulation, which is constituted of a blended Portland, fly ash, blast furnace slag cement [5], foreseen to be used for nuclear waste disposal applications. Consistent with previous results obtained for both powdered samples and dilute systems, it was possible, using a consolidated cement paste (with a water-to-solid ratio akin to that used in civil engineering), to determine that the mineralogy consists of alite (only detected in the *in-situ* hydration experiment), calcite, calcium silicate hydrates (C-S-H), ettringite, mullite, portlandite, and an amorphous fraction of unreacted slag and fly ash. Mineralogy evolution during hydration, spatial arrangement of the different phases and carbonation development in relationship with macro porosity will be also discussed.

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# COMPARISON OF CEMENT MATRICES FOR THE SOLIDIFICATION/STABILIZATION OF LEAD CONTAMINATED SOILS: MECHANISMS AND PERFORMANCE

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In the design of remediation solutions for contaminated soils, solidification/stabilization (S/S) approaches are widely recognized as cost effective and low energy consuming options, especially for the treatment of inorganic contaminants. Despite the universal use of ordinary Portland cement (OPC) for treating heavy metals, Pb contamination remains an issue. This is because cement hydration reaction in the presence of the metal is dramatically delayed, as reported by studies on Pb-doped OPC [1]. Additionally, given its amphoteric behaviour, Pb results highly soluble both at acidic and alkaline pH, the latter being the pH of OPC. Differently from classical *in situ* S/S systems, the Mapei High Performance Solidification/Stabilization (HPSS) process is a recently engineered *ex situ* treatment, which includes a granulation step yielding pellets of the solidified soil [2], that can be efficiently recycled, in accordance to the end-of-waste perspective.

In this study, the suitability of using OPC and calcium aluminate cement (CAC) for the treatment of Pb contamination is investigated by treating a real contaminated soil with the HPSS process. The soil is from an Italian agrarian consortium built in 1898, where the past activities devoted to sulfuric acid manufacturing from sulphides resulted in metal pollution, acidification of the soil and pervasive mobilization of heavy metals. Pb is of special concern for its high concentration (i.e. more than 30000 mg $kg^{-1}$). After a detailed characterization of the starting soil with XRD, different combinations of OPC and CAC were applied as binding agents in the pelletizing process. The effect of the different binders on the S/S performance was analysed with XRD and SEM/EDS: the phase composition combined with the internal microstructure of the pellet yields information on the interaction between the Pb-containing soil particles and the binding system. Leaching tests were carried out in order to assess differences in the stabilization performance, while compressive strength tests were used to characterize the solidification degree in the different systems.

The results indicate that, after the HPSS process, Pb-containing minerals present in the starting soil undergo dissolution, due to the alkaline pH induced by cement, making Pb dispersed within the whole amorphous matrix. Cement hydration is delayed by the formation of an external coating of Pb salts on cement particles, clearly observable in OPC and OPC+CAC systems. In CAC-containing systems ettringite precipitation is increased with respect to OPC system, as CAC provides more calcium aluminates reacting with sulfates from soil. Additionally, the amount of CAC in the formulation positively affects the Pb immobilization performance, virtually reaching 100%. Mechanical tests reveal that, despite the inhibited hydration caused by Pb, CAC acts as a strength provider, leading to better performances during the leaching test. The S/S mechanisms for Pb seem strictly connected to the binding system used. While with OPC alone and combined with CAC, Pb is first stabilized by the surface of cement particles and later by C-S-H, where $Pb^{2+}$ could be hosted [3], in CAC systems the enhanced precipitation of ettringite coupled with the higher strength performance suggest that both physical encapsulation by cement and chemical fixation in the ettringite structure are possible mechanisms involved. Leaching tests on aged pellets suggest that Pb undergoes long-term stabilization by the systems studied.

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# GEOCHEMICAL PERTURBATIONS IN THE CONTACT BETWEEN CONCRETE AND BENTONITE AFTER 13 YEARS OF INTERACTION AT MICROMETRIC TO CENTRIMETRIC SCALE

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The FEBEX experiment was performed in a gallery of the Grimsel Test Site (GTS, Switzerland) for 18 years as a demonstration for the technical capability to manufacture and assemble the engineered barriers of a repository for high level radioactive waste and to monitor the thermo-hydro-mechanical conditions over its lifetime. In this experiment, two metallic heaters were surrounded by a compacted FEBEX-bentonite barrier and hosted horizontally in a granitic drift. A concrete plug was used to seal the drift. The geochemical study of interactions between the system barriers was performed after the dismantling of the experiment.

After 5 years of operation, the heater closer to the gallery entrance was switched off and extracted. Then, a new sprayed concrete plug was applied to seal the drift. This study presents the geochemical perturbations observed at the µm to cm scale from the interface between the bentonite and the concrete plug after 13 years of interaction making use of well-preserved selected samples recovered by the overcoring technique [1].

The overcoring technique maintain the consistency of the interface of both materials, concrete and bentonite, without fractures. Cylindrical samples are later embedded in resin and radially cut into 4 equivalent subsamples for further analyses.

Three different subsamples, named CC-32-4-OC, CC-32-5-OC and CC-32-6-OC, were analyzed by numerous techniques for mineralogical and physical-chemical characterization (e.g. XRD, SEM-EDX, BET specific surface, $^{13}C$ and $^{18}O$ isotopes, TG, soluble salts).

A chemical gradient in the interface is observed at the micrometric scale, mainly by accumulation of Ca at the concrete side and Mg at the bentonite side. At centimetric scale, the mineralogical alteration is dominated by precipitation of calcium carbonates in concrete and magnesium silicates in bentonite. Nevertheless, migration of soluble species, mostly chloride and sulfate in concrete and redistribution of cations associated to exchangeable cations in bentonite, is observed at larger scale.

The representativeness of the study of three overcoring samples confirm with higher confidence previous results observed in hand-picked samples whose interfaces were not fully preserved. The geochemical perturbations after 13 years of concrete-bentonite interaction reaches a limited impact far from the millimetric scale.

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# SURFACE REACTIVITY INTERFACE EXPERIMENTS

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SurfacE Reactivity Interface Experiments (SERIE) are a set of small-scale laboratory experiments developed with the aim to obtain early reactions generated by the contact FEBEX-bentonite and cement mortar. Three types of cement mortars, based on ordinary Portland cement (OPC), CEM I, CEM I with silica addition (low-pH), and CEM II with limestone addition were studied. The bentonite and cement mortar were confined in a methacrylate sleeve containing the contact separated by a PTFE membrane. The prepared columns were exposed to a granitic groundwater flow infiltrated by a piston pump with 1MPa constant head. The effluent was collected to determine the flow rate at the end of the bentonite. Experiments were prepared in duplicate at 23±2ºC. To determine the time evolution of the ongoing processes, experiments at 6 and 18 months were run and compared. The solid materials were studied by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analyses, random powder and grazing incidence X-ray diffraction (XRD) specific surface area (SSA-BET) and Fourier transform infrared spectrometry (FTIR) analyses. The aqueous phase was characterized using ionic chromatography (IC), potentiometric titration (alkalinity) and Vis-spectrophotometry (silica). A more detailed description of the materials and methods is available in the previous pilot experiment [1].

Hydraulic conductivity for effluents collected in all the experiments decrease to be stabilized at $2.3\pm0.8\cdot10^{-13}$ m/s within at 3 months period. pH values (8.1±0.2) and silica concentration (13.6 ±2.6 mg/L) were stable and characteristic of the bentonite buffer. The geochemical and mineralogical results showed in all experiments an increase of Mg in the first hundred microns of bentonite (< 400 µm) and an increase of Ca linked to the development of a carbonation coating (< 200 µm) next to the interface in the cement mortar side. However, the mineral phases found and the intensity of these perturbations was different regarding the type of cement mortar tested. The experiments made with low-pH presented precipitation of brucite in the surface interface of cement mortar material at 6 and 18 months, which was not observed in CEM-I and CEM-II, in spite of the increase of magnesium in the bentonite was significantly higher, specifically in CEM I experiments ($p<0.05$). The carbonation coating was larger in CEM I and CEM II experiments regarding low pH. The XRD patterns registered on the bentonite interface showed an important attenuation of the montmorillonite basal reflections and a wide reflection at 7.4-7.6 Å. In the experiments made with CEM I and CEM II, both effects evolve at 6 and 18 months, while in low-pH experiments this perturbation was only found at 18 months. The maintenance of (hk0) reflections of montmorillonite and FTIR data suggest the presence of a brucite-montmorillonite complex mixed with Mg-tri-octahedral clay minerals (reflections at 1.52-1.53 ϴ) in the bentonite.

The geochemical perturbation determined in these experiments is found to be similar to other larger scale experiments [2], although developed in a lesser spatial extension. Then, these results can help to discuss the early geochemical reactions in the concrete-bentonite system to gain confidence to upscale the processes observed in the real system.

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# THERMODYNAMICS AND KINETICS OF PRECIPITATION OF ZEOLITE AND TOBERMORITE AT CEMENT/CLAY INTERFACES

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The CEMTEX project (CEMent Temperature EXperiments) was set up in the IRSN's underground research laboratory (URL) in Tournemire (France) to fill the lack of knowledge on the effect of temperature on the long-term properties of cement/clay interfaces. In situ experiments were stopped after 1, 2 and 5 years [1]. Diffusion cell experiments were also conducted in the IRSN's LUTECE laboratory (Fontenay-aux-Roses, France) to measure the evolution of solutions and materials over 1 year [2]. In each case, the devices were designed to perform the experiments at 70°C under water saturated conditions and the hydrated CEM-I pastes were directly poured on the argillite surface.

In situ, a layer of phillipsite, tobermorite and C-(A)-S-H formed at the interface [1]. The altered layer became denser and significantly enriched in K-phillipsite over the 5 years. In the cells, the altered layer consisted in calcite/tobermorite/C-A-S-H without zeolite [2]. The occurrence of zeolite and well-crystallized C-S-H was a clear consequence of temperature increase to 70°C and, to our knowledge, was never observed at such interfaces. Therefore, these experiments were a chance to quantitatively assess of the thermodynamics and kinetics of tobermorite and zeolite precipitation under thermo-hydraulic conditions representative of radioactive waste underground disposals.

The geochemical code CHESS and the reactive transport code HYTEC helped to analyze the most significant experimental results, taking into account temperature effect on diffusion coefficients, thermodynamics constants and kinetic rates. The Thermoddem thermodynamic database was used, plus data from the literature (e.g. cationic exchange constants for the clayey phases).

Stability diagrams were first calculated to provide insights in the chemical conditions required to form tobermorite and K-phillipsite versus other secondary silica phases, despite important uncertainties on the thermodynamic formation constants of many zeolites.

The kinetic rate constants of tobermorite-11A precipitation (cell experiment) and K-phillipsite precipitation (in situ experiments) at the CEM I/argillite was obtained for the first time by an inverse modelling based on epitaxial linear growth, translating the temporal evolution of the layer thickness and density in terms of mass rate. The competition with the formation of other Ca-bearing phases (calcite, C-A-S-H...) was investigated by sensitivity analysis.

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# RETENTION OF MOLYBDENUM IN CEMENTITIOUS SYSTEMS

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Cementitious materials are widely used in nuclear waste management, for example for solidification and stabilization of low and intermediate level wastes, as construction materials and backfill in near surface and deep geological disposal facilities, and in certain waste containers. However, the mechanisms governing the retention of various safety relevant radionuclides by cementitious materials on the molecular scale are still not completely understood. Molybdenum-93 (Mo-93) has a half-life of 4000 years and decays by electron capture to stable Nb-93. It is generated in nuclear power plants by neutron activation of the stable molybdenum isotope Mo-92 present in particular in metallic reactor components like stainless steels, and can thus occur in various nuclear waste streams. Mo is a redox-sensitive element, whose aqueous speciation under neutral to highly alkaline conditions is dominated by the thermodynamically highly stable molybdate ($MoO_4^{2-}$) oxo-anion. Under cementitious conditions, powellite ($CaMoO_4$) is supposed to be the solubility-limiting Mo phase, depending on redox potential and dissolved Ca concentration. The sorption of molybdate in cementitious systems is assumed to be mainly due to substitution of sulphate in ettringite and AFm phases [1]; however, the potential role of other hydration phases like C-S-H with respect to molybdate retention remains still an open issue [2].

To unravel the contributions of individual hydration phases on molybdate retention in complex multiphase cementitious materials, we adopted a bottom-up approach, studying the radionuclide interaction with synthesized hydration phases present in cementitious materials (model phases), such as calcium silicate hydrates (C-S-H) with different Ca/Si ratios, monosulphate (AFm) and ettringite (AFt) phases. Molybdate sorption and uptake kinetics by the model phases were studied in static batch experiments under anoxic conditions, using $MoO_4^{2-}$ concentrations below $10^{-6}$ mol $L^{-1}$ to avoid powellite precipitation. As expected, a pronounced uptake of molybdate by AFm-$SO_4$ and AFm-$CO_3$ was observed ($R_d$ ~1,600 L $kg^{-1}$), whereas the uptake by ettringite was found to be distinctively lower ($R_d$ ~120 L $kg^{-1}$). XRD studies on the AFm-phases used in the batch sorption experiments showed an increase in the basal spacing compared to pure AFm-$SO_4$, indicating a structural incorporation of $MoO_4^{2-}$-ions into the interlayer of the AFm-structure, since the size of the molybdate oxo-anions (Mo-O bond length ~1.77 Å) is larger than that of sulphate ions (S-O bond length ~1.47 Å). The dependency of the $R_d$ values on the Ca/Si-ratio of the C-S-H phases (C-S-H 0.9, $R_d$ ~430 L $kg^{-1}$; C-S-H 1.4, $R_d$ ~800 L $kg^{-1}$) suggests electrostatic sorption as the main mechanism of molybdate retention in this case. Moreover, a strong uptake of molybdate in experiments with hydrogarnet (C3AH6; $R_d$ ~3,000 L $kg^{-1}$) was observed. SEM/EDX measurements and TEM investigations indicated the formation of molybdenum-containing AFm-like phases in these experiments.

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# PORE-SCALE REACTIVE TRANSPORT MODELING OF DEGRADATION PROCESSES IN CEMENTITIOUS MATERIALS

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Cementitious materials are used in a wide range of applications in nuclear waste management, for example for the solidification of waste or as construction and backfill material in underground and near surface repositories. In these materials, chemical and microstructural heterogeneities exist in a wide range of length scales (nm to cm). Macroscopic physical characteristics of these materials such as diffusion coefficients and permeability depend strongly on their (micro)structural properties. These properties can undergo changes with time, due to alteration/degradation processes like dissolution and precipitation of solids, which affect the pore structure and pore connectivity. In this context, pore-scale reactive transport models can be regarded as promising tools to realistically describe the evolution of the pore structure and the heterogeneous distribution of hydration phases in cementitious materials. The advantage of these models compared to traditional meso- and macro-scale models (i.e. continuum scale models) is their potential to reduce the level of empiricism in the treatment of the couplings between chemical reactions and the physical properties of the material.

In the framework of the Horizon2020 collaborative project Cebama (Cement-based materials, properties, evolution, barrier functions), a pore-scale reactive transport model is under development and validation. The focus of this study is on degradation processes occurring in cementitious materials as a consequence of the interaction with different groundwaters, leading, for example, to calcium leaching, carbonation or sulphate attack, and their consequences on transport properties. For this purpose, a three dimensional advection-diffusion solver based on the Lattice-Boltzmann method (Palabos) is coupled to a geochemical simulator (PhreeqcRM). The coupling code named *iPP* (**i**nterface **P**alabos **P**hreeqC) was implemented with scalability for high performance computing facilities in mind, thus exploiting MPI parallelization and C++ template meta-programming techniques. Additionally, several optimizations were introduced into the PhreeqcRM code to reduce parallelization overhead due to MPI process communication and to reduce memory footprint, which allows for a significantly enhanced computational scalability on high performance computers. In order to cope with the particular requirements of simulating cementitious materials, such as different scales of heterogeneity involving high contrast in diffusion coefficients, a multi-scale Lattice-Boltzmann approach based on the two-relaxation time (TRT) scheme was implemented. Additionally, the explicit description of the calcium-silicate-hydrate (CSH) phases by a thermodynamic solid solution model was replaced by a discrete phase approach, in order to increase the convergence stability of the geochemical equilibrium calculations. The application of iPP to the simulation of leaching processes leading to degradation of cementitious materials by different types of (ground)waters will be discussed.

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# STABILIZATION OF SOILS CONTAINING SULFATES BY USING HYDRAULIC BINDERS

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Excavation operations during construction produce several tons of soil, which frequently contains high concentration of sulfates (>0.5%). In accordance with the French decree for waste classification for disposal requirements, a soil containing sulfates can only be classified as “an inert and not hazardous waste” if the leachable sulfate concentration is lower than 0.1% or 1000 mg/kg. On the other hand, the reuse of soils containing sulfates for civil engineering proposes can lead to significant risks after their treatment with ordinary cementitious binders because of chemical reactions involving sulfates. These reactions can promote ettringite crystal formation resulting in expansion, cracking and eventually catastrophic damages of materials or structures. To prevent these reactions, the stabilization of soils containing sulfates by adding alternative cementitious binders is studied in this project.

Several cementitious binders having the ability to chemically consume sulfates during their hydration process were used to treat a soil containing sulfates to avoid significant volume expansive reactions (<5%) and increase the mechanical strength (indirect tensile strength>0.2 MPa). The leachable sulfate concentration in treated soil samples was determined by analyzing eluates extracted from leaching tests carried out in accordance with the European standard NF EN 12457-2. All the eluates were then analyzed with the use of the chromatography technique. Complementary analyses were conducted with inductively coupled plasma mass and atomic emission spectrometry. Mechanical properties of the treated soils were evaluated by determining the indirect tensile strength by splitting tests in accordance with the European standard NF EN 13286-42, which consists of diametral compression tests on specimens of compacted and treated soil. Swelling phenomena was evaluated by volume expansion tests on compacted and treated soil specimens in accordance with the French standard NF P94-100. Additionally, microstructural characterizations and mineral phases were analyzed with SEM/EDS.

It was observed that the soil containing sulfates treated with high C3A content cementitious binders had volume expansions superior to 5%, even though the indirect tensile strength was near 0.2 MPa. On the other hand, the soil treated with cementitious binders containing high ground granulated blastfurnace slag (GGBS) level showed volume expansions inferior to 5% and indirect tensile strength values superior to 0.2 MPa. Moreover, after leaching tests it was observed that sulfate immobilization in the solid matrix was about 80%. These preliminary results suggest that GGBS binders are effective for the treatment of soils containing sulfates. Experimental results will be compared with PhreeQC modelling to evaluate how each binder affects sulfate stabilization in the soil.

# ON THE VERY LOW SOLUBILITY OF Np(V) HYDROXIDE SOLID PHASES IN ALKALINE SOLUTIONS CONTAINING (SUB)MILLIMOLAR CONCENTRATIONS OF $Ca^{2+}$

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Within the series of relevant oxidation states of actinide elements in aqueous solutions, An(III)-An(VI), the pentavalent An(V) features the highest mobility in aqueous solutions due to its weak sorption properties and its usually high solubility. The latter is particularly true for amorphous $An^{V}O_2OH$(am) as solubility limiting solid phase. In the case of Np, which exists as Np(V) over a wide range of (pH+pe) solutions conditions, we have recently demonstrated that $NpO_2OH$(am) is but metastable in alkaline NaCl and $CaCl_2$ solutions regarding transformation into higher hydroxide phases, M-Np(V)-OH(s) with M = Na and Ca [1,2,3] respectively. In the present work, the solubility behavior and thermodynamic stability of the ternary solid phase $Ca_{0.5}NpO_2(OH)_2$(s,hyd) was systematically investigated in alkaline NaCl-dominated solutions containing dissolved $Ca^{2+}$ in the concentration range expected in cementitious systems.

All experiments were performed at room temperature under inert Ar atmosphere with $^{237}Np$. The ternary Np(V) solid phase $Ca_{0.5}NpO_2(OH)_2$(s,hyd) was prepared by equilibration of binary $NpO_2OH$(am) in alkaline $CaCl_2$ solutions, as described in our previous work [2], and analyzed by powder-XRD, SEM-EDX, and quantitative chemical analysis. The solubility behavior of $Ca_{0.5}NpO_2(OH)_2$(s,hyd) was investigated in alkaline 0.1, 1.0 and 5.0 M NaCl solutions with $9 \leq pH_m \leq 12$ and additions of 0.4 to 20 mM of $Ca^{2+}$ (undersaturation approach).

Despite the very large excess of $Na^+$ compared to $Ca^{2+}$ ions in the samples (ratio $Na^+$ to $Ca^{2+}$ up to 1250 to 1) the initial $Ca_{0.5}NpO_2(OH)_2$(s,hyd) remained stable and controlled the Np(V) solubility for all $pH_m$ and [NaCl] conditions investigated. For $pH_m$ 9-10.5, the Np(V) solubility decreases systematically with a slope of −2 according to the equilibrium $Ca_{0.5}NpO_2(OH)_2(s,hyd) \Leftrightarrow 0.5\ Ca^{2+} + NpO_2^{+} + 2\ OH^{-}$. At around $pH_m$ 11-12 the solubility curve can be described by the pH independent equilibrium $Ca_{0.5}NpO_2(OH)_2(s,hyd) + (x-0.5)\ Ca^{2+} \Leftrightarrow Ca_xNpO_2(OH)_2^{2x-1}$, leading to very low equilibrium concentrations for Np(V) of log [Np(V)] = −8 to −9. The solubility of $Ca_{0.5}NpO_2(OH)_2$(s,hyd) in alkaline $Na^+$-dominated solutions is, therefore, up to 3 log-units lower than that of the binary phase $NpO_2OH$(am) [1]. The results of the experiments reveal the great stability / low solubility of $Ca_{0.5}NpO_2(OH)_2$(s,hyd) even at trace concentrations of $Ca^{2+}$, and are furthermore in excellent agreement with the chemical and thermodynamic models evaluated in [2,3]. The formation of ternary M-Np(V)-OH solid phases with M = Na, Ca [1,2] significantly reduces the mobilisation of Np(V) in the alkaline solutions typical for cementitious environments. The data are highly relevant for the assessment of realistic source-terms for pentavalent actinides in a repository, where the formation and potential interaction of alkaline solutions with nuclear waste have to be considered due to the large inventory of cementitious material.

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# FRACTURED CORE EXPERIMENTS TO STUDY WATER-ROCK-CEMENT INTERACTION UNDER $CO_2$ STORAGE CONDITIONS

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In wellbores used for $CO_2$ injection in Geological Carbon Storage (GCS), Portland cement is placed between the steel casing and the surrounding rock to prevent gas or fluid leakages. During and after $CO_2$ injection, the resulting $CO_2$-rich acid water may deteriorate the cement and favour undesired leaking. The objective of this study is to understand the processes that take place in the contact between Portland cement and sedimentary rocks under GCS conditions.

In this study, artificially fractured cores made of a half cement cylinder and a half sedimentary rock cylinder (limestone, sandstone and marl) were reacted with synthetic brines at 25ºC and $10^{-3.4}$ bar $CO_2$ and 60ºC and 130 bar $CO_2$ (atmospheric and supercritical $CO_2$ conditions, respectively) by means of percolation experiments. Variation in the aqueous chemistry (concentrations of Ca, $SO_4$, Mg, K, Na, Si, and Al) was monitored over time. At the end of the experiments, the fractured cores were examined by SEM-EDS, XRD, and XCMT to evaluate the changes in the mineralogical content and structure.

Results showed a pH increase in all injected solutions: up to 7-11 in the atmospheric experiments and up to 6 under supercritical $CO_2$ conditions. Ca and Si output concentrations were also higher than the initial ones, whereas a sulphate deficit was observed. Dissolved calcium and silicon and removal of sulphate were higher under supercritical $CO_2$ conditions. Overall, under all conditions, the release of Ca and Si was attributed to dissolution of portlandite and C-S-H from the cement, and the sulphate depletion was caused by gypsum precipitation.

The SEM-EDS analyses showed a significant alteration of the cement and rock surfaces along the fracture walls. On the rock side, dissolution of calcite and precipitation of aragonite and gypsum were detected. On the altered cement wall, precipitation of aragonite and gypsum were identified. Under atmospheric conditions, an extensive layer of a hydrated Mg phase was formed. Under supercritical $CO_2$ conditions, an increase in cement porosity and fracture aperture was visible.

The observed chemical and mineralogical changes allow us to compare the hydrogeochemical response of artificially fractured cores by changing temperature and $P_{CO2}$. Under $CO_2$ supercritical conditions, the main chemical processes were dissolution of calcite and gypsum precipitation. Cement degradation occurred through dissolution of portlandite and C-S-H. Under atmospheric conditions, similar alteration processes occurred although at a slower rate, along with the formation of a Mg hydrated layer on the cement and rock fracture walls. These experiments are providing evidence of the reactivity of cement and sedimentary rock fractures to be considered in the management of GCS systems. Moreover, 2D reactive transport simulations of the variations in the experimental aqueous chemistry and core mineralogy will be used to quantify the kinetics of the acid brine-cement-rock interaction and to evaluate the integrity of the cemented annulus in GCS wellbores.

## Acknowledgements

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# MULTI-SCALE CHARACTERIZATION OF THE SPATIAL HETEROGENEITIES OF MICROSTRUCTURAL AND MINERALOGICAL EVOLUTION OF 14-YEAR IN-SITU CONCRETE-CLAY INTERFACES

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Concrete materials have been extensively used for encapsulation of radioactive waste and as engineered barriers for disposal of radioactive waste, both in near-surface repositories for low/intermediate active waste and geological/deep repositories for high level long-lived radioactive waste. Under its service environment, these concrete structures undergo complex chemical interactions with the geological matrices (e.g. clay, granite). The interaction processes are very slow but important for the long-term durability assessment (> 1000 years). It is well documented that due to the large geochemical contrasts between cement-based materials and clay, chemical reactions are expected to induce modifications in both the chemical and physical properties of both the clayey and cementitious materials which influence the long-term stability of the repository.

The Boom Clay has been considered as a potential host rock for intermediate and high-level radioactive waste in Belgium. We sample concrete-clay interfaces at the underground research laboratory (HADES) located at 225 m in depth at Mol, which is representative for disposal conditions (Phung et al. 2017). An in-situ engineered analogue of concrete/clay interface undergone 14 years of interaction since 2003 has been sampled and characterized. Such relatively long interaction time for an in-situ engineered analogue provides a bridge between laboratory-derived data and the long-term and large scale of safety assessment modelling.

An integrated multi-technique approach was proposed to map the spatial variability of microstructure evolution, considering the heterogeneous spatial distribution of minerals and phases of both materials. The spatial heterogeneity of the full core size samples was first analyzed at the core scale (100 mm in diameter) by 3D µ-tomography to localize the large heterogeneities and the region of interest (ROI). The ROI were impregnated with $^{14}$C PMMA technique to obtain quantitative 2D mapping of the total connected porosity by autoradiography (Gaboreau et al. 2012; Gaboreau et al. 2011). Results from 2D autoradiography allow to spatialize and quantify porosity evolution in both clay and concrete sides. Mineralogical mapping (Gaboreau et al. 2017) were computed from the localized areas based on the feedback of porosity evolution at a micro-scale. Several mineralogical mappings allow spatializing and quantifying mineralogical reaction pathways. Both quantitative 2D porosity and mineralogical mapping obtained on the same impregnated $^{14}$C polished section has allowed to link porosity evolution with mineralogical evolution at the interface and to improve the knowledge on reaction pathways at the concrete-clay interface.

Results obtained from multiscale/multitool approach show that there exists variation in mineralogy and porosity along the interface as well as far away from the interface. This is the consequence of either decalcification or carbonation resulting in clogging or opening of the pores and mineralogical changes. In overall, the decalcification seems to be dominant compared to carbonation at concrete side, while precipitation due to carbonation induces porosity decrease at clay side.

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# THERMODYNAMICS OF Tc(IV) IN AQUEOUS SOLUTIONS: APPLICATION TO COMPLEX MIXTURES INCLUDING CEMENTITIOUS SYSTEMS

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An appropriate understanding of the solubility and hydrolysis of Tc(IV) in dilute to concentrated saline systems is required for an accurate assessment of technetium source term in repositories for radioactive waste disposal. Although a limited number of experimental studies is available for dilute simple systems, virtually no thermodynamic studies dealing with the solubility and hydrolysis of Tc(IV) in more complex, close-to-real systems are available in the literature.

In this work, the solubility of Tc(IV) was investigated from undersaturation conditions in 0.1–5.61 m NaCl, 0.1–4.58 m KCl, 0.25–5.15 m $MgCl_2$ and 0.25–5.25 m $CaCl_2$ solutions in the $pH_m$ range 1.5–14.6. Experiments were performed at $t = (22 \pm 2)$ °C in Ar gloveboxes with < 2 ppm $O_2$. Strongly reducing conditions were chemically set for each independent solubility sample with $Na_2S_2O_4$, Sn(II) or Fe powder. All investigated systems were equilibrated for up to 600 days. Technetium concentration, $pH_m$ and $E_h$ values were monitored at regular time intervals. The redox speciation of technetium in the aqueous phase was quantified for selected samples using solvent extraction and XANES. Solid phases of selected experiments were characterized by XRD, SEM–EDS and chemical analysis. Additional solubility experiments were conducted in “simulated systems”, based on reported ground water and cementitious pore water compositions with complex mixtures of $NaCl–KCl–NaOH–KOH–MgCl_2–CaCl_2$.

Solid phase characterization and solubility data indicate that $TcO_2 \cdot 0.6H_2O(am)$ is the solid phase controlling the solubility of Tc(IV) in all the evaluated systems. Solvent extraction and XANES analysis confirm the predominance of Tc(IV) in the aqueous phase. Solubility data in combination with spectroscopic evidences reported in the literature are best explained considering the formation of the previously unreported trimeric technetium species $Tc_3O_5^{2+}$. In the near-neutral pH region, the pH-independent behavior of the solubility is consistent with the chemical reaction $TcO_2 \cdot 0.6H_2O(am) + 0.4\ H_2O(l) \Leftrightarrow TcO(OH)_2(aq)$. The amphoteric behavior of Tc(IV) is confirmed by the formation of the species $TcO(OH)_3^-$ in dilute NaCl and KCl systems with $pH_m \geq 11$. Changes in the aqueous speciation are observed in concentrated alkaline $MgCl_2$ and $CaCl_2$ brines, where the formation of $Mg_3[TcO(OH)_5]^{3+}$ and $Ca_3[TcO(OH)_5]^{3+}$ ternary species is proposed based on the slope analysis of solubility data and DFT calculations. These results allow deriving comprehensive chemical, thermodynamic and (SIT, Pitzer) activity models for the system $Tc^{4+}–Na^+–K^+–Mg^{2+}–Ca^{2+}–H^+–Cl^-–OH^-–H_2O$. Tc(IV) solubility investigated in “simulated systems” is in good agreement with qualitative predictions based on pure systems.

# SUPERPLASTICIZERS BEHAVIOUR UNDER DEEP DISPOSAL CONDITIONS, DEGRADATION AND COMPLEXATION EFFECTS

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The most widely accepted option for the long-term management of radioactive waste materials considers their disposal in deep underground facilities (examples are Finland, Belgium, France, Sweden, etc.). Such installations should ensure the safety of the waste disposal and minimize possible future external waste perturbation. Concrete and concrete-based materials are widespread in those facilities. Superplasticizers (SPs) are organic polymers used to improve several concrete properties such as workability [1]. The hyperalkaline conditions developed in cementitious environments, can cause chemical transformations of these polymeric materials (degradation, aging, etc.) with the subsequent production of new organic compounds with different chemical properties. Several organic compounds have a high capacity to form stable complexes with some radionuclides of interest from the point of view of radiological and toxicological doses [2]. Therefore, the understanding on the nature and strength of the interactions between radionuclides and organic admixtures present in the concrete formulations (and their degradation products) is of outmost importance to conduct adequate assessments of the future performance of the disposal facility.

The work presented in this contribution tries to discern the effect that polycarboxylic ether-based (PCE) SPs present in the concrete admixtures used in the deep disposal repository may have on radionuclide mobility [3]. The approach followed to study the degradation of superplasticizers has been based in a two-step process. In a first step, a literature review has been carried out to decipher possible superplasticizer degradation products. In a second step, based on the information gathered from the literature review, an experimental study has been done to analyse the degradation of a commercial PCE superplasticizer (Glenium®27) and an in-house synthesized PCE. To this aim selected superplasticizers have been treated with different treatments likely to accelerate their degradation, i.e. hydrolysis, temperature and radiolysis (Figure 1). In parallel, a solubility study has been performed to discern the possible effect of Glenium®27 on nickel behaviour. Over and under-saturation experiments with nickel hydroxide have been carried out in the presence of concrete leachates and concrete synthetic porewater. Additionally, experiments with superplasticizer spikes in solution have been performed to complement system understanding.

Our results indicate that under standard deep disposal conditions Glenium®27 will be stable, and not altered by temperature, radiolysis and/or hydrolysis processes. This means that the generation of labile small organics compounds, that may complex radionuclides from the disposed wastes increasing their mobility, due to superplasticizers degradation will be almost negligible. This is a key argument to support the use of superplasticizers as a concrete admixture for building up the future nuclear waste disposal facilities.

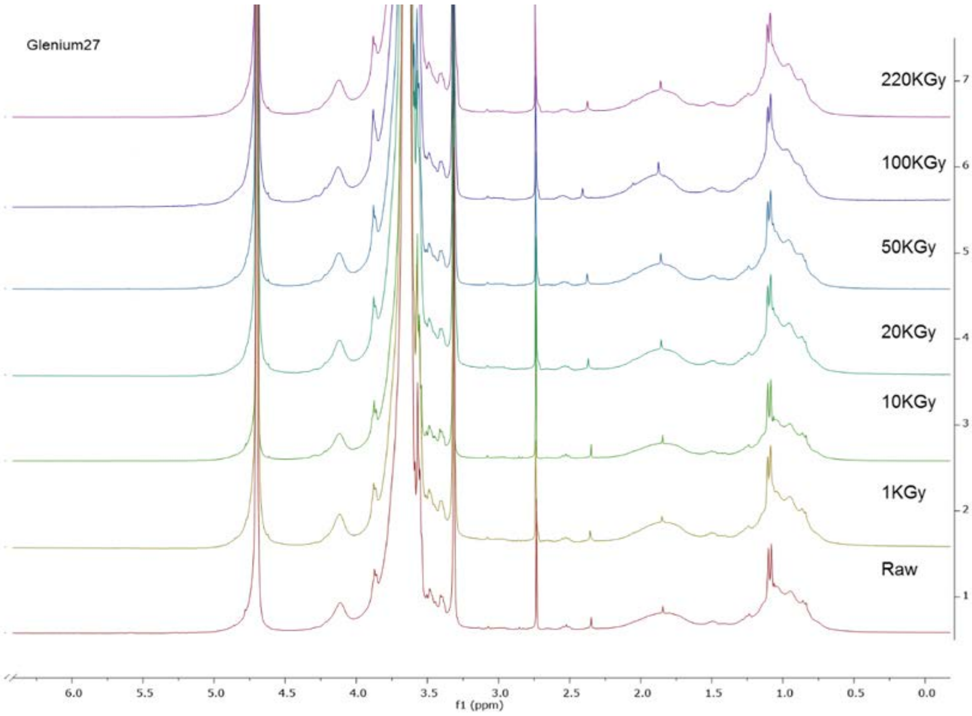

Figure 1. H-NMR spectra of Glenium®27 samples exposed at 1-220 kGy. For comparative purposes the spectrum of the unaltered material is also included.

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# SORPTION BEHAVIOR OF SMALL ORGANIC COMPOUNDS ONTO CEMENTITIOUS MATERIALS: INTERACTIONS AND COMPETITION EFFECTS WITH THORIUM

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Radionuclide behaviour under repository conditions is expected to be affected by organic molecules in solution generated by the degradation of anthropogenic organic materials (AOM) already present within the waste. The radionuclide mobility can be improved in presence of such organic molecules due to the formation of aqueous complexes inducing a solubility increase coupled with a sorption reduction. Thus, it is a topic that has generated special interest during the last decades. Besides radionuclide aqueous complexation, certain organic ligands (i.e. gluconate) are known to strongly adsorb onto the surface of cementitious materials; thereby limiting the number of specific sites available for radionuclide sorption and increasing their mobility [1]. In cementitious media, radionuclide behaviour can also be altered by the presence of major ions (e.g. Ca or Mg) due to the formation of radionuclide aqueous complexes as well as organic aqueous complexes with those ions [2, 3]. Moreover, the presence of large amounts of Fe is expected to form very stable complexes with some organic compounds and competing with organic-radionuclide interactions.

This work focuses on the solubility and complexation of Th under the presence of single/mixture relevant complexing agents (Isosaccharinate (ISA), phthalate and adipate) and their interactions towards sorption capacities onto hardened cement pastes (HCP) and/or pure cement phases (C-S-H) in the presence/absence of dissolved Fe concentrations. In parallel, the sorption behaviour of these organics in binary systems is also investigated. Several batch sorption-desorption experiments with both single and mixture of organic compounds and HCP at different degradation states (I, II and carbonated) or C-S-H gels at variable Ca/Si ratios are performed. Competition effects are assessed between the studied organics in iron-containing systems at different concentration.

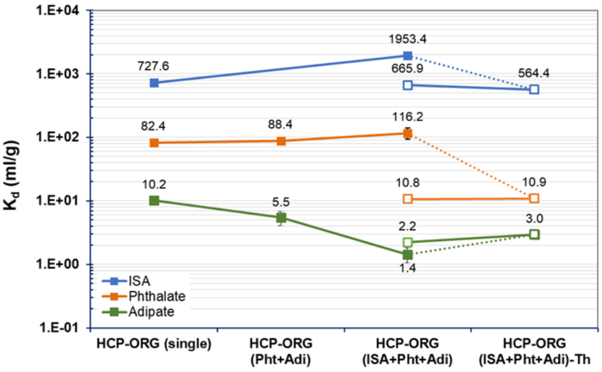

Figure 1. Distribution coefficients ($K_d$) for binary (single and mixture of organics) and ternary systems (including Th).

Our results let us to conclude that, at the range of organic concentration studied in this work (i.e. $10^{-3/-5}$ M), no competition effects are noticed from the studied organics on Th. Hence, a potential combined effect of cocktail of organics is not effective over Th mobility at the studied conditions. The organic adsorption was found to decrease as follow ISA > Phthalate > Adipate, with ISA retention by HCP (degradation state II) much higher than the rest (Figure 1). There is a clear influence of iron on the organic adsorption capacity in cementitious media at the organic concentrations investigated in this work, especially in the case of ISA; resulting in a decrease of ISA sorption to cement due to the formation of Fe-ISA complexes.

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# EXPERIMENTAL AND MODELING EFFORTS TO PREDICT LONG-TERM INTERFACIAL GEOCHEMISTRY OF SALT WASTE WITH CONCRETE VAULTS AT U.S. DOE DISPOSAL SITES

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The United States Department of Energy (U.S. DOE) processes, or is exploring the potential to process, low-level radioactive liquid waste into a solid, monolithic waste form using cementitious binders. The liquid waste contains a high concentration of sodium (5 M), sulfate, and nitrates as well as minor concentrations of heavy metals, radionuclides, and chemical solvents. At the Savannah River Site (SRS; Aiken, South Carolina), mixed product, known as saltstone, is pumped 0.5 km from the mixing plant to a series of circular concrete tanks (115-m diameter) for long-term disposal. At other facilities, the solidified waste form, known as caststone, potentially could be cast into concrete containers for near-surface burial. Performance assessments for these disposal facilities indicate that exposure risks may be driven by the long-term durability of concrete vaults relative to external carbonation exposed to atmospheric and subsurface carbon dioxide and to internal corrosion from contact with salts wastes.

The hydraulic and chemical properties of the high-performance vault concrete and of non-radioactive saltstone simulants are well documented [1, 2] and the presumed mechanism for degradation at the vault/waste interface is sulfate attack [3]. However, previous short-term laboratory experiments to produce a reaction between saltstone and vault concrete have shown no obvious degradation unless the vault concrete is placed in direct contact with some aggressive formulations of the salt solution simulant itself [4]. Due, in part, to the uncertainty and potential for reactions at the salt waste/vault concrete interface, assessments have applied overly-bounding assumptions regarding the predicted long-term durability of the vault container that could impact the confidence of the disposal approach.

The current study uses a combination of material leaching characterizations and geochemical modelling to predict the potential for deleterious reactions at the interface between saltstone materials and high-strength vault concrete. The results of leaching experiments, including pH-dependence, liquid-solid ratio dependence, and mass transport leaching, provide the basis and verification data for development of geochemical and reactive transport models using LeachXS/ORCHESTRA [5] of a concrete/waste interface. Environmental scanning electron microscopy (ESEM) was used to qualitatively characterize changes in the mineralogy and morphology of materials near the interface compared to that of non-disturbed samples. This presentation will provide an overview of the ongoing experimental and modelling work relative to the long-term chemical durability of concrete containment systems.

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# IMMOBILIZATION OF OILY NUCLEAR WASTES WITHIN GEOPOLYMERS

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The UK nuclear stockpile of intermediate level waste (ILW) currently is approximately 150,000 m$^3$. This waste is by far the most problematic and diverse stockpile, due to its heterogeneity and in many instances their incompatibility with the solidification/stabilization practices typically adopted for the treatment of these wastes. Currently oily nuclear wastes are disposed of using a cementitious disposal route based on Portland cement. Cementation of ILWs including oils and other organic species present challenges such as a low waste loading and leaching of radionuclides, therefore, other disposal routes to overcome these issues need to be developed. One of the most promising routes for disposing of these wastes is via solidification using geopolymers. These binders are produced via a chemical reaction between an aluminosilicate precursor and an alkalis source to produce ceramic-like solids. When properly design and cured, geopolymers develop key properties for encapsulation of ILW, including formation of a zeolite-type structure with the ability to chemically bind some radionuclides that might be present in these wastes, and a highly homogeneous and compact structure making the material highly impermeable, so oils can be physically trapped within the waste form.

In this study, the effect of geopolymer mix design in their ability to encapsulate simulated oily nuclear wastes is determining. Understanding how the geopolymer matrix interacts with the oil, under the exposure of gamma irradiation is of upmost importance. These interactions will be studied extensively using optical and electron microscopy, along with other extensive analysis techniques.

# MECHANISMS OF ANION EXCHANGE IN HYDRATED CALCIUM ALUMINATES

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Hydrated calcium aluminates (AFm) are layered double hydroxide (LDH) phases, meaning that their structure consists in the stacking of layers bearing a permanent positive charge, compensated for by hydrated exchangeable interlayer anions. One of forms of AFm commonly found in cement is the one containing interlayer $Cl^-$, and is often referred to as “Friedel’s salt”.

As AFm are probably the most efficient anion-sorbing phases of many cements, determining their mechanisms of anion retention is of prime importance to the understanding of the mobility of anions in cement-based materials, and hence to our capacity to build robust reactive transport models. This has implications and applications in numerous settings. For example, many concepts of (nuclear) waste disposals sites make use of cement materials to build access structures and tunnels. In this configuration, cement will act as the interface between the storage site and its surroundings. Quantifying the potential retention by cement components, and in particular by AFm, will thus improve the modelling of potential anionic radionuclides mobility in such settings.

The quantitative modelling of anion retention can only be performed if the mechanisms are understood at the macroscopic (aqueous chemistry) and molecular scales. Indeed, determining the sorption sites at the molecular scale allows deciphering if sorption is due to reversible adsorption or to irreversible sorption (e.g. incorporation) phenomena and the nature and density of the sorption sites. All these information can be used to build robust geochemical models that allow modeling the data observed at the macroscopic scale.

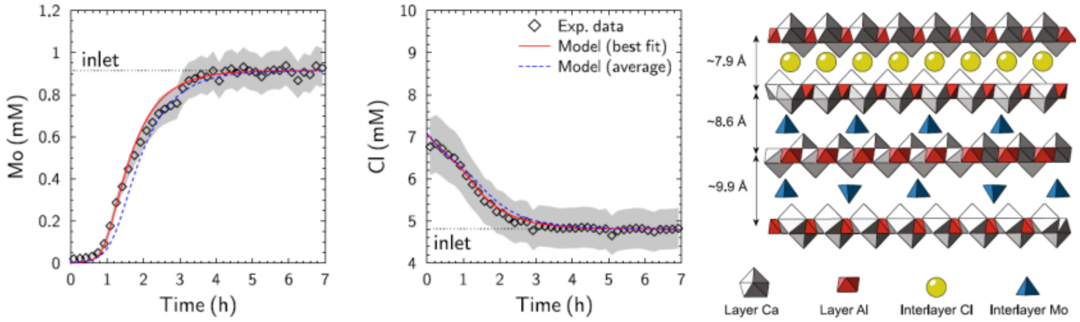

**Figure 1.** Modelling of Mo sorption by AFm initially containing interlayer $Cl^-$. Left: data (open diamonds) and modelling (using a per experiment model – red solid line or an average model over all experiments performed – bue dotted line) of Mo concentration as a function of time, after a Mo-containing solution was percolated though an AFm suspension. The red area materializes the data uncertainty. Middle: same figure, but for $Cl^-$ concentration as a function of time. Right: structure model for Cl-/$MoO_4^{2-}$ exchange. When the interlayer contains Cl-, the layer-to-layer distance is ~7.9 Å. When $MoO_4^{2-}$ replaces $Cl^-$, the layer-to-layer distance expends to ~8.6 Å and ~9.9 Å, depending on $MoO_4^{2-}$ configuration in the interlayer and on the relative humidity. After Marty et al. (2018)

Here, we combined several chemical and physical methods, including flow-through experiments, microprobe analyses, and synchrotron high-energy X-ray scattering to quantify the mechanisms of molybdenum (Mo) and selenium (Se) adsorption, and the sorption reversibility, by AFm initially containing Cl. It was shown that the sorption is due to reversible adsorption phenomena. For example, Mo adsorbed in the interlayer as tetrahedral $MoO_4^{2-}$ by replacing mainly $Cl^-$ at the same crystallographic site, with an Mo:Cl exchange stoichiometry of 1:2, and with a layer-to-layer distance increase due to the larger radius of $MoO_4^{2-}$ as compared to $Cl^-$ (see figure 1 for the general scheme of exchange). However, because experiments were conducted at high pH values to remain in the AFm chemical stability field, it was observed that $OH^-$ played a significant role in the sorption, competing with $MoO_4^{2-}$ for adsorption sites. Selectivity constants could be determined for all three anions. However, when $OH^-$ replaced $Cl^-$, the sorption site became unavailable for further $MoO_4^{2-}$ sorption. Thus, the $Cl^-$/$OH^-$ competition must be considered when modelling anion sorption by AFm.

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# CEMENTITIOUS MATERIALS AGING IN CARBONATE-ROCK/CEMENT-PASTE INTERFACES WITH IMPLICATIONS FOR DEEP GEOLOGICAL DISPOSAL SITES

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In deep geological disposal sites for radioactive waste, interfaces between cementitious materials, used either as engineered structures or as waste forms, and host-rock are often found. Such interfaces might lead to chemical and structural alteration of both the cement and the rock. In the case of carbonate rocks, carbonation of the cement hydration products (e.g. portlandite, C-S-H, and ettringite) leads to pH decrease in the paste. Portlandite carbonation results in subsequent decalcification of C-S-H that leads to changes in the cement strength and may lead to structural failure. Furthermore, the mobility of trace constituents (e.g. radionuclides) may increase in response to changes in pH, porosity, and mineralogical gradients.

As carbonate rocks have not been previously considered as host rocks for a deep geological repository of nuclear waste, their interaction with cement phases has not been studied extensively. The objective of the present study is to characterize the long-term performance of interfaces between cementitious materials and carbonate rock with respect to primary phases and trace constituents.

The present study compares the performance and interactions between Ordinary Portland Cement (OPC) and low pH cement with two typical carbonate-bearing rocks from the Negev region: chalk and marl of the Mount Scopus group, from the Northern Negev, Israel. The two rocks, as well as the two types of cements, were studied for their solid phase characterization, pH dependence leaching test (EPA 1313), and semi-dynamic transport tests (EPA 1315 egress and ingress using LiBr as a tracer) using cement/rock simulant pore solutions. The samples were held at 30 °C during curing and testing. The samples' porosities were measured and XRD mineralogical analyses were conducted. The LeachXS/ORCHESTRA platform was used for developing a geochemical reactive transport model that considers: mass transport, cement chemistry, geochemical speciation, and multi-ionic diffusion.

The experimental results of EPA 1313 and EPA 1315 tests were used for calibration and validation of a cement aging model. Simulation results show propagation of a carbonation front from the cement – rock interface into the cementitious materials and the redistribution of constituents and phases. Amongst other things, the rate of carbonation was found to depend on the cement and rock types.

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# CORROSION OF IRRADIATED STEEL IN CEMENTITIOUS ENVIRONMENT: SPECIATION OF CARBON-14

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Safety assessment shows that $^{14}C$ is one of the main contributors to the annual dose from a cement-based deep-mined geological repository for low- and intermediate-level radioactive waste (L/ILW) in Switzerland. For current safety assessment it is assumed that $^{14}C$ mainly contributes to the dose in its organic form, e.g. as $^{14}C$-bearing organic compounds, which are weakly retarded by the cementitious near field. A compilation of activity inventories revealed that $^{14}C$ in L/ILW in Switzerland is mainly associated with irradiated steel (~75 %). $^{14}C$ is produced according to the nuclear reaction $^{14}N(n,p)^{14}C$ by the activation of nitrogen impurities in stainless steel exposed to thermal neutron flux in nuclear reactors. Slow corrosion of irradiated steel will give rise to the release of $^{14}C$ in the deep-mined geological repository. Although the inventory of $^{14}C$ in the irradiated waste forms is well known, the chemical speciation of $^{14}C$ in the cementitious environment upon release from irradiated steel is still poorly understood. The present study is aimed to fill this knowledge gap.

To this end a corrosion experiment with irradiated steel is currently being carried out. The experimental design includes a reactor system to perform the corrosion experiment with irradiated steel and analytical methods suitable to quantify the $^{14}C$-bearing compounds in the liquid and gas phases. Identification and quantification of these compounds is a particularly challenging task because the inventory of $^{14}C$ in irradiated steel is low and the corrosion of steel in the alkaline conditions of a cement-based repository is very slow (few nm/year). Therefore, the concentrations of the $^{14}C$-bearing compounds in the liquid and gas phases are expected to be extremely low. Compound-specific radiocarbon analysis (CSRA) is the only suitable analytical technique to determine the compounds at the given concentration level.

CSRA for dissolved compounds, mainly carboxylic acids [1], is based on a combination of chromatographic separation of the individual $^{14}C$-containing carboxylic acids using high performance ion exclusion chromatography (HPIEC) and $^{14}C$ quantification by accelerator mass spectrometry (AMS) [2]. The first results from the corrosion study with irradiated steel show that the analytical approach can be successfully applied to determine the total organic $^{14}C$ content (TO$^{14}$C) in solution. In addition, individual $^{14}C$-bearing compounds could be identified. The type of aqueous $^{14}C$-bearing compounds formed during the corrosion of irradiated steel was previously identified in corrosion studies with non-irradiated iron powders [3]. The concentration of the $^{14}C$-bearing compounds was found to increase very slowly with time in line with the low corrosion of stainless steel in alkaline conditions [4]. The CSRA method for $^{14}C$-bearing compounds will be presented including first results from the corrosion experiment with irradiated steel conducted in conditions relevant to the cementitious near field of an L/ILW repository.

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# UPTAKE OF Be(II) BY ORDINARY PORTLAND CEMENT IN THE DEGRADATION PHASE I

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Beryllium is a chemotoxic element used in nuclear reactors as reflector or moderator due to its low thermal neutron absorption cross section and its specific chemical / structural properties. For this reason, beryllium is also found in specific waste forms in repositories for the disposal of radioactive waste. In contrast to other alkali-earth elements, beryllium is characterized by an amphoteric behavior involving the formation of cationic and anionic hydrolysis species under acidic and alkaline pH conditions, respectively. In the hyperalkaline pH conditions defined by cementitious systems, two $Be(OH)_3^-$ and $Be(OH)_4^{2-}$ species are expected to dominate the aqueous speciation of Be(II) [1, 2]. There are virtually no experimental studies investigating the uptake of beryllium by cementitious materials, although a weak sorption can be hypothesized based on the negative charge of the Be(II) aqueous species prevailing in the aqueous phase. In this framework, this contribution focuses on the sorption of beryllium on fresh Portland cement (degradation phase I, pH ≈ 13) under a range of initial beryllium concentrations $[Be]_0$ and solid-to-liquid ratios (S/L). The main goal of this study is to provide a quantitative assessment of the Be(II) uptake in cementitious environments relevant in the context of nuclear waste disposal.

All experiments were performed in an Ar-glove box at T = (22 ± 2) °C. Ordinary Portland cement (CEM I 42,5 N BV/SR/LA type) was used as sorbent material in all the experiments. Artificial cement porewater (ACW) with pH = 13.1, $[Na]_{tot} = 0.03$ M, $[K]_{tot} = 0.08$ M and $[Si]_{tot} = 10^{-3}$ M was prepared based on the original porewater composition reported elsewhere for the investigated cement formulation [3]. Batch sorption experiment were conducted with $10^{-6}\text{M} \leq [Be(II)]_0 \leq 10^{-2.5}$ M and $2\ g\cdot L^{-1} \leq [S/L] \leq 50\ g\cdot L^{-1}$, where the solubility limit of $\beta$-$Be(OH)_2(cr)$ was considered in the definition of $[Be(II)]_0$. Sorption kinetics were monitored for up to 60 days. Total concentration of Be(II) in the aqueous phase was quantified by ICP–MS after ultrafiltration with 10 kD filters. The detection limit of ICP–MS (calculated as $3\sigma$ of the blank signal) for the quantification of beryllium in the conditions of our experiments is ≈ $10^{-8}$ M.

Preliminary results show a relatively strong uptake of Be(II) by ordinary Portland cement in the first degradation phase. In all investigated systems, the concentration of Be(II) in the aqueous phase after equilibration with cement is well below the solubility limit defined by $\beta$-$Be(OH)_2(cr)$ at pH ≈ 13, *i.e.* [Be(II)] ≈ $10^{-4}$ M, thus confirming that experimental observations are primarily driven by sorption phenomena instead of solubility. Relatively slow sorption kinetics are observed (sorption equilibrium achieved > 10 days), suggesting that additional processes beyond surface complexation might be involved in the uptake of Be(II). Further results from on-going experiments will be extensively discussed in this contribution.

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# IMMOBILIZATION OF LOW-LEVEL WASTE CONTAINING NITRATE IN GEOPOLYMERIC SYSTEMS

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Geopolymers are considered as an alternative waste forms for the immobilization of low-level radioactive waste containing strontium and cesium ions. Liquid low-level waste often contains high concentrations of nitrate ions. The main goal of this work is to examine the effect of nitrates on the immobilization of cesium and strontium in geopolymeric systems. The study has been conducted on both low and high Si/Al molar ratio systems (1 and 1.7 respectively), yielding semi-crystalline and amorphous matrices respectively.

Geopolymer pastes were prepared by the alkali activation of metakaolin at room temperature. $NaNO_3$ salt was added to the activation solutions in different amounts, in order to reach $NO_3^-$/Al ratios of 0.125 and 0.25. Blank samples were cast with no $NaNO_3$ added. $CsNO_3$ and $SrNO_3$ salts were added to the mixture, at a concentration of 3000 ppm, as waste simulants. The various formulations were analyzed using XRD, isothermal calorimetry and semi-dynamic and pH-dependent leaching tests.

XRD analyses had confirmed that high Si/Al matrices were amorphous. For the low Si/Al matrices, XRD revealed the presence of an amorphous phase, together with zeolites A and X. No nitrate bearing zeolites were detected.

The samples were sequentially leached for 3 months using the ANS/ANSI 16.1 method after one month of curing at RH of 100% and room temperature. Leached amounts of $Cs^+$ ions were found to be higher for low-Si/Al samples than for high Si/Al samples (12-21% vs. 2-4% respectively). Within each Si/Al ratio, $Cs^+$ Leaching was higher for samples with higher content of $NaNO_3$.

$Sr^{2+}$ leaching was considerably lower than that of $Cs^+$. Leached amounts of $Sr^+$ ions were also higher for low-Si/Al samples than for high Si/Al samples (0.3% vs. 0.15% respectively). No effect of $NaNO_3$ presence was found on $Sr^{2+}$ Leaching.

# INVESTIGATION OF THE UPTAKE OF Th, U, Np, Pu AND Am BY CALCIUM-SILICATE-HYDRATE PHASES

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Cementitious materials have been considered as construction material and technical barrier in prospective repositories for the long-term storage of high-level nuclear waste. Calcium-silicate-hydrate (C-S-H) phases are a major component of hardened cement paste (HCP) and mainly responsible for its retention capability. During cement degradation, the C-S-H phases change their composition from a high calcium-to-silicon (C:S) molar ratio of 1.8 in fresh HCP to a C:S ratio of 0.7. Thus, for the long-term safety assessment it is important to investigate the retention capability of the C-S-H phases regarding their changing composition for the different constituents of the radioactive waste. In particular, the long-lived actinides plutonium ($t_{1/2}(^{239}\mathrm{Pu}) = 2{,}44 \times 10^4$ a) and neptunium ($t_{1/2}(^{237}\mathrm{Np}) = 2.14 \times 10^6$ a) contribute significantly to the long-term radiotoxicity of the waste, but also americium and uranium.

We investigated the sorption of different redox stable actinides (Th(IV), U(VI), Am(III)) as well as the uptake of the redox sensitive Np(V) and Pu(III) on C-S-H phases in dependence of solid-to-liquid (S/L) ratios between 0.5 g $L^{-1}$ and 20.0 g $L^{-1}$ and C:S ratios between 1.8 and 0.7. In addition, the oxidation state and the coordination environment of the sorbed Pu(III) on C-S-H phases was investigated by high-energy resolution X-ray absorption near-edge structure (HR-XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy.

The experiments were performed with a contact time of 72 h and radionuclide concentrations between $1 \times 10^{-7}$ mol $L^{-1}$ and $1 \times 10^{-8}$ mol $L^{-1}$ in the sorption samples and $1 \times 10^{-6}$ mol $L^{-1}$ in the samples for the spectroscopic investigations, respectively.

The batch experiments showed a similar quantitative uptake (> 97%) of all investigated radionuclides by C-S-H phases, independent of the actinide oxidation state and the C:S ratio. The average distribution coefficients $R_d$ were approx. $10^5$ L $kg^{-1}$ [1] and agree with literature values that range from $R_d(\mathrm{Eu(III)}) > 2.7 \times 10^4$ L $kg^{-1}$ [2] to $R_d(\mathrm{U(VI)}) = 1 \times 10^6$ L $kg^{-1}$ [3]. The spectroscopic studies by Pu $M_5$-edge HR-XANES and Pu $L_3$-edge EXAFS showed oxidation of the initially added Pu(III) to Pu(IV) [1] and indication of incorporation of Pu(IV) in the interlayer of C-S-H phases, respectively.

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# UNDERSTANDING CEMENTITIOUS BACKFILL INTERACTIONS WITH GROUNDWATER COMPONENTS

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Cementitious backfills perform a number of safety functions that are important to the development of safety cases for ILW concepts for geological disposal. These include maintaining alkaline porewater conditions and providing a high sorption capacity for radionuclides. In the UK, the Nirex Reference Vault Backfill (NRVB) has been developed for such a role [1]. To improve our understanding of its long-term performance, a detailed program was undertaken to investigate potential cement alteration pathways that result from interaction of the NRVB with groundwater solutes. The objective was to demonstrate a capability to interpret the chemical and physical evolution of the backfill as a result of these interactions with groundwater, through a combined experimental and modelling study. To simplify the system, interactions with different groundwater components were considered separately, focusing mainly on sodium sulphate and magnesium chloride solutions. This helped develop an understanding of backfill attack by sulphate, magnesium and chloride, and may be of relevance to interactions with associated components of wastes as well as groundwaters.

The experimental program consisted of flow-through experiments using the selected solutions, and performed under conditions of constant flow, over timescales of up to 860 days. Elemental analysis and pH of the egressing eluent were determined throughout the experiments. At the end of the experiments, detailed solid analyses were performed on samples from various locations in the NRVB using a wide range of techniques. These were supported by dynamic leaching experiments performed on crushed samples of the altered backfill and on unaltered NRVB monoliths, in the same solutions. In the sodium sulphate experiment, sulphate attack resulted in the formation of ettringite, thaumasite and gypsum. For the magnesium chloride case, the results were dependent on the concentration of the magnesium in the ingressing solution. At higher concentration, precipitation of brucite at the upstream surface of the NRVB led to clogging and termination of the experiment after about one month. At lower concentration, no such clogging occurred, despite almost all the ingressing magnesium being removed by the NRVB over timescales of more than two years. For both systems, high pH values of the eluent were maintained over the full periods studied; for the sodium sulphate experiment the final pH was 12.7 (after 180 sample volumes) and for the low concentration magnesium chloride case pH 11.5 (after 749 sample volumes).

To aid the interpretation of the experimental data, reactive transport modelling was applied using the PHREEQC geochemical program. The experimental pH and major-element concentration profiles were selected as data sets for fitting. A “top-down” modelling approach was applied involving representation of the NRVB by a simple set of mineral phases, and including further model detail (effects of observed secondary mineral phases, kinetic dissolution of solids and lateral transport processes) only where they improved the overall fits. The resulting models were considered to be simple while maintaining consistency with the major features of the experimental data sets. The models provided good fits to the full sodium sulphate data set and to most of the data for the low concentration magnesium chloride experiment. This has helped to provide mechanistic interpretations of the evolution of NRVB, based on relatively simple sets of secondary mineral phases, as well as early kinetic control of mineral dissolution and diffusion-restricted release of portlandite components at longer times.

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# THE DFG SPP 2005 “CONCERT” PROJECT: STUDYING PARTICLE-PARTICLE INTERACTIONS RELEVANT FOR CEMENT PASTE RHEOLOGY

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The CONCERT project is a collaborative project between the Universities of Jena, Weimar, Hannover and KIT, within the priority program “Opus Fluidum Futurum” of the German research foundation (DFG). It started in summer 2018. The main topic of the project is to predict rheological properties of superplasitcized cement pastes and their transient evolution during cement hydration based on fundamental particle/aggregate interactions.

The experimental and modelling program conducted at KIT-INE and Uni Jena is focused on fundamental particle-particle interactions. The aim is to characterize the surface chemistry of relevant mineral phases (e.g. $SiO_2$, $C_3S$, $C_3A$) by means of zetapotential measurements as a function of solution composition (electrolytes: KCl, $K_2SO4$, $CaCl_2$), pH, and in absence and presence of selected superplasticizers, and to develop or adapt electrostatic surface complexation models for the selected mineral phases.

Particle-particle interactions are assessed experimentally by means of atomic force microscope (AFM) force distance measurements in sphere-plate geometry, using AFM cantilevers modified with corresponding mineral particles, at equivalent solution conditions.

Aim of the work at KIT and Uni Jena is to develop a coupled surface complexation modelling – charge regulation code, which will allow modelling of electrostatic particle-particle interactions as a function of solution composition beyond the classical DLVO approach.

Finally, the charge regulation code and measured adhesion forces will be used to interpret the rheological behavior of mineral suspensions of varying complexity from pure mineral particle suspensions to complex superplasticized cement pastes, which will be investigated by the project partners.

Here we present first zetapotential and force distance data measured on $SiO_2$ as a function of electrolyte (KCl, $K_2SO4$, $CaCl_2$) and pH (3-11). The AFM tip was in this case a commercial sharp silicon tip (Bruker SNL-10, 0.06 N/m, 2 nm tip radius), and the substrate a Quartz powder (Millisil W 12) embedded in epoxy resin and polished. Zetapotential measurements were performed on a Quartz powder with particle sizes < 5 µm in equivalent solutions.

At low pH (pH ~3) the magnitude of the diffuse layer potential at the $SiO_2$ surfaces is low (only slightly negative) for all electrolytes and weak attractive forces (~0.3 nN) between AFM tip and substrate upon approach are likely dominated by van der Waals interactions. Pronounced adhesion forces (~1 nN) are observed upon retraction of the tip from the surface.

With increasing pH the zetapotential drops to strongly negative values for 5 mM KCl and $K_2SO_4$. This decrease of zetapotential is as expected less pronounced in 50 mM KCl. Correspondingly, we observe by AFM at pH 11 more (5 mM KCl and $K_2SO_4$) or less (50 mM KCl) strongly repulsive interaction forces, which even outcompete adhesion. For 5 mM $CaCl_2$, the decrease in zetapotential with increasing pH is counter balanced by adsorption of $Ca^{2+}$ at the $SiO_2$ surface. Correspondingly, the AFM-tip experiences attractive forces (~0.2 nN) and strong adhesion (~1.7 nN) in this electrolyte even at pH 10.9.

Studies on the macroscopic rheological properties are underway.

# RELATIONSHIP BETWEEN QUANTITATIVE MINERALOGICAL MAPPING OF CEMENTITITIOUS MICROSTRUCTURE AND LEACHING EXPERIMENTS: AN INNOVATIVE CHARACTERIZATION OF THE RADIONUCLIDE MIGRATION

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The migration of radionuclides through cementitious barriers in the context of radioactive waste repositories is characterized by transfer parameters such as diffusion coefficient and distribution factor (Rd) for sorption. These parameters, which are usually determined from diffusion and batch experiments respectively, are macroscale properties. However, the cement-based materials are highly heterogeneous with many solid phases such as hydrate, unhydrated binder grains or aggregates. Consequently, the role of each component of the hardened cementitious materials remains poorly characterized among the solid phase mix. Independently on the uncertainties induced by the heterogeneity, there is a need (i) to identify the solid phases contributing to the radionuclide transfer in-situ, within the own microstructure of a sample, and (ii) to observe the evolution of the elements of interest within this microstructure under a leaching or a contamination. This work presents the combination of several technics, in particular the quantitative mineralogical mapping, to investigate the radionuclide behavior at the microstructure scale once it migrates. Focusing on specific radionuclides (Ba, Sr, Cs) as trace elements or contaminants, this contribution aims to identify the radionuclide-bearing phases in a pristine material and after leaching or contamination. Moreover, an innovative information on the foreseen influence of innate trace elements is presented.

Cement CEM V from Ciments Calcia (Rombas - CEM V/A (S-V) 42.5 N CE PM-ES-CP1 NF "PMF3") was deeply characterized in terms of chemical composition by X-ray fluorescence spectrometry and ICPS-MS so as to provide trace element content. As expected, this measurement showed that many trace elements are present. Hardened cement pastes were casted with a water-to-cement ratio of 0.4. The HCP chemical composition was estimated with the same procedure than unhydrated cement. The concentration of the trace element in pore solution have been measured confirming the presence of trace as solute species. Leaching tests on hardened cement pastes were performed with different solid-to-liquid (S/L), indicating various trends of the major/trace element leaching as a function of the S/L ratio. These trends are related to surface sorption or dissolution/precipitation mechanisms. The rates of removable Ba or Sr show the importance of the remaining unhydrated binder content. A relationship between the quantitative mapping and the sorption parameter of these elements in the cement-based materials is established revealing the influence of C-(A)-S-H and calcite in the behavior of Ba and Sr in solution. Alternatively, if Ba and Sr were innate elements, HCP samples were exposed to Cs by electro-diffusion tests. Quantitative mapping evaluated that Cs is well bound to the cementitious matrix. These results are discussed regarding the existing Kd data as given by Ochs et al. (2016), in particular on Cs for which there is a lack of data to fully cover the range of degraded states.

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# RADIONUCLIDE RELEASE FROM SPENT FUEL UNDER ANOXIC / REDUCING CONDITIONS IN CEMENTITIOUS SOLUTION

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The release of radionuclides from spent $UO_2$ fuel under representative conditions of the Belgian "Supercontainer concept" is being investigated in the present study. Hence, dissolution experiments using high burn-up spent nuclear fuel (SNF) samples are currently performed in highly alkaline (cementitious) solution and anoxic/reducing atmosphere.

The $UO_2$ material was sampled from a fuel rod segment, which was irradiated in the Gösgen pressurized water reactor (Switzerland) during four cycles. The fuel rod achieved an average burn-up of 50.4 GWd/$t_{HM}$. As leachant, a synthetic Ca-bearing solution representative of concrete pore water at the early stage of cement alteration was prepared and used in the experiments, the so-called Young Cement Water with calcium (YCWCa, pH ~13.5). Three cladded specimens of about 20 mm length, each comprising a complete pellet plus two half pellets (thereby including two inter-pellet gaps), were prepared by dry cutting in a hot cell and absence of $O_2$. Then, the samples were introduced in autoclaves and exposed to YCWCa under anoxic/reducing conditions. Anoxic/reducing conditions in the autoclaves were established using an Ar/$H_2$ gas mixture or pure argon. The solution was completely changed after one day in order to reduce the amount of Cs in solution as well as to remove any potential U(VI) likely present as a pre-oxidized layer on the SNF surface. The duration of the leaching experiments is two years in batch mode. Gas aliquots and liquid aliquots of 10 mL were periodically taken to analyze the amount of radionuclides released into the gaseous and aqueous phases.

Results obtained after six of the seven planned samplings regarding the release of the fission gases (Kr and Xe), $^{90}Sr$, $^{137}Cs$ as well as actinides are presented.

# ALTERATION OF CHEMICO-PHYSICAL PROPERTIES OF ORDINARY CEMENT PASTE USED IN NUCLEAR WASTE DISPOSAL SUBJECTED TO COMBINED CARBONATION AND LEACHING DEGRADATION

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Cementitious materials are essential for Belgium's current nuclear waste disposal research as they are considered as construction materials and engineered barriers (EBS) for surface and deep-geological disposal facilities. As different mechanisms after disposal will produce gas phases inside the EBS, the cementitious material must not only retard the fluid migration from the waste into the surrounding host rock, but concurrently have a high enough transport ability to prevent pressure built-ups and, thus, potential fracturing. Due to the material's long-term exposure to the surrounding geochemical environment, aggressive water will be able to penetrate into cement through pore spaces and interact with the cementitious matrix leading to chemical degradation, especially from leaching and carbonation. Here, we are presenting the approach and results of the ongoing research on the combined effect of combined leaching and carbonation on physical and transport properties of Ordinary Portlandite Cement paste (OCP).

In order to investigate and quantify the combined alteration effect, we implement both experimental work and physico-chemical modelling. Experimental work is conducted on OCP (CEM I 52.5 N) samples which were cured for 28 days. The composition of these samples varies exclusively in their water-cement ratios from 0.4 to 0.6. After curing, the microstructure, mineralogy and transport properties of all samples are characterized to provide reference information in order to analyze effects of subsequent alteration experiments. Characterization techniques for both characterization and post-mortem analysis include nitrogen adsorption, He-pycnometry, MICP, TGA, XRD, permeability, diffusion, and SEM imaging with EDX analysis.

Alteration experiments were conducted under advective flow conditions for each cement paste composition. For each, the investigation was conducted on four similar specimens, through which fluid was streamed to initiate pure leaching, pure carbonation, combined leaching and carbonation, as well as a reference sample with host rock (Boom clay) like carbonate conditions. This is done to derive the combined alteration kinetics and rates and the influence of individual leaching and carbonation on the cement paste's characteristics. In order to simulate more realistic experimental conditions and enhance applicability of results to sub-surface environment, all alteration experiments were conducted under full saturation of the pore space. This represents a contrast to usual studies of degradation, especially carbonation, which usually only partially saturate pores by equilibrating samples with relative air humidity and using gaseous $CO_2$. Here, we immerse samples in a water solution with a controlled pH, ionic strength and dissolved carbonate content. As the degradation mechanisms are relatively slow processes, experiments are accelerated by adding ammonium nitrate and sodium bicarbonate for increased leaching and carbonation rates, respectively. Ratios and amounts of these accelerants are refined by 1D modelling (HP1).

Results show the feasibility of accelerating experiments. A decrease of permeability at early experimental stages indicates dominating influence of carbonation due to pore clogging. However, unlike in diffusive transport regimes, advective flow conditions do not result in a clear identifiable alteration front. Post-mortem analysis (MICP, TGA) shows that both carbonation and leaching have an overall far lesser effect on mineralogy and parameters such as pore size distribution and porosity as expected. However, significant permeability changes indicate more localized effects in the capillary pore system, where alteration is limited to specific capillary systems. Further, SEM/EDX analysis attest to this theory as reaction products such as calcite can predominately be found in larger capillary pores. The discrepancy between permeability and mineralogy changes can be explained, as fluid flow is governed primarily by only the size of largest connected pore system. Therefore, small microstructural changes can cause a significant change in transport properties (pore clogging). As these findings only represent alteration kinetics under advective conditions, we will repeat similar experiments under diffusive transport conditions, where we expect to see significant differences.

# REACTIVE TRANSPORT MODELLING OF CEMENT HYDRATION AND DEGRADATION. APLICATION TO USFD EXPERIMENTS.

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Within the framework of the European project CEBAMA, a low-pH cement mix is being used in a set of chemical alteration experiments. During cement hydration, the mixing water is partially consumed to form hydrates. Low-pH cement mixes include a substantial amount of supplementary cementitious materials that, if combined with superplasticizers, enables to reduce the content of water. If proper curing is not considered, self-desiccation may occur, leading to a decrease in the rate of hydration. The effect of curing can only be considered if an open system is assumed. However, modelling of cement hydration using geochemical simulators have traditionally entailed the hydration process as a closed system, with no interaction with the environment.

The simulated experiments have been conducted at the University of Sheffield [1], also within the framework of CEBAMA. Cylindrical specimens of hardened cement paste (HCP) have been cured for 28 days at a temperature of 40 ºC with a relative humidity (HR) of ≥95%. Subsequently, samples were exposed to synthetic groundwaters of different composition representative of granitic, saline and clay host-rocks. During groundwater-cement interaction, further hydration and leaching processes overlap in time. The modelling of these two simultaneous phenomena is the main novelty of the present work, which will allow to assess the impact of curing and leaching conditions on the resulting mineralogy of the altered HCP.

The role of curing conditions and internal relative humidity is studied by coupling hydration, moisture transfer and reactive transport processes in a single model. The model is used to evaluate the effect of internal moisture evolution and the interaction with the environment on the degree of hydration and the chemical composition of the cementitious system. The hydration of HCP samples is simulated with a 2D axisymmetric model implemented in iCP [2]. The approach is based on thermodynamic modelling coupled with a set of dissolution kinetic reactions for the binder. The rate of dissolution of each mix component is considered to be slowed down by a decrease in the internal RH by a humidity-dependent factor. In order to relate RH changes with the water content evolution calculated in the geochemical simulator Phreeqc, the adsorption/desorption isotherms are used [3]. The evaporable water content is updated in the model as water is consumed during hydration. Moisture transfer is solved in Comsol Multiphysics using a non-linear diffusion-based model. Hydration process then continues with the updated water content. From 28 days on, the model accounts for further hydration that occurs simultaneously with the interaction of the samples with groundwater.

Model results describe first the hydration of the HCP samples during 28 days in the curing chamber. Once HCP samples are in contact with different groundwaters, cement pastes present differences in mineralogical composition and porosity values. Self-desiccation occurs at early ages triggering moisture in-diffusion from the curing chamber. The degree of hydration after 28 days is around 0.85, while it keeps on increasing to reach almost a fully hydrated cementitious system after several years. Thus, hydration is highly influenced by groundwater interaction. As a result of this interaction, different secondary minerals are expected to appear for the different composition groundwaters impacting porosity and transport properties.

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# IMPROVING THE QUALITIY AND EFFICIANCY OF NUMERICAL SIMULATIONS AIMED TO ASSES TRANSPORT PROPERTIES OF CEMENTITIOUS MATERIALS

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Simulation of dissolution/precipitation processes with a pore-scale reactive transport model increases the insight in coupled chemical-physical transport processes. However, modelling of the dissolution processes has two major drawbacks, firstly, it requires an accurate description of the microstructure. Secondly a large number of times steps is needed, especially when the buffering of the capacity of the solid phase is high. To obtain an accurate description of the microstructure model, we developed a new hierarchal multiphase simulated annealing porous media reconstruction algorithm, which takes several SEM images as input to obtain a 3D representation of the microstructure. To address the second problem we propose an approach to reduce the number of required time steps. The efficiency of the approach is demonstrated on the equilibrium dissolution processes. The underlying idea is that the number of time step iterations can be reduced if the buffering is sufficient to transfer the system to a steady state, i.e. that the Concentration field around solid is time-invariant. Combing the two approaches strongly increases the quality and numerical efficiency of transport simulation in cement paste. The new porous media reconstruction approach increases the quality of diffusivity prediction by a factor of 10 compared to simulations using a microstructure models derived from traditional approaches such as CEMHY3D and the new reactive transport approach decreases the calculation time for numerical calcium leaching in cement by a factor of 50 while increasing the error only negligibly.

# REACTIVE TRANSPORT MODELLING OF CEMENT - CLAY INTERACTION ACCOUNTING FOR ELECTROSTATIC EFFECTS IN THE CLAY

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Cementitious materials are part of virtually all nuclear waste repository concepts. Many concepts also contain clay materials, either in the host rock or bentonite barrier. The enormous material contrast between cement and clay leads to interactions, which could be shown in many laboratory and large-scale URL experiments. Within the interaction zone, relevant properties of the clay material are altered (e.g., swelling behavior, permeability, specific retention).

Reactive transport modelling can reveal the numerous interrelated interaction processes, or even predict their long-term evolution. Previous modelling results from OPC - Opalinus Clay interaction indicate that a Mg-enrichment measured in the clay at 7 mm from the interface coincides with a high pH front entering from the cement side [1]. In contrast, low pH cement - clay interfaces show enriched Mg in both cement and clay directly at the interface [2]. New modelling indicates that the pH front enters the clay to a smaller extent. Other features of clay - cement interaction like decalcification, sulphur enrichment, and carbonation, as well as redistribution of the cations occupying the clay exchanger, can be reproduced for both interfaces (OPC and low pH).

The current model includes the hydration of the cement based on clinker and microsilica dissolution rates from reference measurements. Thermodynamic data of all cement phases and discretized solid solutions is taken from Cemdata07 and 18. From the onset of cement hydration, the cement porewater is connected to the Opalinus Clay porewater. This leads to diffusion over the interface controlled by chemical gradients, which change with hydration evolution. The solute transport in the Opalinus Clay occurs in two porosity domains: the porewater in the Donnan porosity is influenced by the negative charge of the clay minerals and therefore dominated by cations. Its composition is in Donnan equilibrium with the free porewater, which is charge-balanced. Its chemical composition can lead to porosity clogging. In turn, no clogging is assumed in the Donnan porosity due to unfavorable activities and geometry. In contrast to the close to equilibrium reaction rates of the cement hydrates, the clay mineral reactions are restricted by extremely slow rates known from literature.

The modelling approach can consistently represent chemical and phase measurements of different interfaces from the Mt Terri CI project. It helps to understand the numerous coupled interaction processes, which left behind a complex chemical and mineralogical zonation parallel to the interface.

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# COMPARATIVE STUDY OF RADIUM AND STRONTIUM BEHAVIOR IN CONTACT WITH CEMENTITIOUS MATERIALS

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Radium is a nuclide that needs to be studied for its importance for the safety assessment of repository of spent nuclear fuel. It is necessary to examine its mobility, which is influenced, among other things, by the retardation via sorption on materials of engineered barriers, including cement materials. The uptake and diffusion of radium and strontium, its assumed analogue, in presence of cementitious materials were studied. Ra and Sr behavior is characterized by the distribution coefficient between liquid and solid phases, $K_d$.

A comparative study of sorption behavior of radium and strontium was done on several cementitious materials: three hardened cement paste (HCP CEM I, CEM II and CEM III) and two types of concrete based on two of HCP used (both concretes are actually utilized in the storages of radioactive waste in the Czech Republic, Concrete CEM I and CEM III); all crushed and sieved on fraction ≤ 0.4 mm; and on CSH phase.

The cementitious materials were analyzed by X-ray diffraction and used to the study of equilibrium sorption of the $^{223}$Ra (used as an analogue of the critical radionuclide $^{226}$Ra) and $^{85}$Sr (used as an analogue of $^{90}$Sr). Sorption experiments with $^{223}$Ra were carried out strictly in a carrier-free arrangement with the concentration of Ra approx. $10^{-12}$ mol/L, while those with Sr were done with the initial concentration of Sr $c_0 = 3.5\cdot10^{-4}$ mol/L labelled by $^{85}$Sr or as carrier-free. In addition, all the cementitious materials used contain Sr, which may affect the experiment. The conditions, under which experiments were held, included the variable temperature (22, 50, 65, and 80 °C) and the liquid-to-solid ratio $V/m$ (10 to 1000 L/kg). The starting solution was Portlandite water (saturated $Ca(OH)_2$).

A comparative study of sorption on the CSH phase was supplemented by experiments with $^{133}$Ba and also the isotopes of interest ($^{226}$Ra and $^{90}$Sr; all isotopes were used in a concentration range of $5\cdot10^{-10}$ – $5\cdot10^{-7}$ mol/L. These experiments were performed in equilibrated CSH solution.

The evaluation using linear sorption isotherm revealed that obtained $K_d$ values for Ra uptake reach the values in the range of 70 – 650 L/kg, while that for Sr 10 – 130 L/kg on real cementitious materials. $K_d$ values in the range of $V/m$ from 10 to 600 L/kg are mostly comparable for Sr (10 – 20 L/kg), but the $K_d$ for Ra are rising in general. Sorption experiments with the CSH phase confirmed a significant difference between Sr, Ba and Ra at the $K_d$ values, as expected from previous studies. Similarly, the difference between real cements and pure CSH phases was confirmed. Values of $K_d$ for Sr were in the order of hundreds, for barium in the order of thousands, and for radium increased to the order of tens of thousands L/kg. The kinetics of Sr and $^{223}$Ra uptake was evaluated by a set of six models based on the different rate-controlling processes, and describing the sorption in heterogeneous systems. The DM (two-film) model in a case of Ra, and the DIL (diffusion in inert layer) model in a case of Sr proved to be the most convenient.

Through diffusion experiments over a 0.5 cm wide layer formed by pressing of crushed HCP CEM II were performed with Portlandite water. Ra, as in the case of the sorption study, was carrier-free, Sr with a carrier ($c_0 = 3.5\cdot10^{-4}$ mol/L). $K_d$ values determined by evaluation of diffusion experiments was around 9 L/kg for Sr, and 150 L/kg for Ra.

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# INFLUENCE OF TEMPERATURE PULSE ON A CEMENTITIOUS NEAR FIELD

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The Swiss repository design for high level waste is based on a bentonite backfill surrounding the waste canisters. We investigated the performance of a CEM III/B based concrete as alternative backfill material replacing the bentonite.

Of special interest is the influence of temperature on the mineralogy, transport and long-term interaction with the surrounding host rock. Increased temperatures as expected in a backfill, accelerate not only the reaction of the cement and other materials, but affect also the composition of the hydrates and of the pore solution.

In a first step we modelled the effect of temperature on a completely hydrated cement (see Figure 1). The stable phases as a function of temperature were calculated based on the PSI-TDB coupled with Cemdata18 database plus crystalline C-S-H phases from the Thermoddem database, as shown in Figure 1. The kind and the volume of C-S-H phases formed depend strongly on the temperature. The formation of α-C2SH at high temperature agrees with experimental observations in blended Portland cement.

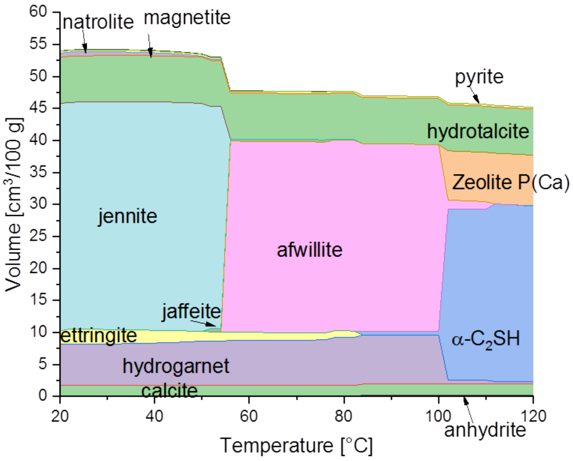

*Figure 1: Effect of temperature on the calculated volume of hydrates and solution in a completely reacted CEM III/B using the PSI-GEMS TDB plus the Cemdata18 database plus crystalline C-S-H phases from the Thermoddem database.*

We used a reactive transport model to investigate the temporal geochemical evolution of the near-field in contact with the adjacent host rock. The models include the effect of thermal pulse on transport and chemical reactivity. We considered that at elevated temperatures the system evolves faster due to the increase of solute diffusivity with temperature, the change of solid solubility with temperature (decrease or increase) which depends on the solid, and the change of kinetic dissolution/precipitation rates with temperature.

Porosity clogging at the concrete/Opalinus Clay interface is very likely to occur. Clogging times are highly uncertain. After clogging, mass fluxes between concrete and Opalinus Clay will be largely reduced which will slow down concrete degradation.

# QUANTUM CHEMICAL MODELING OF U(VI) SORPTION ON CALCIUM SILICATE HYDRATE

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Cementitious materials as commonly used for radioactive waste solidification and in the construction of geological repositories for highly radioactive waste may affect the release of radionuclides. Calcium silicate hydrates (CSH) are major constituents of cement and its degradation products and have been identified as the main sorbing phase for actinide ions. A mechanistic understanding of these sorption processes is an important prerequisite for thermodynamic and transport modeling of safety aspects. For reaching this goal, quantum chemical (QC) calculations offer a complementary approach to the commonly applied spectroscopic methods of investigation at the atomic scale. The detailed structure of CSH, which is at best nanocrystalline, is still unknown and considered to be similar to tobermorite. We use 14 Å tobermorite, ideal and defective, as a model of CSH phases. C/S ratios of 0.67, 0.83, and 1.0 are modeled by varying content of $Ca^{2+}$ cations in the interlayer.

We applied a density functional method together with the plane-wave based projector augmented wave (PAW) approach to account for core electrons, as implemented in the program VASP [1]. Sorption systems were represented by periodic supercell models. To calculate reliable sorption energies, a simulated annealing (SA) procedure has been invoked [2]. We examined the incorporation of $UO^{22+}$ into the interlayer region and adsorption on the (001) surface. We used chemical intuition and a half-automatic search to identify suitable sorption sites for uranyl. As a common defect and also to account for the low crystallinity of CSH, we studied also sorption sites at missing bridging Si tetrahedra.

According to our model results, sorbed uranyl ions are mostly four-coordinated. With increasing C/S ratio, absorbed uranyl coordinates up to two OH ligands instead of aqua ligands in the first coordination shell. When uranyl is sorbed in the interlayer, the OH ligands bridge uranyl ions with interlayer $Ca^{2+}$ cations, which is not the case when $UO^{22+}$ adsorbs on the surface. Structural parameters of the absorption and adsorption complexes were determined to be similar. Thus, U(VI) species adsorbed at the (001) surface of tobermorite or incorporated in the interlayer will not easily be distinguishable by geometric parameters. For both types of sorption complexes structural parameters were calculated as measured by EXAFS [3], but not all of them are simultaneously present in a single sorption complex. Therefore, we conclude that several species contribute to the EXAFS result. A preliminary comparison of energies shows that adsorption on the surface tends to be only somewhat favorable compared to interlayer sorption, at the same C/S ratio. Thus, we expect that both sorption mechanisms may occur simultaneously.

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# THERMODYNAMIC MODELLING OF AN & FP UPTAKE IN C-S-H

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Calcium silicate hydrate (C-S-H) phase with so-called “defect-tobermorite” structure is abundant in most cementitious waste forms. C-S-H can incorporate Na, K, Al cations [1], Zn [2], as well as actinides/analogs An (Th(IV), U(VI) [3]; Cm(III), Eu(III) [4]) and fission products FP (Sr [5], Ba [6], Ra [7]) relevant for radioactive waste disposal. Previous attempts to extend C-S-H thermodynamic solid solution models with such cations [2,8-10] were only partially successful because they did not account properly for cations binding onto specific structural sites; the resulting models were not incremental (i.e. adding new end-member(s) would lead to re-parameterization of the whole model), and not precisely describing some uptake isotherms measured at different Ca/Si mole ratios.

Recently, we presented a more rigorous, structurally consistent sublattice solid solution model CNKASH [11] that can accurately describe the solubility, non-gel water content, and mean silicate chain length (MCL) of variable-composition C-S-H “gels” [12]. The model assumptions included possible atomistic defects in tobermorite structure [13], and that charges acting on interlayer cationic (IC) sublattice sites originate in bridging tetrahedral (BT) sites from the deprotonation of silanol groups. Thus, any end member was constructed using a template BT:IC:IW:DU, where IW is $H_2O$ or vacancy in the interlayer water site, and DU is a dimeric unit of tobermorite structure. Ca and Al can enter both BT and IC sites, whereas Na or K can enter IC sites. Moieties and vacancies were chosen to yield realistic non-gel water content at various Ca/Si ratios. The model has been implemented in GEMS codes and parameterized [12] using the GEMSFITS code (http://gems.web.psi.ch). Extensions with end members for Na, K and Al could be parameterized incrementally (i.e. keeping previously fitted input properties all fixed).

Achieved levels of precision and incrementality pave the way for the efficient use of available sorption isotherms and the knowledge of An & FP binding sites in C-S-H via further extensions of our CNKASH model to cover disposal-relevant applications of thermodynamic modelling of waste-cement interactions. It is known [5-7] that in C-S-H, the sorbed Sr, Ba, Ra occur mostly in IC sites, whereas An and REE may also occur in BT sites or form surface precipitates [3,4]. Using this knowledge, the necessary end members and interaction parameters for each cation can be defined, and their properties then fitted against the uptake isotherms at different Ca/Si mole ratios. This incremental fitting strategy is fairly feasible using code tools such as GEMSFITS. Verification can be done by comparing blind model predictions with isotherms that have not yet been used in the parameterization process.

This presentation is aimed at summarizing the current progress in extending the CNKASH solid solution model with An & FP end members, first of all, for those cations that have already been added to previous C-S-H solid solution models [8, 9, 14]. Pros, cons and perspectives of the new CNKASH model and its enhancements with An & FP parameters will be discussed, along with examples of the quality of fits and of the uptake prediction and model verification.

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# TRITIATED WATER DIFFUSION IN FRESH AND CARBONATED CEMENT PASTES: EFFECT OF A DRYING/RESATURATION CYCLE

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In the French radioactive waste management context, cementitious materials will be widely used as engineered barriers, backfill materials or confinement matrices for some Intermediate-Level Long-Lives waste. In a waste disposal facility, during the construction and the operation phases, the ventilation of underground galleries/shafts will impose specific conditions (relative humidity, presence of $CO_2$) that will modify the degree of water saturation ($S_w$) of cement materials (surfacial drying) and induce a potential carbonation. The aim of this study is to investigate the effect of a drying/resaturation cycle on the effective diffusion coefficient of tritiated water (HTO) in fresh and carbonated cement pastes.

Samples used are disks (2 mm thick) of a CEM V/A hardened cement paste (HCP) prepared with a water to cement ratio of 0.43 and cured at least 27 months in an artificial cement pore water (ACW ; pH~13.5) [1]. The drying stage consisted of storing HCP samples (during several months at 20±1°C under Ar atmosphere) at fixed relative humidity (RH) imposed by saturated saline solutions. Thus, initial $S_w$ values obtained range from 0.63 to 0.85. Afterward, HCP samples were resaturated with ACW (under vaccum). Additionally, a fully saturated sample was used as a reference. Carbonated samples were prepared in conditions representative of atmospheric carbonation [2]. An accelerated carbonation process was performed in a climatic chamber ($P_{CO2}$ = 3% vol ; RH=55 % in order to obtain a maximal carbonation rate). Through-diffusion experiments were performed, in at least duplicate, using standard two-reservoir set-ups. The effective diffusion coefficient, $D_e$(HTO) and material capacity factor, $\alpha$ were obtained by modelling the HTO cumulative activity curves (in the downstream reservoir) with a routine based on an analytical solution of Fick laws (with fixed initial and boundary conditions).

$D_e^{ref}$(HTO) value, obtained for the reference sample is $3\pm1\ 10^{-13}\ m^2.s^{-1}$ which is in agreement with literature data for this materials [1,3]. For fresh HCP samples, $\alpha$ values are similar to water accessible porosity (0.33±0.02). No significant HTO retention is then assumed in HCP samples.

For fresh HCP, the drying/resaturation cycle results in a slight non-linear increase of $D_e$(HTO) values as initial $S_w$ values diminish. This result is consistent with the reported description of the drying effect on HCP microstructure [4]. For high initial $S_w$ (0.85), water is mostly drained from the capillary porosity with no specific effect on HCP microstructure. As this process is reversible the final $D_e$(HTO) value (after resaturation) is similar to $D_e^{ref}$(HTO). For intermediate initial $S_w$ (0.63), the water molecules, distributed as multilayers at C-S-H particles surfaces, partly desorb and cause small changes in the mesopore distribution by opening/closing pores (MIP measurements) which ease HTO diffusion through the pore network. The impact on $D_e$(HTO) value is an increase by a factor of 2 ($5.4\pm0.4\ 10^{-13}\ m^2.s^{-1}$).

For carbonated HCP samples, the drying/resaturation cycle results in decreasing the water accessible porosity (0.21±0.01) and increasing of $D_e$(HTO) value ($12\pm2\ 10^{-13}\ m^2.s^{-1}$). These results are consistent with a combination of porosity clogging (precipitation of $CaCO_3$ in pores) and presence of microcracks (decalcification of C-S-H) as described in Auroy *et al* study [2]. The increase of $D_e$(HTO) value supports the conclusion that for CEM V HCP, microcracks could be the main pathway for diffusion of HTO in carbonated samples.

Comparing to the reference sample (fully saturated non-carbonated HCP), these results suggest that HTO diffusion is favoured during a drying/resaturation cycle. For a blended cement, this effect may be enhanced if coupled with carbonation.

## Acknowlegment

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# MOLYBDENUM ADSORPTION ONTO CEMENT HYDRATES. THE ROLE OF C-S-H AND AFM PHASES

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Cementitious materials have good properties as solidification/stabilization agents for radioactive waste[1]. Their potential for retaining many contaminants is great due to their high sorption capacity. This capacity is related to the chemistry and structural characteristics of different pure phases that constitute the hydrated cement paste. Among different pure phases, several authors proposed AFt, AFm or C-S-H gels as viable cement constituents for oxyanion immobilization via sulphate or silicate substitution[2]. In this work, molybdenum was selected as targeted oxyanion mainly due to the scarcity of data related with its retention under cementitious conditions. Molybdenum-93 is an activation product from steel corrosion with a half-life of 4.000 years. The main parameters affecting the mobility of this element in cement pore water are pH, redox potential (Eh), and the calcium concentration. Under aqueous cementitious conditions, Mo speciation is dominated by molybdate ($MoO_4^{2-}$). The mobility of $MoO_4^{2-}$ under cementitious conditions could be controlled by different processes involving sorption, ionic exchange or precipitation, depending on the characteristics of the pure phase and on its contacting waters.

Our work, included in the frame of CEBAMA European Project, deals with the study of molybdenum retention onto different pure cement phases. The main goal is to analyze the retention mechanisms of molybdenum under cementitious conditions by developing a bottom-up approach, starting with the study of cement single phases to hydrated cement pastes. Tested phases included AFt, C-S-H gels (three C/S ratios 0.8, 1.2 and 1.4) and mixed phases with different AFm/AFt ratios (S(VI)/Al (0.5, 1, 2, 2.5)). Experimental work started with the synthesis and characterization of the targeted solids and their equilibrium solution in order to stablish a well characterized starting point. Our solid and liquid characterization were in agreement with other data reported in bibliography which indicates the presence of (i) stable single phases in the case of AFt and C-S-H gels, and (ii) AFm/AFt mixtures with variable S(VI)/Al ratios. From solubility experiments, we determined that the solubility product reported for $CaMoO_4$ (7.9±0.33)[3] allows describing all the experimental results obtained using different contacting solutions. Kinetic studies showed very low molybdenum retention capacities for AFt, C-S-H gels (0.8 and 1.2) and AFm/AFt (S(VI)/Al=2 and 2.5) while C-S-H 1.4 and mixed phases containing higher AFm proportions (S(VI)/Al=0.5 and 1) gave not only good retention values but also fast retention kinetics. Isotherm experiments, restricted to those latter, revealed that the phase with highest AFm proportion (S(VI)/Al=0.5) retained molybdenum more efficiently, achieving elimination percentages close to 100%. Mixed phase with S(VI)/Al=1 and C-S-H 1.4 also presented good retention capacities for molybdenum but lower than that observed for AFm with S(VI)/Al=0.5. The comparison of our results with other studies reported in bibliography indicated that the retention process may be ruled by edge sorption mechanisms[4].

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# THE IMPACT OF RECYCLED CONCRETE SCABBLINGS ON THE HYDRATION AND PERFORMANCE OF NUCLEAR ENCAPSULATION GROUTS

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Concrete scabblings - where the outer layer of radioactively contaminated concrete is removed from the bulk - arising from nuclear decommissioning are classified as intermediate (ILW) or sometimes low-level waste (LLW), and as such require disposal. The disposal route for ILW wasteforms in the UK is through encapsulation in a cementitious grout matrix. Nuclear encapsulation grouts contain high levels of blast furnace slag, with a 3:1 GGBS:OPC ratio used to reduce thermal cracking from heat of hydration at early ages, and to maintain the pore solution pH in an appropriate range to limit the solubility of radionuclides within encapsulated waste.

In order to improve the waste to container volume ratio, a co-disposal method has been proposed whereby the scabblings are used as a filler material within the grout. As such, the impact the material has on the properties of the encapsulation grout have been investigated.

Two high strength (50 MPa) concretes were used to produce synthesized scabblings; prepared with either CEM I or CEM IIA (with 20% PFA replacement). Both were crushed and ground to a powder, with half of each powder then undergoing accelerated carbonation, (so as to simulate the binder composition at the depth to which radionuclide contamination is observed [1]). The 4 resultant powders were then used to replace binder within encapsulation grouts, with replacement levels of 10, 20 and 40%. Performance was then monitored over a period of up to 90 days.

Isothermal calorimetry was used to investigate hydration of the grouts at ages up to 28 days, and results were compared to mixes where quartz had been used as an inert filler at the same replacement percentages, to account for the filler effect[2][3]. The mixes containing scabbled material showed increased hydration compared to quartz, suggesting there is latent hydraulic material remaining in the scabblings, contributing to grout hydration above and beyond solely the filler effect.

After the first 24 hours of hydration, mixes containing carbonated material were found to show slightly increased strength and bound water content, compared to equivalent non-carbonated samples. This suggests increased hydration within the first 24 hours, in line with the previously reported positive effect of carbonates on slag hydration [4][5]. Despite a slight increase in early age strength, the addition of carbonated fines as opposed to uncarbonated fines had a more significant impact on the rate of initial reaction. At additions up to 40% of uncarbonated material, the dormant/induction period remains constant, while the early peak of aluminate hydration is accelerated when compared to mixes prepared with an inert filler. Use of carbonated material extends the dormant period proportionally to the percentage replacement, while the aluminate peak was also decelerated. Carbonate dissolution during hydration buffers the pH of the pore solution below 12.5 for significantly longer (up to 6 hours for 40% inclusion) than that of the uncarbonated material (1 hour for 40% inclusion), affecting the early hydration reactions. Finely ground powders of both original concretes, whether carbonated or not, affect the hydration kinetics of encapsulation grouts, and can’t be considered as inert fillers.

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# THERMODYNAMIC DATA FOR MAGNESIUM PHOSPHATE CEMENTS

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Magnesium potassium phosphate (MKP) cements show fast setting, high early strength and low pH such that MKP is used for rapid repairs and as solidification/stabilization agent for low-level nuclear wastes and wastes containing heavy metals. MKP cements harden in the presence of water due to the reaction of potassium dihydrogen phosphate ($KH_2PO_4$) with magnesia ($MgO$) resulting in the formation of K-struvite ($MgKPO_4 \cdot 6H_2O$). Different experimental studies showed that a number of other hydrates, such as $MgHPO_4 \cdot 3H_2O$ (newberyite), $MgHPO_4 \cdot 7H_2O$ (phosphorrösslerite), $Mg_3(PO_4)_2 \cdot 8H_2O$ (bobierrite), $Mg_3(PO_4)_2 \cdot 22H_2O$ (cattiite) and $Mg_2KH(PO_4)_2 \cdot 15H_2O$ are also formed during hydration.

Thermodynamic models have been developed to better understand the changes in hydrating cements and applied successfully to different cement types including Portland cement, blended Portland cement, calcium sulfoaluminate cement, or alkali-activated cements. The reliability of such model predictions relies on the accuracy and completeness of the underlying thermodynamic database. While during the last past two decades, significant effort has been made to complete thermodynamic data for calcium, silicon and aluminium based cements, much less effort had been focused on magnesium phosphate cements.

However, only limited thermodynamic data are available for magnesium phosphate hydrates; data for newberyite, cattiite, K-struvite and bobierrite have been reported [1, 2]. For other phosphate hydrates, such as $Mg_3(PO_4)_2 \cdot 4H_2O$ or $Mg_2KH(PO_4)_2 \cdot 15H_2O$, no measured solubility data exists. Thermodynamic data for magnesium phosphates have also been estimated from the free energy and enthalpy of the oxides, a procedure which can lead to accurate estimations in some cases, but can deviate in the order of several to several tenth of kJ/mol to the data derived from solubility measurements, which makes predictions of solubility and relative stability based on such data difficult. This lack of a complete and reliable thermodynamic database for hydrating MKP cement system prevents the efficient use of thermodynamic models to predict the effect of varying mineral composition, temperature and the environment in such systems. Thus, the present paper describes a consistent thermodynamic database for magnesium phosphate hydrates based on solubility measurements for newberyite, phosphorrösslerite, farringtonite, $Mg_3(PO_4)_2 \cdot 4H_2O$, bobierrite, cattiite, K-struvite, and $Mg_2KH(PO_4)_2 \cdot 15H_2O$ carried at different temperature and a critical review of existing thermodynamic data and solubility measurements from literature.

The formation of the different hydrates is mainly governed by pH of the magnesium potassium phosphate cement system. Newberyite, phosphorrösslerite and $Mg_2KH(PO_4)_2 \cdot 15H_2O$ are intermediate phases, which form at early hydration stage when pH of cement system is still low. Afterwards, these intermediate hydrates are either partially or fully transformed to the more stable phases, such as K-struvite, bobierrite, cattiite, depending on pH development in the MKP cements.

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# 5 YEARS MONITORING OF CEMENT-CLAY INTERFACES: HTO AND $^{36}$CL$^{-}$ DIFFUSIVITY AND ITS RELATION TO POROSITY CHANGES

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Multiple barrier concepts have been developed by several countries for the deep geological disposal of radioactive wastes. In these concepts, the properties of natural and several engineered barriers are used to isolate the waste from the biosphere. Cement is widely used as waste matrix and backfill and often comes in contact with clay rich host rocks. The geochemical differences between clay and cement pore water lead to mass fluxes across interfaces and cause dissolution-precipitation reactions. These reactions induce the formation of regions with modified transport properties, which may influence relevant safety aspects of the geological repository. The precipitation of new phases may cause a local reduction of the porosity and leads over long periods to a complete clogging of the pore space. Whether porosity clogging takes place or not is a fundamental issue regarding gas transport and radionuclide diffusion in the context of a geologic repository for radioactive waste. Accordingly, the development of cement-clay material interfaces has to be studied in detail.

Due to the small extents of altered zones and the mechanical fragility of cement-clay interfaces the sample preparation for the experimental investigations of this system is very challenging. A special cell was therefore developed that allows studying the evolution of the diffusive behavior of reacting interfaces by means of macroscopic through-diffusion experiments and simultaneously investigating the porosity evolution with neutron imaging. To simplify the system, high-porosity cement and Na-montmorillonite were used as model components for the interface samples. Evolution of cement-clay interfaces were repeatedly monitored with various non-destructive methods over a period of five years. Diffusion experiments were performed using HTO and $^{36}$Cl$^{-}$ as tracers, the latter to study the effect of porosity changes on the anion accessible porosity.

Results of HTO diffusion experiments indicate a strong decrease of the diffusive flux across the samples within the first year of interaction, and only a moderate further reduction during the successive four years. The interface remains partially permeable for diffusive transport of Cl$^{-}$ and HTO after five years observation time. As expected, the diffusivity of $^{36}$C$^{l-}$ is clearly lower than that of HTO. Preliminary data indicate also a decrease of the diffusion coefficient but no complete blocking of the anion flux.

Investigations of the local porosity changes by neutron imaging showed that a small zone of clearly reduced porosity developed within the Na montmorillonite clay, mainly within the first year. This zone is very likely responsible for the observed reduction of the HTO and $^{36}$Cl$^{-}$ diffusive flux with time. It hinders mass transport, which in turn also reduces further reactions near the interface. Overall, this leads to the observed slowdown of both, tracers flux reduction and porosity reduction with time.

Interestingly, not all samples showed the same behavior. In some cases, the diffusive flux of HTO was not or only weakly affected by reactions. In these same samples, no clear porosity reduction within the Na-montmorillonite was observed by neutron imaging. At present, we are revealing potential reasons that triggered the different behavior. For this purpose, we also perform chemical analyses of the interface regions. It is also planned to perform reactive transport simulations in order to test their sensitivity to various model parameters and feedbacks.

# ZEOLITES - SECONDARY MINERALS IN DEGRADED PORTLAND CEMENT/CLAY SYSTEM: SYNTHESIS, STRUCTURE CHARACTERIZATION, AND THERMODYNAMIC STUDY

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The safety of deep underground nuclear waste repositories has to be guaranteed on a geologic time scale. After thousands of years, Portland cement (PC) will have partially degraded to low Ca/Si C-S-H gel and aluminoferrite minerals. Together with the aluminosilicate minerals in the adjacent rock, this chemical environment facilitates the formation of secondary zeolite minerals [1]; cements, zeolites and clays can co-exist in the long-term. Several naturally occurring zeolites, such as natrolite, chabazite, zeolite P(Ca), zeolite X, and Y, have been detected experimentally in 3-year-old specimens. However, the experiment-derived solubility products show a high variability compared with literature values [2]. Although zeolites are used in diverse areas and present in different cementitious systems, their stability domains are largely unknown and no/very little experimentally derived thermodynamic data is available due to the high structural variations of zeolites. This draws forth the objective to determine the thermodynamic data of pure zeolites experimentally and systematically.

In this study, natural and commercially available zeolites were collected and hydrothermal methods were used to synthesize pure zeolites in the temperature range from 80 to 200 °C. Different cations (Na, K, and Ca), alkali concentrations, Al/Si ratios, Al and Si sources, and seeding were explored to obtain different types of zeolites. The solid products were collected and characterized by TGA, XRD, and FT-IR in order to know the water content and (extra-)framework structures. Zeolites dissolution experiments were conducted at different temperatures to obtain the experimental solubility products ($K_{SO}$). The values of Gibbs free energy, enthalpy, entropy, and heat capacity were computed using the geochemical modelling code package GEM-Selektor.

XRD and TGA results indicated that the as-synthesized zeolites were highly pure phases and no carbonation occurred during the synthesis process. Until now, Na-based zeolites, with the frameworks of FAU, GIS, LTA, CHA, CAN, SOD, PHI, ANA, NAT, and MER, have been synthesized directly. Their Ca- and K-endmembers were obtained by hydrothermal cation exchange methods, except of analcime (ANA) and natrolite (NAT), which showed negligible cation exchange ability towards $Ca^{2+}$. Regarding the FT-IR results, the minimum transmittance peak typically fell in the range of 1100-900 $cm^{-1}$, assigned to asymmetric stretching vibrations of Si-O(Si) and Si-O(Al) bonds. This peak shifted to lower wavenumbers when the extra-framework cation was exchanged by cations with weaker electronegativity. In subsequent batch dissolution experiments, higher aqueous concentrations were measured at higher reaction temperature, indicating an increasing solubility at increasing temperature. For the K- and Ca-exchanged zeolites, the negligible amount of leached $Na^+$ indicated that complete cation exchange processes were achieved. By using GEM-Selektor software, the values of enthalpy, entropy, and heat capacity were computed based on the changes in experimental solubility products with temperatures. It was found that the thermodynamic properties of zeolites were largely determined by their frameworks.

The determination of thermodynamic data for zeolites, as secondary minerals between degraded PC/rocks interfaces, would close an important gap in long-term thermodynamic predictions needed in the context of radioactive waste disposal.

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# SYNTHESIS OF CEMENT/CLAYSTONE INTERACTION AND ITS IMPACT ON MASS TRANSFER AND TRANSPORT PROPERTIES BASED ON 10-YEAR FIELD EXPERIMENT

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Cementitious materials used as support and waste matrix in designs of deep geologic repositories of radioactive waste will variably impact interfaces between components of the engineered barrier system and its interface to the confining claystone. Of concern are possible deleterious effects on clay stability, such as diminished retention properties, or enhanced (radionuclides) or diminished transport properties (water saturation of bentonite, gas escape).

The CI Experiment (Cement-Clay Interaction) at the Mont Terri rock laboratory provided samples over 10 years of interaction along claystone interfaces with 3 different types of concretes, pastes and mortar (OPC, two types of low-alkali cementitious products), see [1] for preliminary results after 5 years, and [2] for details on micro-XRD work.

Findings elaborated by a combination of high-resolution analytical techniques applied to interface samples recovered after 2, 3, 5 and 10 years document complex but systematic chemical/mineral zonation patterns in both the cement matrix and the adjacent Opalinus Clay. While not all details of chemical zonation could be resolved in terms of mineral identity, the pattern can be coherently understood. Regions of well-detectable alteration are confined to a few millimeters, less pronounced on the clay-side, and with only sulphate redistribution in cements extending beyond 10 mm. Patterns of progress of reaction fronts with time suggest a rapid initial development and consecutive slowing down of reaction progress.

Effects on transport properties are more difficult to derive, but paired with evidence from accompanying laboratory work [2] also suggest an overall decrease of mass transfer rates with time. Of note – but also explainable - is the relative minor overall difference between extents of alteration of OPC (with very high initial pH) and the two low-alkali cementitious products (with internal pH evolving rapidly to below 12-12.5). This would indicate that there is no compelling advantage of the latter materials just for the purpose of trying to minimize interactions with dense clay materials.

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# INTERACTION OF FE(III) WITH CALCIUM SILICATE HYDRATES

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Thermodynamic modelling of the hydration process of Portland cement (PC) allows the composition of the hydrate assemblage and the pore solution to be predicted as a function of time. While the hydration process can be adequately modelled for PC it is still challenging to correctly model the hydration of slag-containing cements due to the limited information that is available about the behavior of Fe(0) in these cements, in particular also the interaction of Fe(II,III) with calcium silicate hydrates (C-S-H). PC typically contains Fe(III)-bearing $C_4AF$ (~3-4% $Fe_2O_3$). However, the iron content can rise up to 6% in slag cements, e.g. PC blended with ground granulated blast furnace slag containing Fe(0).

The current understanding of the fate of Fe during cement hydration has significantly improved over the last years as several studies have focused on the speciation of Fe in cementitious systems (e.g. [1] and references therein). For example, it has been demonstrated that Fe(III) can substitute Al(III) in Al-containing cement phases, such as ettringite, AFm phases and Fe-siliceous hydrogarnet (e.g. [1] and references therein). Nevertheless, the sorption behaviour of Fe(III) by C-S-H has not yet been investigated although C-S-H is the main hydration product of PC and blended cements which therefore largely determines the chemical and physical properties of cement pastes. In addition, C-S-H phases are chemically stable over a very long period of time in degrading cementitious systems and further, they have a high immobilization potential for cations (e.g. Sr(II) [2], Np(IV) [3] and many others). Thus, C-S-H plays a crucial role in the control of radionuclide release from the cementitious near field of a repository for radioactive waste.

In this study the interaction of Fe(III) with C-S-H has been investigated by wet chemistry experiments and synchrotron-based X-ray absorption spectroscopy. Kinetics of the sorption process and sorption isotherms were determined on C-S-H phases with different Ca/Si ratios using $^{55}$Fe radiotracer to quantify the Fe(III) uptake. For the spectroscopic studies, Fe(III)-doped C-S-H phases with different Fe(III) loadings were prepared and analysed by extended X-ray absorption fine structure (EXAFS) spectroscopy. The EXAFS data were modelled with the aim of developing a mechanistic understanding of the Fe(III) interaction with C-S-H. Preliminary results show that Fe(III) strongly binds to C-S-H and further that Fe(III) can be incorporated in the interlayer of C-S-H phases.

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# MODELLING MULTICOMPONENT DIFFUSION IN CEMENT-CLAY SYSTEMS

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Cement based materials represent a large fraction of the material present in geological radioactive waste repositories, and is present in the engineered construction material as well as in cemented waste-forms. Because cement-based materials have a very contrasting chemical composition in comparison with the surrounding host material, the resulting concentration gradients in pore water may lead to diffusion controlled chemical interactions near the interfaces.

Local changes in chemical composition can lead to mineral precipitation or dissolution and in this way have an impact on physical parameters such as local porosity tortuosity and mechanical strength. Insight into the extend and rate of the chemical evolution of the materials on both sides of the interface is important in support of performance assessment studies [1].

However, because reaction and diffusion rates are very slow, it is difficult to gain this insight from experiments only. For that reason, reactive transport models are often used as additional tool to estimate long term chemical and physical changes. Such models may incorporate a wide range of different chemical and physical processes such as complexation, adsorption, precipitation, (multicomponent) diffusion, reaction kinetics etc [2,3].

In this work we focus on including the effects of electromigration according to the Nernst-Planck equation in reactive transport modelling of such systems. Including this process in reactive transport models is usually very computationally intensive. However, in this work we present a numerically efficient way to include the required calculations in a reactive transport model. We discuss in what way the new approach is different from the usual procedure [4,5].

Secondly, we demonstrate the model for a cement-clay system as defined within the CEBAMA project, and we will discuss under which conditions the effects of electromigration are significant and thus important to include.

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# CHEMO-MECHANICAL BEHAVIOR OF PORTLAND AND LOW-PH CEMENT IN CONTACT WITH ARGILLITE

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The argillaceous layer (argillite) of Callovo-Oxfordian age has been chosen as a possible host-rock for deep geological disposal of intermediate-level long-lived and high-level radioactive wastes in eastern France. In contact with this clayey host-rock, high volumes of cementitious materials would be used for the shape of galleries as well as mechanical plugs in gallery and shaft seals. Concrete and the clayey rock will react with each other due to their strong different physicochemical properties. In addition, a temperature of 70°C may occur at the cement/clay interface due to the presence of high-level radioactive waste.

The CEMTEX project (CEMent Temperature EXperiments) focuses on the understanding of the chemo-mechanical behavior of cement/clay interfaces at 70°C depending on the cement formulation. In situ experiments with ordinary Portland cement (OPC) and two low-pH binders were performed over 5 years in the IRSN's Underground Research Laboratory (Tournemire, France). Chemo-mechanical characterizations (XRD, TGA, SEM-EDS, microstructural analyses, nano-indentation) were performed after dismantling.

Decalcification and carbonation were observed for all cement paste samples. A layer composed of phillipsite (zeolite), tobermorite (well-crystallized C-S-H) and calcite was also noticed at the cement/argillite interface. In the case of OPC paste/argillite, the mineralogical evolution led to an opening of the macroporosity in the hardened cement paste linked to portlandite dissolution. Nevertheless, precipitation processes caused a relative decrease of the total connected porosity within both materials in the altered zone. In the case of low-pH cement paste/argillite, a layer of gypsum was present in the argillite. Magnesium enrichment was also visible in the decalcified hardened cement matrix. This enrichment could be related to the precipitation of M-S-H phases, but this hypothesis remains to be confirmed.

Despite changes in porosity and mineralogy, first nano-indentation measurements made on OPC paste/argillite showed that these degradation processes were not sufficient to alter significantly the mechanical properties of the cement paste matrix. This preliminary result will be confirmed by further measurements. Chemical characterizations showed that the presence of clayey host-rock has a stronger effect on low-pH cement matrix than OPC matrix. The reason of this difference is likely due to the lack of Portlandite. Nano-indentation tests on the low-pH paste/argillite cement system are in progress, to confirm this observation.

# CHEMICAL AND MICROSTRUCTURAL EVOLUTION OF LOW-PH CEMENTITIOUS MATERIALS EXPOSED TO CALCAREOUS WATER: LAB EXPERIMENTS AND MODELLING

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Two types of cementitious binders are considered today for the design of radioactive wastes geological disposal in France: an ordinary Portland cement binder (for the main part of the facility infrastructure) and low-pH binders (for sealing systems). The latters were formulated to induce a less aggressive alkaline plume and to decrease the temperature hardening. The behaviour of low-pH cementitious materials in a clayey environment has been studied in the literature over the last decade. The option for vertical shaft seals also includes a low-pH concrete plug at the interface between the roof of the argillaceous hostrock and the upper calcareous rock, a natural aquifer. In these conditions, the low-pH concrete plug will be exposed to the constant flow of carbonated water, susceptible to be more aggressive (Mg perturbation, hydrolysis, carbonation…) for the cementitious matrix compared to clayey pore waters.

Due to the lack of study on the ageing of low-pH cementitious materials in contact with calcareous water, IRSN has started new experiments in the laboratory and under in situ conditions. The first ones consist in immerging a set of low-pH cement pastes (CEM IIIA + silica fume) in a high volume of synthetic carbonated solution in equilibrium with dolomite and calcite. The second ones consist in immerging more than a hundred of cylindrical samples exposed to a natural flow of calcareous water during several years in the Tournemire URL. The samples were made of cement paste and concrete for two low-pH formulations (CEM III/A+ SF and CEM I + SF + FA). The present study focuses on the results acquired in the first approach.

Solid analyses (SEM-EDS, XRD, microtomography and autoradiography) exhibit a strong perturbation after only 2 months of interaction. All samples show a full destructuration over several thousands of micrometres from the surface, with a total porosity growing up to 90% linked to hydrolysis. The first two-millimetres are strongly altered with the precipitation of M-S-H and decalcification, as already observed in previous studies [1]. The bulk of the material seems also disturbed with a porosity increase from 15 to 30%. The experimental results were modelled in terms of chemical and mineralogical evolutions with the Hytec reactive transport code, using the recent developments by EMPA and IRSN on M-S-H thermodynamics [2,3].

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# MULTI-METHOD AND MULTI-SCALE APPROACH FOR STUDYING CHLORIDE-36 MIGRATION THROUGH LOW pH CEMENT PASTES

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Because of its long half-life and high mobility, $^{36}Cl^-$ present in spent nuclear fuel and in low- and intermediate-level radioactive waste is of potential concern in the context of nuclear waste disposal. Understanding the mechanism of $^{36}Cl^-$ migration in hardened cement paste at trace concentrations through a cementitious material is of great importance, which depends on several interconnected factors, such as the initial chemical composition (i.e. hydrated cementitious phases), the total stable chloride content present in the solid and on the micro- and pore structure. Low-pH cement-based materials were developed within the nuclear waste disposal context in the late 90´s and in general, there is a lack of data and parameters (i.e. microstructure, diffusion and adsorption coefficients among others) which are needed to predict and assess the long-term behavior of $^{36}Cl^-$ in a repository system considering this material.

This work combines a multi-scale experimental methodology and a macroscopic numerical approximation to mechanistically study the mass transport of $^{36}Cl^-$ through low-pH cement pastes and to quantify its effective diffusivity and geometrical factor (i.e. tortuosity/constrictivity) and possible retardation processes. Batch sorption experiments have indicated a very weak uptake (Kd < 0.40 L kg$^{-1}$) of $^{36}Cl^-$ at trace concentrations (< $10^{-6}$ mol L$^{-1}$) associated with surface processes in the calcium-(aluminum) silicate hydrate (C-(A)-S-H) phases combined with the competition of natural chloride ($1 \cdot 10^{-3}$ mol L$^{-1}$) for sorption sites. Confirmation at the molecular scale of the presence of chloride in a structure similar to $CaCl_2$ $2H_2O$ or C-S-H phases with low Ca:Si ratio has been provided by chlorine K-edge X-ray absorption spectroscopic (XAS) measurements. On the other hand, capillary porosity (10 - 30 nm) and gel pores (<10 nm) in C-(A)-S-H phases have been identified by mercury intrusion porosimetry (MIP) as the dominant pathway for $^{36}Cl^-$ transport in studied cement pastes. Effective diffusion coefficients ($D_e$) were obtained ($\sim 1 \cdot 10^{-12}$ m$^2$/s) by inverse modelling of through-diffusion experiments considering Fickian diffusion as the only transport process and the Archie´s law, $D_e = \varepsilon^m_{acc} D_w$ (with $m$ [-] as empirical constant, $D_w$ [m$^2$/s] as the diffusion coefficient of the tracer in water, and $\varepsilon_{acc}$ as the accessible porosity [-] which is related to the constrictivity ($\delta$) and tortuosity ($\tau$)). A finite element method to solve the partial differential equations has been used neglecting sorption as observed experimentally in our study. However, to obtain a good fit of the experimental data a very small (unrealistic) accessible porosity was needed. These findings are indicating that the porosity-effective diffusion correlation, which is generally described by empirical laws such Archie´s law is not applicable in these systems, probably due to the heterogeneous small pore scale (< 10 nm) network of the C-(A)-S-H phases. For this reason, the application of a more complex multi-porosity approach model is needed to properly explain the experimental findings and migration of $^{36}Cl^-$ in low-pH cement pastes, which are mainly composed of C-(A)-S-H gel phases, highlighting the relevance of considering appropriately the transport processes in nanopores.

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# ATOMISTIC MODELING OF FLUID TRANSPORT IN CEMENT IN $CO_2$ STORAGE ENVIRONMENTS

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The enormous potential of the carbon capture and sequestration (CCS) technology to reduce the carbon footprint has attracted several studies in the recent past [1,2]. Cementitious materials are widely utilized in CCS operations for zonal isolation of the $CO_2$ storage wells. The degradation and deterioration of concrete in these extreme conditions pose several environmental risks such as groundwater contamination and fugitive gas leakages. To minimize these risks and to optimize CCS operations, a proper understanding of the fluid transport pathways in wellbore cement is important.

In this work, we employ atomistic computer simulations to model $CO_2/H_2O$ fluid interactions with cement's main hydration phase: calcium silicate hydrate (C-S-H). The molecular level investigations contribute to an improved understanding and quantification of fluid migration through wellbore leakage pathways. The effects of the cement chemistry and pore size distribution are taken into account by varying the C/S ratio of the atomistic C-S-H models from 0.83 to 1.75 and the pore sizes from 1 to 5 nm, respectively. To begin with, the intercalation potential of $CO_2/H_2O$ fluid mixtures is investigated using grand canonical Monte Carlo (GCMC) simulations for the C-S-H porous systems in equilibrium with binary $CO_2/H_2O$ bulk mixtures at 323 K/90 bar and 348 K/130 bar, mimicking the T/P conditions of sequestration. Increasing the C/S ratio decreases the adsorption of $CO_2$ as water competitively adsorbs on the calcium cations, blocking access of $CO_2$. The equilibrium compositions and structures obtained from the GCMC simulations are used as an input for classical molecular dynamics (MD) simulations using ClayFF potential [3]. The structural properties (i.e density profiles and preferential orientation) and fluid transport (i.e diffusion behavior) of the nano-confined $CO_2$ and $H_2O$ molecules are presented.

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# IODINE UPTAKE BY AFM PHASES

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Iodine-129 is an important dose-determining radionuclide emanating from low and intermediate level radioactive waste (L/ILW) repositories. The thermodynamically stable species of iodine under the alkaline and reducing conditions of a cement-based L/ILW repository is iodide ($I^-$). A good candidate for the immobilization of the hazardous $I^-$ anions are AFm phases due to their interlayer anion exchange capacity. AFm phases are layered double hydroxides (LHD) which form during the hydration of cement. They consist of a positively charged main layer, $[Ca_4(Al,Fe)_2(OH)_{12}]^+$, and a negatively charged interlayer, $[X\cdot nH_2O]^{2-}$, where X represents either two monovalent anions or a bivalent anion. The ability of AFm phases to bind iodine was investigated in two sets of experiments.

The formation of binary solid solutions between the iodine AFm end member (I-AFm) and the common AFm phases hemicarbonate ($OH\_CO_3$-AFm), monocarbonate ($CO_3$-AFm) and hydroxy-AFm (OH-AFm), was examined. The samples were characterized by TGA, FTIR, XRD and liquid phase analyses, and the obtained data were used to construct solid solution models based on the thermodynamic modelling program GEMS. The formation of a continuous solid solution was found between the AFm end member pair I-$OH\_CO_3$. The progressive substitution of the $I^-$ anion is reflected by a gradual decrease of the interlayer distance from 8.83 Å in the I-AFm phase down to 8.20 Å for $OH\_CO_3$-AFm, visible by a gradual peak shift of the basal reflexion from one end member to the other. In the cases of the I-$CO_3$ and I-OH pairs the solid solutions are incomplete and miscibility gaps with the compositions $0.5 \leq CO_3/(2I+CO_3)$ and $0.1 \leq OH/(I+OH)$ exist, indicated by the presence of two coexisting phases at compositions near $CO_3$-AFm and OH-AFm.

In addition, the sorption of $I^-$ on $OH\_CO_3$-AFm, monosulfate ($SO_4$-AFm) and sulfide-AFm (HS-AFm) was studied in a series of batch sorption experiments. In the sorption experiments, $OH\_CO_3$-AFm showed the highest affinity for $I^-$ with a mean distribution coefficient ($R_d$) value of $48 \pm 10$ $L\cdot kg^{-1}$. The $R_d$ value obtained for the HS-AFm was determined to be $35 \pm 7$ $L\cdot kg^{-1}$. The weakest sorption was observed for the $SO_4$-AFm with a mean $R_d$ value of $27 \pm 5$ $L\cdot kg^{-1}$.

The experimental data suggests that iodine can be incorporated in the AFm interlayer where anion exchange leads to the formation of solid solutions. The solid solution formation is favored by end members with similar crystal symmetry. Further, the sorption of $I^-$ is dependent on the type of the interlayer anion with a stronger sorption displayed by AFm phases with a singly charged anion in the interlayer (HS-AFm) than by AFm with divalent ions ($SO_4$-AFm).

# BEHAVIOR OF MINOR ELEMENTS IN BLENDS OF CEMENT AND SLAG

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An effective approach to lower the $CO_2$ emission from cement production is to replace Portland cement in concrete with low-$CO_2$ supplementary cementitious materials (SCMs). Today, SCMs such as blast-furnace slag from pig iron production and fly ash from coal combustion are used, which leads to significant $CO_2$ reductions and also it is a means to utilize by-products from industry. However, the availability of these SCMs gets more and more limited and new sources of SCMs need to be explored. Possible candidates for suitable SCMs are slags from other metallurgical processes than pig iron production, such as e.g. steel slags, copper slags, and slags from pyro-metallurgical recycling processes. These slags consist of a glassy Ca-Al-Si phase containing different minor elements, such as e.g. $Sr^{2+}$, $Zn^{2+}$, and $Pb^{2+}$, depending on the type of slag, the treatment process, and the raw materials. Currently, the slags are being slowly cooled and used as partial replacement of aggregates in concrete. However, their possible use as SCMs will result in a more sustainable outcome and higher added value. For use as SCMs, fast cooling of the slag can be performed in order to obtain a more glassy, and thus more reactive, material. However, the presence of minor elements affects the glass structure and thus influences the slag reactivity [1]. Furthermore, the hydration of cement has been observed to be affected [2]. The removal process of minor elements from slag is often challenging, and, for use of alternative slag types as SCMs, an improved understanding of the impact of minor elements on the hydration of cement-slag systems is thus of high importance.

In the current work, the behavior of the minor elements present in a non-ferrous metallurgy slag have been investigated in blends of Portland cement with 30 wt.% replacement by slag. The hydration of the blends was followed up to 28 days of hydration by XRD and TGA in order to identify the hydrate phases forming. Furthermore, the pore solution was extracted over time and analyzed by ICP-MS. To get an improved understanding of the role of the minor elements in the slag and their effect on slag reactivity, SEM-EDX was additionally applied to locate the minor elements in both the slag and the hydrated cement matrix.

The work elucidates the difference in hydrate phase assemblage as a result of the presence of minor elements released from the slag into the pore solution. The minor elements are observed to be either incorporated in hydrates such as the C-S-H phase or forming new compounds, such as hydroxides, consistent with the work done by Gineys et al. [2].

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# A CONTINUUM MODEL COUPLED DIFFUSION, MICROSTRUCTURE AND GEOCHEMICAL TO DESCRIBE COMBINED CARBONATION-LEACHING OF CEMENT PASTES IN A CLAY ENVIRONMENT

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Concrete materials which are used or envisaged as an engineered barrier in both in near-surface repositories for low/intermediate active waste and geological repositories for high level long-lived radioactive waste are potentially subjected to complex chemical interactions with their immediate surrounding environments. Several chemical contrast may exist between the concrete and (potential) surrounding materials in Ca and H concentrations but also in $CO_2$ concentrations as is the case e.g. of Boom Clay (Phung et al. 2017). Therefore, a combination of different chemical degradation processes including carbonation and leaching should be taken into account to assess the long-term performance of these concrete structures.

This study aims at developing a reactive transport model to predict the evolution of the microstructure, mineralogy and transport properties of cement pastes (CP) due to combined carbonation and leaching under accelerated conditions in which the CP samples are submerged in a Boom Clay suspension (batch experiment) with an elevated $CO_2$ concentration. 1D reaction – diffusion model at continuum scale coupled with geochemical reactions and an evolution of transport properties is implemented in a reactive transport code HPx (Jacques et al. 2018). From a chemical point, the model combines carbonation and leaching of several elements (Ca but also Si, Na, K, Al) and continuous cement hydration similar to the processes expected to occur in the long-time experiment under saturated conditions.

Besides the prediction of the changes in porosity, diffusivity, permeability and mineralogy, the model also enables to answer the question whether clogging occurs in CP interface. Results show an increase in total porosity of CP interface due to leaching. This indicates that clogging at the CP side might not occur. Verification with experimental results from accelerated degradation experiments shows a good agreement.

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# PREDICTING THE EVOLUTION OF HYDRATION HEAT OF LARGE-SCALE CEMENTED WASTE CONTAINERS FROM ISOTHERMAL CALORIMETRIC MEASUREMENTS

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Cement binders in combination with supplementary cementitious materials and admixtures are often used as matrix material in the conditioning of waste (e.g. evaporator concentrates, precipitation sludge) originating from the nuclear industry. The conditioned waste is then stored in large steel drums for eventual safe disposal. Although the resulting cemented waste form does not have load-bearing functionality, certain minimum quality of the waste form has to be complied with in terms of mechanical stability. Two main concerns are the possibility for thermal cracking and delayed ettringite formation if temperature in the cemented waste form exceeds a certain threshold value (~ 60ºC) due to heat of hydration. Therefore, the choice of blended cement recipes, waste sludge loading and water to cement ratio dictates the temperature distribution within the cemented waste drums.

Maximum temperature can be determined via adiabatic calorimetric tests or through isothermal or semi-adiabatic tests in combination with hydration heat evolution models. The difficulty with the adiabatic calorimeter is that a large quantity of waste sludge is necessary to carry out tests. The same applies to semi-adiabatic calorimeter tests, although the quantity of waste sludge needed is somewhat lower compared to adiabatic tests. Therefore, the best approach is to use isothermal calorimetric tests, which need only a few tens of grams of cement-sludge samples and couple them with hydration heat models to predict theoretical maximum temperature.

There exist several hydration heat models, which follow either the equivalent age or affinity law approach, within which both empirical and phenomenological models have been proposed. Such models have been shown to perform reasonably well for pure as well as blended cements in civil engineering applications. However, to the authors' knowledge there are no literature data to suggest that such hydration models perform well for the case of nuclear waste sludge because of the possible interaction of the waste sludge with blended cement. This information, i.e. the suitability of existing models, is crucial from the point of view of optimizing the number of calorimetric experiments.

In the preliminary phase of this study, the performance of an existing phenomenological model for blended cements is explored. A particular advantage of this approach is that once the model parameters are calibrated, it is possible to predict the temperature evolution for various compositions of the binder. The model results are compared against several isothermal experiments. Preliminary indications are that the waste sludge does not significantly influence the hydration heat evolution. In a next step, the model parameters that are established using isothermal calorimeter are used to validate semi-adiabatic measurements, by taking into account heat losses. Finally, based on the phenomenological model with its parameters, the temperature evolution in a hypothetical large-scale container of approximately 200 L is examined.

# $UO_2$ DOPED DISOLUTION STUDIES UNDER CEMENTITIOUS STORAGE CONDITIONS

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The effect of the presence of the cement water in the $UO_2$ solubility [1, 2] is influenced by pH due to U(VI) hydrolysis. In order to improve the understanding of relevant parameters such as type/concentration of dopant, pH and Eh in the behavior of the nuclear fuel matrix dissolution under deep repository conditions, leaching experiments are undergoing by using $UO_2$-based model systems. In the frame of the DISCO project [Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions. EURATOM H2020-NFRP-2016-2017-1. Project ID: 755443] several leaching tests in both, anoxic and reducing atmosphere, are being carried out for $UO_2$ doped with Cr and Al, between others. DISCO project aims to study spent fuel matrix dissolution in reducing repository environments and novel types of fuel (MOX, doped) behave like the conventional ones.

The main goal of these empirical studies is to have a picture of the potential role of doping materials on the matrix corrosion in cementitious systems of modern LWR fuels. Samples used as model fuels were fabricated at CIEMAT by a classical powder method and doping the $UO_2$ with 0.06%$Cr_2O_3$, 0.02%$Al_2O_3$-0.05%$Cr_2O_3$ and 6.6%$CeO_2$. The composition of Young Cement Water, YCW (pH 13.7) is based on previous data from SCK-CEN [3]. Static dissolution experiments in LDPE and PP containers are ongoing as batch tests with similar surface area to volume ratio (SA/V). The experiments are being carried out in a glove box (< 2 ppm $O_2$) with argon atmosphere control. To determine uranium release ICP-MS analysis are performing, as well as test dissolution rate. Differences in U concentration between filtered and ultrafiltered samples will provide quantitative data of the possible colloid formation, favoured by the calcium and other complexing agents existing in the leachant, mainly hydroxyl ions. The pH and redox parameters of the leached are being monitored during the experiments in order to control the system and its influence as function of the time. Microstructural analysis characterization is performing by SEM, XRD and Raman spectroscopy to identify secondary phase formation.

Results acquired will be useful in comparative terms within the framework of DISCO project in which similar experiments are ongoing under the similar conditions but with $H_2$ atmosphere at high pressure.

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# HTO AND CHLORIDE-36 DIFFUSION ON PORTLAND-TYPE AND LOW PH CEMENTITIOUS MATERIALS

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Cementitious materials are widely used in radioactive waste management mainly for waste solidification and construction of concrete containers. Within deep geological repository the cementitious materials are considered also for construction elements (ramps, linings, seals). The radionuclide transport properties are the part of the characterization of these materials.

Experimental work within the CEBAMA project focuses on alteration and interaction studies on two types of cementitious materials (OPC – cement paste based on Portland type CEM II, w:c = 0.45, and RPM – CEBAMA reference mix paste with low pH leachates) in contact with groundwater (GW) from Underground Research Facility Josef and with bentonite suspension (Czech Bentonite 75, B75) in pressure vessels during three sampling campaigns (9/18/27 months) for OPC samples and two campaigns (9/18 months) for RPM samples under in-situ (10°C) and high temperature (95°C) load. The main goal was to understand how the interaction processes affect the transport properties of cementitious materials. The performed HTO and chloride ($^{36}$Cl) through-diffusion experiments on evolved cylindrical cement samples (thickness of 8 mm, diameter of 50 mm) at laboratory temperature provided three types of datasets: depletion concentration curves in input reservoirs, breakthrough curves in output reservoirs and concentration profiles in samples.

Based on powder x-ray diffraction (XRD) of cementitious samples and on chemical analyses of solutions after the interaction six main results were concluded: In the case of temperature, both the OPC and RPM samples were influenced in terms of mineralogy composition. The heated OPC samples contained the newly-formed hydrothermal mineral katoite (C3ASH4) and lacked those phases which are stable under lower temperatures such as calcium aluminium oxide carbonate hydrate and hydrocalumite. Higher temperature accelerates the dissolution of the various minerals, especially ettringite, which results in increasing concentrations of sulphates in solution. The high-temperature RPM samples were found to contain completely transformed minerals such as ettringite and brownmillerite. The solutions of OPC samples were enriched with potassium and calcium in contrast to the RPM samples, where sodium dominated. A comparison of the OPC samples stored at 100% relative humidity at 10°C after 9, 18 and 27 months and RPM samples after 9 and 18 months revealed only minor changes in terms of mineralogy and thus no progress with concern to curing and stable material maturity.

The high temperature load raised up values of HTO effective diffusion coefficients ($D_e$) on samples of both cementitious materials studied, in case of OPC samples even in one order of magnitude, which could be related to dissolution of material under higher temperature. The $^{36}$Cl through diffusion experiments showed different behaviour: while the OPC samples have a high chloride uptake capacity (the fast depletion of activity $^{36}$Cl in input reservoir was observed), the RPM samples have a strong diffusion resistivity of chloride (almost no depletion in input reservoir, effective diffusion coefficients are below the values of $10^{-14}$ $m^2s^{-1}$). Contrary to temperature the interaction time (9/18/27 months) was not so significant on diffusion results.

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# COUPLED THERMO-HYDRO-CHEMICAL-MECHANICAL MODEL OF MORTAR-BENTONITE INTERACTIONS

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Double interface tests were performed by CIEMAT during the PEBS Project (Long-term performance of Engineered Barrier System) to study the interactions of corrosion products, bentonite, and mortar at the ambient geochemical conditions of the repository expected to occur after 1,000 to 3,000 years [1]. The cells were hydrated with a synthetic argillaceous water and heated at 60ºC during 18 months. The coupled THCM model was performed with a 1-D mesh, which accounts for the hydration equipment (water tank, the water pipe and the filter), the lime mortar, the bentonite and the magnetite powder [2].

Model results show that the lime mortar, the bentonite and the magnetite powder are fully saturated at the end of the test. The computed water content, saturation degree and water intake reproduce the measured data at the end of the test. The computed concentration of $Cl^-$ increases in the mortar and decreases in the bentonite due to the diffusion from the bentonite into the mortar. The concentrations of $Cl^-$ become uniform after a few days. The computed concentrations of dissolved $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ show also the effect of diffusion. However, they are subjected also to cation exchange reactions. $SO_4^{2-}$ and $Al^{3+}$ diffuse from the mortar into the bentonite. These species are also subjected to mineral dissolution/precipitation. Portlandite dissolution in the mortar and the diffusion of dissolved $Ca^{2+}$ into the bentonite lead to the precipitation of calcite, CSH1.2 and CSH1.6 near the interface. The computed concentration of exchanged $Ca^{2+}$ also increases in the bentonite at the end of the test. The computed concentrations of dissolved and exchanged $Mg^{2+}$ decrease from their initial values in the mortar near the hydration boundary and in the bentonite near the mortar interface due to the precipitation of brucite and sepiolite. In addition, sepiolite shows some precipitation peaks in the bentonite. Sepiolite, CSH1.6 and CSH1.2 precipitation lead to the decrease of the concentration of dissolved $SiO_2(aq)$. The model predicts that anhydrite precipitates in the mortar and in the bentonite, but anhydrite is transformed into gypsum after the cooling phase. For the most part, the numerical model captures the main trends of the mineralogical observations. However, there are some discrepancies, especially for ettringite precipitation in the mortar, which is not computed with the model, and brucite precipitation in the bentonite that is not observed in the laboratory. The porosity changes due to mineral dissolution/precipitation at the end of the test are small and limited to the mortar and a few mm in the bentonite. The porosity increases 8% in the mortar near the bentonite interface due to portlandite dissolution. On the other hand, the porosity decreases 1.5% in the bentonite in a 0.2 mm thick zone near the mortar interface due to calcite and brucite precipitation.

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# COUPLED THERMO-HYDRO-CHEMICAL-MECHANICAL MODEL OF THE INTERACTIONS OF THE SHOTCRETE BUFER WITH THE COMPACTED BENTONITE IN THE FEBEX IN SITU TEST

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FEBEX (Full-scale Engineered Barrier Experiment) is a demonstration and research project for the engineered barrier of a high-level radioactive waste repository. The project includes the FEBEX in situ full-scale test performed at Grimsel, Switzerland. The tests started on February 1997 and finished in 2015.

The interactions of the bentonite and the shotcrete plug of the FEBEX in situ tests have been modelled with a non-isothermal variably-saturated 1-D reactive transport numerical model. The model was performed normal to the interface at a radial distance from the axis of the gallery equal to 0.75 m. The simulation extends from 2002 when the concrete plug was constructed to 2015 when it was dismantled. The initial and boundary thermal and hydrodynamic conditions for the 1-D model where taken from a previous detailed 2-D axisymmetric THM model of the bentonite-concrete interface [1].

Model results show that the computed temperature after 13 years of simulation (from 2002 to 2015) is about 30ºC in the bentonite which fit the temperatures measured along the borehole drilled through the concrete plug. The bentonite is almost saturated at the bentonite-contrete interface after 13 years. The computed concentrations show a decreasing of $Cl^-$ concentration in the bentonite due to the diffusion of $Cl^-$ from the bentonite into the concrete. The concentration of dissolved $Ca^{2+}$ increases in the concrete due to the dissolution of portlandite in the concrete and solute diffusion from the bentonite. The concentration of $Ca^{2+}$ decreases near the bentonite-concrete interface due to the precipitation of calcite near the bentonite-concrete interface. Calcite dissolves in the bentonite and precipitates near the bentonite-concrete interface. Portlandite dissolves in the concrete interface. The concentration of dissolved $Mg^{2+}$ decreases due to the precipitation of brucite and sepiolite near the bentonite-concrete interface. The front of brucite and sepiolite precipitation moves from the bentonite-concrete interface into the bentonite. The model does not predict the precipitation of the Friedel salt. The concentration of dissolved $SiO_2$(aq) in the concrete increases due to the dissolution of CSH1.8 and the diffusion of the silica from the bentonite into to the concrete. The decrease of the concentration of dissolved silica in the bentonite is caused also by the precipitation of sepiolite near the bentonite-concrete interface. Ettringite precipitation is very small and nonuniform. The high pH front penetrates 7.5 cm into the bentonite after 13 years. The porosity decreases slightly in the bentonite near the concrete-bentonite interface due to the precipitation of brucite, calcite and sepiolite. The porosity in the concrete, on the other hand, increases near the interface due mostly to the dissolution of portlandite.

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# INTERACTION OF STRONTIUM CHLORIDE SOLUTION WITH CALCIUM ALUMINATE PHOSPHATE (CAP) SYSTEM

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Processing of contaminated water in Fukushima Naiichi Power Plant results in various aqueous secondary wastes [1]. Encapsulation of these wastes with conventional cement matrices based on Portland cement (PC) is challenging because of the potential hydrogen gas generation, and associated risks of fire and explosion, due to the radiolysis of the water contents intrinsically present in the conventional cement matrices as pore solution and hydration products. In order to overcome this issue, we have been developing a new cement matrix based on calcium aluminate phosphate (CAP) system with reduced water content [2]. Differing from the conventional cement, solidification of this system is based on acid-base reaction. Because the water content is not crucial once the system is mixed, it is possible to reduce its water content by a mild heating at 60-90ºC without compromising the integrity of the solid products [2].

The present study investigates the interaction between strontium and CAP system. Radioactive strontium $^{90}$Sr is, together with salt, one of the major contamination in the aqueous secondary wastes [1]. The investigation was conducted focusing on the aqueous solution of strontium chloride $SrCl_2$ and the powder of CAP precursor, in order to study the initial interaction between strontium ions and CAP system when they are mixed in the aqueous environment. Powders of CAP precursors (i.e. Secar 51, sodium phosphate monobasic di-hydrate $NaH_2PO_4 \cdot 2H_2O$ and sodium polyphosphate $(NaPO_3)_n$) were mixed in dry state, and introduced to the 0.1 mol/L solution of strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$) at different amounts. The mixed solution was continuously stirred at room temperature, and 10 mL of the solution was sampled periodically for ICP analysis. At the end of the reaction, the mixture was filtered and the solid component presented in the systems was recovered for analysis using XRD, TG and SEM.

The ICP analysis of the solution indicated a rapid interaction of $SrCl_2$ and CAP precursor powders, which appears to complete in a few hours. The strontium concentration in the solution was found to decrease proportionally with the CAP powders introduced to the system, indicating that strontium ions are forming solid product(s) through the reaction with the CAP powders. The behaviour of chloride ions was more complex, but it also indicated a general decrease in its concentration with the amount of CAP precursor powder introduced to the system. The aqueous reaction typically resulted in two types of solid products; dark powders typically sink at the bottom of the container, and less-dense cloud-like suspension staying in the middle of the solution. The XRD analysis revealed that the dark powders contain unreacted Secar 51 and its conventional hydration products gibbsite and hydrogarnet, whereas TG analysis suggested the additional presence of $\beta$-$SrHPO_4$ in the cloud-like suspension. Strontium also appeared to be dispersed in the amorphous binding phase(s) in SEM.

The results obtained indicate that CAP system can incorporate strontium into the resulting solid phase. The incorporation mechanism might be associated with the formation of strontium phosphate salts and possibly bound to the amorphous binding phase.

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# CEMENT-ROCK INTERACTION IN THE FRAMEWORK OF EXPERIMENTS AT THE GRIMSEL TEST SITE

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Several experimental and modeling studies of Portland cement – rock interaction have been performed within the HPF, LCS and CIM projects at the Grimsel Test Site (Switzerland). Within HPF, laboratory and in situ injection of high-pH solutions into fractured granite were performed. In LCS, pre-hardened cement was placed in a borehole intersecting a fracture. Modeling studies of a natural analogue (Eastern Springs at Maqarin, Jordan) and an industrial analogue (DM borehole at Tournemire, France) were also performed. The different rock structures (impermeable clay rock, fractured porous limestone, fractured tight granite) imposed very different transport regimes translating into very different spatial extents of alteration. In the new CIM experiment at Grimsel, currently at the planning stage, a solution containing tracers will be circulated in small borehole (5.6 cm diameter) drilled into a larger 15-year-old mortar-filled borehole (38.8 cm diameter). Solute transport and retention through the mortar and into the host granitic rock, together with the alteration of mortar and granite, will be investigated.

At Tournemire (concrete-mudstone interaction), transport control by diffusion resulted in a very small spatial extent of alteration. Porosity was clogged at the cement – rock interface (mm scale) due to the precipitation of C-A-S-H, calcite and ettringite, together with clay dissolution (source of Al and Si). Porosity of the concrete increased due to portlandite dissolution. At Maqarin, long term circulation of portlandite-saturated solutions along a fracture resulted in intense mineral alteration along the fracture and in the wall rock (cm scale), due to the porous nature of the rock (matrix diffusion). Primary aluminosilicate dissolution also provided Al and Si for C-S-H/C-A-S-H and ettringite precipitation. The relative magnitudes of fracture flow vs. rock matrix diffusion control the extent of fracture-rock interface clogging vs. fracture clogging.

In the HPF and LCS in situ experiments at Grimsel (year scale), there is very limited mass transfer from the fracture to the rock matrix due to the very small granite porosity. pH buffering by reaction is limited and primary aluminosilicate dissolution (fault gouge) controls also C-S-H/C-A-S-H and ettringite precipitation in the rock fracture. Mineralogical changes are only minor. Fracture heterogeneity is an important control in the spatial distribution of alteration within the fracture.

In the new CIM experiment, an important topic is the study of tracer transport and retention through the mortar, and very importantly transport (if any) through the mortar-rock interface. Clogging of porosity at that interface will play a key role.

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# MICROCHEMICAL AND MICROMECHANICAL CHARACTERIZATION OF HYDRATED CALCIUM-HYDROSILICATES WITH COUPLED RAMAN- AND NANOINDENTATION MEASUREMENTS

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A new type of hydraulic mineral phase, the hydraulic calcium-hydrosilicate (hCHS) is characterized by its CaO / $SiO_2$ ratio, which can vary between two and one [1]. The reaction kinetics of hCHS differs from that of classical clinker phases due to the highly reactive silicate species present in the structure, which involve silanol groups. No portlandite is formed during hydration. Without buffering by portlandite, solved species e.g. pH, c($Ca^{2+}$) and c($SiO_4^{4-}$) must be controlled for a reproducible reaction. Variation of the solution chemistry results in the formation of different C-S-H phases, which changes the mechanical properties. Celitement, a new cement type, is based on hCHS. It is produced by mechanochemical activation of Calcium-Silicate-Hydrates (C-S-H) in a milling process. Celitement does not contain other hydraulic phases as calcium aluminate or calcium ferrate, which gives the potential to reduce the calcium content in cement by $^2/_3$ and thus significantly reduce the $CO_2$ output during processing.

The deformation behavior of hardened cement paste is a direct function of the mechanical properties and interactions of its microstructural constituents. In order to investigate the underlying microstructural mechanisms, nanoindentation tests were carried out, giving details of the mechanical properties of the individual microstructural components. In the past, the nanoindentation technique has been coupled with an elemental mapping of the indented hardened cement paste surface with EDX, in order to obtain information on the elemental distribution, i.e. the phase composition for each indent [2]. In the case of hCHS based cements the EDX assignment does not work as hCHS (synthesized with a molar CaO/$SiO_2$ of 1.1 in the present study) reacts isochemically upon hydration, resulting in a C-S-H phase with the same chemical composition. Thus, a homogeneous distribution of the main elements Ca and Si is observed throughout the sample. In the presented study, nanoindentation mapping tests were in addition coupled with Raman mappings, yielding in depth insight into the mechanics of the mineralogical phases constituting the hardened cement paste. Therefore, it was possible to identify fresh C-S-H with varying density (LD, HD) as well as C-S-H from the raw material in hardened Celitement paste by their specific Raman spectra and simultaneously acquire data of their mechanical properties: hardness, indentation modulus and creep. Combination with EDX data for the distribution of alkalis in the same area of interest give additional detailed insight into the reaction pattern of hCHS.

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# REDOX, SOLUBILITY AND SORPTION BEHAVIOR OF PLUTONIUM IN THE PRESENCE OF ISOSACCHARINIC ACID AND CEMENT

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The final repository for short-lived low- and intermediate-level (L/ILW) nuclear waste in Sweden (SFR1) is located in a crystalline host rock formation near Forsmark. In the post-closure period, cementitious materials will buffer the pH of the intruding ground water in the alkaline range ($10 \leq pH \leq 13.3$) over a long time–scale with strongly reducing conditions expected as a result of the anaerobic corrosion of steel containers.

Residual amounts of plutonium present in the inventory of SFR1 contribute to long-term radiological risk potentially arising from the waste due to the long half–life of $^{239}$Pu ($t_{½}$ $^{239}$Pu = $2.41 \cdot 10^{4}$ a) [1]. A large inventory of cellulose is disposed of in SFR along with the waste. α-D-isosaccharinic acid (HISA) is the main degradation product of cellulose under the hyperalkaline pH conditions defined by cementitious systems [2]. The strong complexation of ISA with An(III) and An(IV) requires dedicated research efforts with focus on the Pu–ISA–cement system, for which almost no experimental studies are available in the literature.

All experiments were conducted in an Ar glove box at $T = (22 \pm 2)$ °C. Reducing conditions were buffered using hydroquinone (HQ) ($pe + pH_m \approx 10$), Sn(II) ($pe + pH_m \approx 1.5$) or $Na_2S_2O_4$ ($pe + pH_m \approx 0$). Systematic solubility experiments were conducted from undersaturation conditions with aged $^{242}Pu(IV)O_2$(ncr,hyd) solid phase in 0.1 m NaCl–NaOH solutions at $8 \leq pH_m \leq 13$. Experiments were performed in the absence and presence of ISA ($10^{-6}$ m $\leq m(ISA)_{tot} \leq 0.1$ m) and Ca(II) ($3 \cdot 10^{-4}$ m $\leq m(Ca)_{tot} \leq 0.02$ m). The impact of ISA on the uptake of plutonium by ordinary Portland cement was assessed with series of sorption experiments using pre–equilibrated pore water at $pH_m = 12.5$ and the step-wise addition of a Pu(VI) stock solution. Supernatant solutions and solid phases of selected samples were exhaustively characterized by advanced analytical techniques including synchrotron-based techniques at the INE–Beamline for Actinide Research at the KARA facility.

A pronounced increase of plutonium solubility by up to 3 $\log_{10}$–units was observed in the presence of ISA and Ca(II), compared to ISA-free systems. Slope analysis on the solubility data in combination with solid phase characterization and DFT calculations indicate the formation of $Pu(IV)(OH)_3ISA_{-H}^{-}$, $Pu(OH)_3ISA_{-2H}^{2-}$ and (in strongly reducing solutions with $pH_m < 11.5$) $Pu(III)(OH)ISA_{-H}(aq)$. The presence of Ca(II) promotes the formation of two quaternary complexes $CaPu(OH)_3ISA_{-H}^{+}$ and $CaPu(OH)_3ISA_{-2H}(aq)$. A comprehensive thermodynamic model is derived for the system $Ca^{2+}–Pu^{4+}–Pu^{3+}–OH^{-}–Cl^{-}–ISA^{-}–H_2O(l)$.

The presence of ISA decreases the uptake of Pu by cement, although sorption is importantly affected by the order of addition of components and by kinetics. The results obtained in this work represent a realistic empirical basis to quantitatively assessing the impact of ISA on the uptake of Pu by cement.

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# RETENTION OF AN(III)/LN(III)-MALATE COMPLEXES IN CSH PHASES

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Concrete widely serves as an engineering barrier and for waste conditioning in nuclear waste repositories. Organic additives are commonly used for tuning the physico-chemical and mechanical properties of fresh concrete. A variety of organic additives, like modified lignosulphonates, polyacrylates and poly(hydroxo)carboxylates contain strong complexing functional groups, which can interact with radionuclides (RN) forming stable complexes. In the worst-case scenario of water intrusion into the waste repository, the concrete degrades, so that the soluble organic additives will be leached out and may complex the RN. It is still controversially discussed in literature how these additives influence the RN retention in concrete. CSH phases are the main binding phases remaining after concrete degradation. For a long-term risk assessment in nuclear waste repositories, the interaction of the RNs with cement additives in presence and absence of CSH phases must be known. Am(III) and Cm(III) are chosen as representatives for RN which will determine the radiotoxicity of the nuclear waste. As cement additive malic acid (α-hydroxydicarboxylic acid, Mal) was chosen.

Extended X-ray absorption fine structure (EXAFS) spectroscopy was used for the determination of the structural properties (coordination numbers and atomic distances) of Am(III)-Mal complexes at highly alkaline pH values and of the ternary Am(III)/Mal/CSH system. In aqueous solution at pH 10 a polynuclear Am(III)-Mal-precipitate is formed showing a tridentate coordination of the ligand and a probable 2:4 Am(III)/Mal stoichiometry. At higher pH values a polynuclear Am(III)-hydrolysis species is dominating. In the binary system Am(III)/CSH two species appear in dependence on the C/S ratio. At C/S 0.4 one species which show pronounced O, Si, and Ca peaks in the FT of the EXAFS spectrum is present. This clearly can be assigned to an incorporated Am(III)-species. At C/S $\geq$ 0.8 another species appears which possesses weak O, Si, and Ca peaks in the FT. This can be interpreted as sorbed-like species. In presence of Mal another additional sorbed-like species occurs which is different to the species in the binary system.

Complementary to the EXAFS investigations, time-resolved laser-induced fluorescence measurements with Cm(III)/CSH and Cm(III)/Mal/CSH were conducted. Lifetime measurements revealed the existence of two fluorescing species within the Cm(III)/CSH system at C/S 1.0 which is in agreement with literature. [1] One species shows a long lifetime of 800µs ($n_{H2O}$= 0) and the other species having a shorter lifetime of 200µs ($n_{H2O}$= 3 ± 0.5). This can be interpreted as one species being incorporated in the CSH bulk within the Ca-O-sheets (substitution for Ca) and one Cm(III) species which is intercalated in the CSH interlayer or on the edges bound to a few water molecules. In presence of Mal the lifetimes don't change significantly but the Cm(III) emission spectra show more pronounced peaks than without Mal. This can be assigned to a highly ordered or crystalline species evolving when Mal is present.

Batch experiments with C-14 labeled Mal show that it is retained on CSH phases although the log $K_d$ value is smaller than for Cm(III) and Am(III). These experiments show that Mal influences the speciation of metal ions in CSH phases by being partly sorbed on CSH phases.

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# LEACHING CHARACTERISTICS OF CEMENTITIOUS MIXTURES CONTAINING HIGH CONTENT OF FLY ASH

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Fly ash can be utilized as a substitute material in cement mixtures, such as CLSM (Controlled Low Strength Material) and grout, which in infrastructure applications may come into contact with runoff, infiltration or groundwater. Grout and CLSM are also used extensively in closure of former defense nuclear materials production facilities. Evaluation of the potential for leaching of constituents of potential concern (COPCs, e.g., heavy metals) from formulations containing fly ash is important to ensure environmental protection. Leaching of trace elements from CLSM and grout mixtures containing high content of fly ash that were cured for different periods was examined using the Leaching Environmental Assessment Framework (LEAF). Evaluation of the expected and bounding concentrations to be released will allow definition of criteria for fly ash usage in infrastructure applications.

Cubic blocks of cement mixtures with and without fly ash (Table 1) were manufactured and cured for periods of 7, 28 and 90 days. Colombian fly ash CMC-CerD was chosen as a bounding case because of its high concentration of COPCs and its low pozzolanic activity. Following the curing, the cubes were tested according to a monolith leaching procedure (NEN 7375:2004 similar to EN15863 and EPA 1315) designed for determination of the inorganic constituent leaching rates from construction materials and wastes. Twenty trace elements were measured in the leachates and the cumulative releases (mg/m$^2$ external geometric surface area) for the entire test were determined. Major and trace element composition and pH dependent leaching (EPA 1313) were determined for the fly ash and each of the grout and CLSM formulations. All data (leachate and total concentrations) were uploaded to the program LeachXS™ which enables database management, comparison of leaching data for different tests or materials, modelling, and outputting data such as cumulative release per unit area and fluxes.

**Table 1.** Component ratios used in preparation of CLSM and grout.

| Type | Fly ash | | Portland Cement | | Fine Aggregate | | Water | | Total | Admixture[1] |
|---|---|---|---|---|---|---|---|---|---|---|
| | kg | % | kg | % | kg | % | kg | % | kg | kg/m$^3$ |
| CLSM with fly ash | 400 | 18.9 | 120 | 5.9 | 1250 | 61.9 | 250 | 12.4 | 2020 | 1.0 |
| Reference CLSM | – | – | 150 | 7.7 | 1500 | 76.9 | 300 | 15.4 | 1950 | 1.0 |
| Grout with fly ash | 800 | 44.4 | 400 | 22.2 | 200 | 11.1 | 400 | 22.2 | 1800 | 0 |
| Reference grout | – | – | 800 | 45.7 | 650 | 37.1 | 300 | 17.1 | 1750 | 0 |

[1] Air entrainment agent (olefin sulfonate)

Concentrations of constituents of potential concern (COPCs) in the cementitious mixtures containing fly ash are clearly enriched compared with the corresponding reference materials with very high enrichments (up to greater than 6 times) of B and Se. Similarly, in the leaching test (pH dependence and monolith), the mixtures containing fly ash leached higher concentrations of COPCs compared to the reference blends. However, although the grout with fly ash contains higher concentrations of COPCs due to its larger content of fly ash, COPCs were leached in lower concentrations due to the high content of cement which plays a strong role in stabilizing COPCs.

The beneficial use of coal fly ash incorporated into these cementitious mixtures for safe application in the Israeli environment was examined using the methodology set in EPA (2014).

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# FORMATE AND ACETATE STABILITY UNDER REPOSITORY RELEVANT CONDITIONS: WHAT CAN WE LEARN FROM THE LITERATURE?

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Safety assessment studies for low and intermediate level radioactive waste (L/ILW) repositories have shown that carbon-14 ($^{14}C$) is an important dose-determining radionuclide due to its potential release in the form of dissolved or gaseous species facilitating its migration from the disposal site into the biosphere. Cvetkovic et al. [1] identified $^{14}C$-formate and $^{14}C$-acetate as the main $^{14}C$ bearing organic compounds released during anoxic corrosion of irradiated steel under repository relevant conditions. The fate of these $^{14}C$-bearing organic compounds after their release from the steel waste, however, is still largely unknown. After closure, the repository will gradually become saturated with water but partially saturated conditions might exist for up to 100’000 years due to gas production in the near field [2]. Hence reactions both in gas and aqueous phase might influence the fate of $^{14}C$-acetate and $^{14}C$-formate.

Thermodynamically, formate and acetate are unstable under the alkaline conditions prevailing in the repository near-field and, depending on the redox conditions, they decompose to $CO_2$ or $CH_4$. However, at moderate temperatures and pressures, most of these redox reactions are extremely slow and formate and actetate can be metastable for very long times due to the high activation energies hindering spontaneous decomposition [3]. In the past, little attention has been paid to the abiotic decomposition of formate and acetate in water at temperatures below 100°C because microbiological activity is expected to be the main driving force for the decomposition. In contrast, extensive research has been carried out under high temperature and pressure conditions in the gas phase (catalysis) and under hydrothermal conditions found in sedimentary basins, oil-field brines and geological hydrothermal fluids. Decomposition can occur both in the gas phase and in the aqueous phase. Formate decomposes either via dehydrogenation (release of $H_2$) or decarboxylation (release of $CO_2$) [4]. Acetic acid decomposition in the gas phase occurs either via decarboxylation producing methane and $CO_2$ or ketonisation producing ketene or acetone and $H_2O$ [5]. Under hydrothermal conditions, decomposition occurs mainly by decarboxylation and oxidation [6]. The aqueous speciation of the organics and the presence of catalytic surfaces may considerably reduce the activation energy needed for the decomposition reactions to proceed within a reasonable time scale [4,6].

Products arising from the decomposition of formate and acetate ($H_2$, CO, $CO_2$) may further react via abiotic synthesis processes such as Fischer-Tropsch (FT) type reactions to form longer chain hydrocarbons [7]. These abiotic synthesis reactions occur mainly in the gas phase but were also observed in aqueous solution. In the latter case, only the formation of a few low molecular weight organic compounds in small quantities has been documented so far whereas in the gas phase FT reactions were found to produce large quantities of a variety of organic compounds such as hydrocarbons, carboxylic acids and alcohols.

This contribution presents a summary of insights obtained from the literature concerning the chemical stability of formate and acetate in the gas and aqueous phase. Decomposition processes are discussed in relation to their relevance for L/ILW repository conditions.

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# PROGRESSION OF THE GEOCHEMICAL INTERACTION AT THE CONCRETE-BENTONITE INTERFACE UNDER SIMULATED ENGINEERED BARRIER CONDITIONS

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A set of 6 identical scale-model tests (HB) was designed to study the temporal evolution of the concrete-bentonite interaction in the engineered barrier system of a deep geological repository. HB tests reproduce the thermal and hydraulic regimes expected during the re-saturation of the bentonite barrier. The tests consisted of a 7cm-high FEBEX bentonite cylinder in contact with a 3cm-high CEM I 42.5 R/SR concrete slab. Sequential dismantling was scheduled for 6, 12, 18, 54, 82 and 136 months. Once dismantled, the bentonite and concrete blocks of the experiments were sliced into 1cm-thick cylindrical sections to determine the physical, chemical and mineralogical changes of both materials over time. After 136 months, the bentonite block was almost fully saturated. The degree of saturation of the bentonite in the vicinity of the concrete-bentonite interface was 95% while close to the heater the degree of saturation was 80%. As bentonite was confined inside a stainless steel cell, slight differences in dry density values were observed. By the heater, dry density reached 1.69 g/cm$^3$ whereas close to the interface reached 1.61 g/cm$^3$. Temperature at the interface was around 40ºC.

$Cl^-$ and $SO_4^{2-}$ tended to concentrate near the heater in all the experiments, due to evaporation processes and the thermo-hydraulic gradient generated by the simultaneous heating and hydration of the concrete-bentonite column. Sequential dismantling of the set of experiments confirmed that the $Cl^-$ front moves faster than $SO_4^{2-}$ one, since $Cl^-$ behaves as a conservative ion while $SO_4^{2-}$ is controlled by dissolution/precipitation processes. $Cl^-$ and $SO_4^{2-}$ mass balances indicate that the overall content in the bentonite block increases due to the highly saline solution used for hydration. Due to the leaching of the concrete matrix, $Ca^{2+}$ increases in the exchange complex of the bentonite with respect to the untreated FEBEX bentonite in the whole bentonite column. On the contrary, an overall decrease of $Mg^{2+}$ was observed in the bentonite column, except for the heater zone, where it was accumulated. The first dismantled experiment (6 months) already provided evidences of depletion of exchangeable $Mg^{2+}$ in the bentonite in the contact with the concrete, being the extension of the affected zone up to 4 cm depth in the experiment dismantled after 136 months. The depletion of $Mg^{2+}$ is in agreement with the formation of Mg-rich phases (serpentine–like or 2:2 or 2:1:1 sheet silicate), being the extension of precipitates <1 mm. Cement leachates favoured the precipitation of carbonates and C(A)SH gels and sulfate-rich phases on the concrete side of the interface. Gypsum and ettringite were soon detected (12 months), whereas calcite was not initially observed but became the dominant phase after 136 months. According to stable isotopes, calcite found in the interface was $^{13}C$-depleted if compared to $\delta^{13}C$ values measured in both, bentonite and concrete. This fact points to dissolution and re-precipitation processes involving the dissolved carbon in bentonite leachates. Al tended to decrease from the bentonite interface and to increase within < 1mm thickness at the concrete matrix. The dismantling of this set of experiments suggests that the extension of the mineralogical alteration front in the bentonite decreases or at least does not show an appreciable evolution with increasing temporal scales. Mercury intrusion porosity data points to a decrease of bentonite and concrete porosity at the interface due to the precipitation of newly-formed phases. On the contrary an increase of BET specific surface area in the first two millimetres of bentonite occurs.

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# GAS PERMEABILITY AND HYDRAULIC CONDUCTIVITY OF CONCRETE CORES FROM THE PLUG OF THE FEBEX IN SITU EXPERIMENT

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The FEBEX in situ was a full-scale experiment planned to test the feasibility of the engineering barrier (EB) concept following the Spanish deep geological repository design for high-level radioactive waste in granite formations. After a first partial dismantling in 2002 a shotcrete plug (cement CEM II A-L 32.5 R) was used to confine the bentonite buffer [1]. The plug was constructed in two stages: a first section (S1) in contact with the bentonite buffer with a thickness of one meter and a second one of two meters (S2), giving a total plug length of 3 meters. After 28 days of hardening the quality control in section S1 provided mean strength values of 32 MPa and mean hydraulic conductivity values of $4.3{\cdot}10^{-11}$ m/s. At the time of the final dismantling of the experiment in 2015, the plug had been operational for 13 years.

The aim of this study was to experimentally investigate the transport processes through the concrete plug and assess the performance of the plug after 13 years operation.

Gas permeability and hydraulic conductivity of concrete core samples taken during dismantling at different positions in section S1 were tested in custom-built setups, in order to examine the effects of the bentonite pore water or the granite groundwater on the transport properties of the plug. Both were measured in core samples drilled onsite during dismantling and preserved to keep the degree of saturation they had when the plug was dismantled. The tests were performed in triaxial cells.

The setup for the gas permeability tests allowed the change of the injection pressure at the upper part of the sample and the control of the confining pressure. The backpressure was kept atmospheric and the gas outflow was measured by means of different range gas flowmeters. The pressure paths followed consisted in an increase of confining pressure from 1 to 2 MPa. The injection pressure kept constant at 0.2 MPa during the whole tests. The results show that the increase in confining pressure did not cause a noticeable reduction of gas permeability. The mean gas permeability value computed was in the order of $10^{-11}$ m/s.

The hydraulic conductivity was measured in the core samples after they had been saturated with deionized water. These tests took place in constant head permeameters in which the samples were saturated with an injection pressure of 0.6 MPa under a confining pressure of 0.8 MPa. Once the sample was saturated, a hydraulic head of 0.1 MPa was applied and the outflow was measured. The hydraulic conductivity values obtained were in the order of $10^{-10}$ m/s, higher than the initial values.

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# SURFACE COMPLEXATION MODELING OF NICKEL SORPTION UNDER VARYING GEOCHEMICAL CONDITIONS

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Radioactive nickel, Ni-63 is one of the significant radionuclides, because it has relatively long half-life (96 years) and shows high portion of radioactive wastes generated from nuclear power plants (NPPs). According to the Safety Analysis Report (SAR) of the Wolsong Low and Intermediate Level Waste (LILW) disposal facility in South Korea, it is expected that the amount of radioactive nickel accounts for 25.4% of the total radioactivity. In addition, due to the large amount of nickel in a reactor vessel, a significant amount of radioactive nickel will be generated and can be an important contributor to the safety assessment as LILW source term in repository. Generally, the migration of radionuclides in soil and groundwater is largely controlled by its sorption and desorption behaviors at the solid/water interface. Therefore, knowledge of the sorption of radionuclides at solid/water interface is vital for predicting the risk caused by long-term disposal of radioactive waste, and for assessing the migration of radionuclides in the environment. For a long-term safety assessment of the disposal facility, reactive transport models utilize the distribution coefficient (constant-Kd) model to describe the mobility of radionuclides in the subsurface environments. However, Kd value is sensitive to the varying pH conditions due to the reaction between groundwater and cement. The LILW generated from NPPs will be disposed in the Wolsong disposal facility, which has been built as underground concrete silo type. Wolsong disposal facility utilizes lots of cementitious materials by engineered barrier system, backfill, and solidified materials. After closure of disposal facility, these cementitious materials will interact with groundwater, which then will change the pHs to hyper-alkaline conditions (pH 10.5-13.1). In this study, surface complexation model (SCM) was developed to describe nickel sorption onto minerals as background geochemical conditions vary after cement-groundwater interaction. A non-electrostatic GC-SCM approach simulated the measured Nickel sorption very well for the entire pH ranges. Without SCM model, a constant Kd model based on simple batch sorption results may mislead the Nickel sorption by precipitation process, especially at high pH condition.

# THERMAL TREATMENT OF RADIOACTIVE CONCRETE WASTES FROM NUCLEAR POWER PLANT DECOMMISSIONING

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The treatment and disposal of contaminated concrete waste is a major issue for nuclear power plant (NPP) decommissioning due to the very huge volume and large quantities of wastes generated. Most of the intermediate and low level solid radioactive wastes generated during the NPP decommissioning process are concrete and metal used as building materials, which account for more than 70% of total solid waste. The purposes of this study are to characterize the concrete wastes, investigate the dehydration process, and optimize the thermal treatment for Co and Cs spiked concrete samples at various temperatures to reduce the volume of dismantled radioactive solid wastes. Concrete coupons were prepared using Portland cement (Type I/II) with dry ingredients such as sand, fly ash, and crushed rock and water at the ratio of 0.21, 0.37, 0.05, 0.24, and 0.13 in a single batch. A hand mixer was used with the mixing process including loading period, mixing period, and discharging period. After mixing period, the concrete slurry was poured into a paper mold (5cm in diameter and 10cm in height) and cured in the desiccator under the constant moisture content (80-100% RH) for 5-28 days. To make concrete samples contaminated by Co and Cs, 0.4 mL (10ppm) of their solutions were individually spiked at a depth of 0.7 cm using a glass syringe during the curing. Thermal treatment experiments were carried out with various temperature such as 105°C, 200°C, 300°C, 400°C, 500°C, and 600°C for an hour in the furnace. After thermal treatment, these samples were cooled at room temperature and were crushed by rubber hammer. Finally, the crushed concrete samples were sieved and particles size less than 1mm in diameter were used to separate cement paste specimen from the aggregates in the concrete. The collected cement paste and concrete aggregate were characterized by Scanning Electron Microscope (SEM)/Energy Dispersive Spectrometer (EDS) for surface morphology and chemical composition, X-Ray Diffraction (XRD) for mineral identification, Fourier transformed-infrared (FT-IR) for the changes of chemical binding, and X-ray fluorescence (XRF) for the bulk chemical composition as well as total Co and Cs contents. To quantify the total concentrations of Co and Cs in the final concrete samples, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used after digestion. This study investigated the synthetic contaminated concrete samples by Co and Cs, and optimized thermal treatment method to reduce the waste volume. After thermal treatment at 600ºC for an hour, the cement paste was separated from concrete aggregates. These results provide the possibility and optimum condition of thermal treatment to reduce the volume of concrete wastes.

# ESTIMATES OF MINERAL STABILITY CONSTANTS DERIVED FROM PH DEPENDENCE LEACHING TEST DATA FOR GEOCHEMICAL MODELLING OF CEMENT-BASED WASTE SYSTEMS.

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In cement paste and mortar, the retention of specific anions has been described as a solid solution substitution for sulfate in ettringite. Other elements can also substitute in ettringite for respectively, Ca and Al. In literature substitution parameters have been derived for Cr and Se. However, for other relevant trace elements thermodynamic data are missing. This seriously hampers description of release behavior from cementitious or highly alkaline materials in reactive transport scenarios. In this work we have derived substitution parameters for a range of elements based on the assumption, that ettringite or ettringite-like phases control the release of several trace elements by substitution for sulphate, Ca or Al. The pH dependence test (e.g. EPA method 1313 and EN14429) has been used for multi-element geochemical speciation modelling to obtain a chemical speciation fingerprint (CSF), that allows description of the complex interactions between major, minor and trace substances in various matrices. By comparing the leaching of a range of anions in a wide variety of alkaline materials, retention of oxyanions in the pH range 10 – 13 is clearly observed. For metals, retention at high pH is identified, but phases describing this behavior are lacking. At high pH metals are present as negatively charged ions, which might substitute in ettringite or ettringite like phases alternatively, metals may coprecipitate with portlandite. For several other elements gaps in geochemical modelling can be identified, since on the basis of available thermodynamic data in existing databases no minerals or phases can be identified able to describe the observed release behavior. This paper describes the calibration of thermodynamic data for anionic and cationic substitutions in ettringite and portlandite phases based on a range of materials. Filling such gaps on the basis of reasonable assumptions for potential minerals can improve the understanding of release in reactive transport until more specific thermodynamic data can be obtained.

# $^{14}$C DIFFUSION THROUGH CEMENT MATERIALS AND INTERACTION WITH ION EXCHANGE RESINS FIXED IN CEMENT MATRIX

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Cements and concretes have been widely used in I/LLW management in Czech Republic, being used namely as solidification material. Moreover, cement materials are considered also for disposal of high level waste (HLW) in deep geology repository (DGR), hereby being considered both for solidification and construction materials. Studies of the contaminants migration processes are focused mainly on the diffusion. 14C was chosen as a relevant contaminant of I/LLW and spent resins from nuclear reactor operation and as an activation product.

For the diffusion and sorption experiments the cements CEM I, CEM II and CEM III were used as a cement paste and cement mortar with quartz sand. Diffusion processes are studied using through diffusion method, with 14C acetate tracer on the cement paste and cement mortar samples (50mm in diameter, 10mm in length). Additional sorption and leaching test are performed to evaluate retention coefficients of this contaminant. Tested materials were crushed and sieved to different mesh size fractions.

Cement CEM II class was successfully tested as a fixation matrix for the ion exchange resin samples and leaching test of fixed spent ion exchange resins labelled by 14C were performed. The testing process focused on the kinetics of 14C species leaching into three different liquid phases - distilled water, synthetic granitic water and sodium hydroxide.

All these results and obtained data will contribute to improvement to the performance and safety assessment of operating repositories and potential DGR. Moreover, those could also be used as an input for the DGR planning and performance and safety assessment of the DGR part, where cementitious materials will be used for waste fixation and disposal.

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# CEMENT-BENTONITE INTERACTION PHYSICAL MODELS AT THE BUKOV URF – PROJECT INTRODUCTION

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When designing the engineered barriers of deep geological repositories (DGR), it is essential to gain a thorough understanding of the interactions between the various materials used in such barriers under real rock environment conditions. The Interaction Experiment project is being conducted by the CTU, ÚJV and CGS for SÚRAO in the context of the Czech Republic's DGR development program.

The Interaction Experiment (IE) is aimed at the study of interactions between the engineered barriers of the DGR and their interactions with the surrounding rock environment and local groundwater. Thus, the experiment is being conducted under real conditions at the Bukov URF at a depth of 550 m in boreholes drilled into highly-metamorphosed amphibolic paragneisses to amphibolites. The project involves the construction of 10 individual mock-up physical models subsequently emplaced in specially-drilled horizontal boreholes. It is planned that the models will simulate the various processes expected to occur in the future DGR under real rock conditions. The first part of the experiment will involve the heating of five of the mock-up models via heating elements up to 100°C and 200°C, while the remaining five models will be subjected to the local in-situ temperature (15°C). All the models will be artificially saturated with groundwater and fully instrumented so as to obtain detailed information on e.g. water saturation, swelling pressure and temperature distribution. Combinations of the following materials will be used for the construction of the IE models: concrete made from Ordinary Portland Cement (OPC), Low-pH concrete (leachate pH value approx. 11) and Czech Ca/Mg bentonite from the Černý Vrch deposit in the form of pellets and segments. All the materials as well as the surrounding rock environment were characterized in detail prior to the commencement of the loading procedure so as to allow for the study of the changes expected to occur during the interaction process.

It is assumed that the operation of the interaction physical models will continue for at least 3 years. The experiment will result in a detailed description of the chemical and mineralogical processes that occur as the result of the interaction of the various materials (concrete, bentonite, rock), a comparison of the processes underway with respect to the various conditions (heat, saturation etc.) prevailing within the individual models and the mathematical simulation of their THM (thermo-hydro-mechanical) development.

## Acknowledgement:

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# COMPARISON OF EXPERIMENTAL AND MODELLED LEACHING OF CEMENTITIOUS MATERIALS IN NUCLEAR WASTE REPOSITORY ENVIRONMENT

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Leaching of cementitious materials with various calcium/silica -ratios was experimentally studied and the corresponding leaching was modelled. Experimentally measured and modelled hydroxyl releases were compared in order to understand differences between modelling and experiments, and to verify the used modelling method.

Leaching was studied in ion-exchanged water, saline groundwater and saline bentonite porewater. Groundwater compositions were selected corresponding to potential groundwaters that will interact with cementitious materials in a high-level nuclear waste repository in Finland. Studies were performed in deaireated conditions at room temperature. Cementitious samples with various calcium/silica -ratios were prepared using low-alkali Ordinary Portland cement (CEM I 42,5N SR3 MH/LA) and colloidal silica (Levasil 100/45). The samples' water/ binder -ratio was 1. Samples were stored for 365 days in closed vials to obtain low calcium/silica -ratios. The studied calcium/silica -ratios ranged from 3.14 to 0.2.

Leaching was studied using a batch method, where a known quantity of finely grounded hydrated cementitious paste was mixed with a known volume of leachate in closed vials. The prepared samples were continuously agitated at least for 24 hours. After the agitation, samples were centrifuged and leachate was decanted. The leachate pH was measured and a new volume of leachate was added to each individual sample. The process was repeated until a desired pH value was reached. The total amount of released hydroxyls was calculated.

Identical sample compositions were modelled using Gibbs energy minimization program (GEMS, Paul Scherrer Institut) accompanied with use of the thermodynamic database for cementitious materials (CEMDATA 14, Empa).

The modelled hydroxyl release was compared to experimentally measured values. In ion-exchanged water, measured and modelled hydroxyl releases had overall relatively good correspondence. A good correlation between modelled and measured hydroxyl contents was observed with calcium silica -ratios above 1.0. The modelled hydroxyl release was only slightly higher than experimentally measured. With calcium/silica -ratios ≤1.0, the difference between the measured and modelled results increased and the poorest correspondence was observed with a calcium/silica -ratio of 0.2. In saline groundwater and saline bentonite porewater, modelling underestimated the hydroxyl release with high calcium/silica -ratios (>1.0). With low calcium/silica -ratios (≤1.0), modelling overestimated the released hydroxyl contents.

Used modelling method does not account for alkali adsorption, which is a potential source of differences in modelled and measured results in ion-exchanged water. However, the differences were small considering the potential range. Because the scale of differences was small and the modelling tendency was to overestimate the total hydroxyl release, the used modelling method seems to be a viable method to estimate hydroxyl release in ion-exchanged water. In saline groundwater, precipitation of secondary phases was likely responsible for the observed large differences. If the studied modelling method is used to estimate hydroxyl release in saline groundwaters, relevant secondary phases needs to be predefined.

Obtained results are being used to update Safety Case for the Operational Licence of Finlands high-level radioactive nuclear waste repository.

# MODELLING OF THE LONG-TERM DURABILITY OF LOW-PH CONCRETE IN SHAFT SEALS WITHIN A CLAYEY FORMATION

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The French design for a geological disposal of radioactive waste involves several vertical shafts to connect the underground and the surface facilities. These shafts will be backfilled and sealed when the underground facility will be closed. The sealing function plays a significant role for the safety of the disposal by preventing the circulation water, therefore limiting the mobility of radionuclides to the biosphere. The chemical evolution and durability of the shaft seals has thus to be assessed on a long-term basis, in order to identify potential changes in their containment properties.

The aim of this paper is to evaluate the evolution of the seal components on long timespan, focusing on chemical interactions in the concrete plugs surrounding the core, made in swelling bentonite. The plugs have indeed to support constant volume of swelling bentonite (few MPa pressure) in order to ensure its sealing safety role, and their mechanical properties can be reduced due to their chemical evolution. 2D-modelling was performed with the reactive transport code HYTEC [1], taking into account advective and diffusive transport under water saturated conditions, cation exchange and dissolution/precipitation.

The paper addresses a composite sealing system for a vertical shaft (10 m in diameter). The core is made of a mixture of swelling clay (MX80 bentonite) and sand, located in an argillite layer. The upper concrete plug is embedded in a calcareous layer located over the argillite layer. The concrete consisting of a ternary low-pH cement is in contact with different types of materials (MX80 bentonite, limestone and argillite). The study focused on the spatial extent of the altered concrete, in relation with the precipitation of M-S-H at the expense of C-S-H [2], calcite precipitation and ettringite secondary formation. The extent of the attenuated alkaline plume in the core is also estimated, as well as the evolution of the sodium exchangeable fraction in the bentonite, of importance to assess the evolution of its swelling capacity. A sensitivity analysis was done on the hydraulic conductivities of the calcareous formation and the concrete slab. Transient unsaturated water conditions and long-term hydration of the low-pH cement were considered as alternative processes.

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# A GEOCHEMICAL MODELLING APPROACH FOR PREDICTING LONG-TERM WASTE-CEMENT INTERACTIONS

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The concept for a deep geological repository for low- and intermediate-level waste (L/ILW) in Switzerland foresees the use of large quantities of cementitious materials, which shall provide stable mechanical conditions and a high pH chemical environment for a very long period of time [1]. The cement-based engineered barrier of the repository near field includes the cement-stabilised waste matrices, concrete containers for waste emplacement, and the cementitious backfill of the containers and the cavern. Knowledge of the long-term stability and performance of the cement-based barrier is of great importance with a view to assessing the safe disposal of radioactive waste over the period of concern for the deep geological L/ILW repository.

The near field of an L/ILW repository consists of a very heterogeneous mixture of various waste materials, such as metallic and organic waste, which are conditioned by solidifying concrete. The reactivity of the waste matrix and the interaction of the reaction products with the concrete is likely to alter the barrier function of the near field over time. The chemical processes relevant to the degradation of waste materials and the solidifying concrete include the chemical degradation of organic waste and the interaction of the main degradation product, $CO_2$ (and its bases), with hydrated cement, the corrosion of metallic waste, and the long-term alteration of hydrated cement by the dissolution of siliceous aggregates. The geochemical modelling approach outlined in this study was developed with the aim of predicting the temporal evolution of cement-stabilised waste sorts subject to the various chemical degradation processes [2].

The thermodynamic modelling approach is based on the assumption that the waste package can be considered as a “mixing tank” in which the chemical processes are rate determining. The GEM-Selektor v3.3 code was used for the modelling including the Nagra/PSI thermodynamic database and the Cemdata 14.01 database, complemented by additional thermodynamic data for zeolites, Zn/Cu species, and chloride salts. The inventories of the waste sorts were taken from the MIRAM 14 databases [3]. The degradation of organic materials, the corrosion of metals, and the dissolution of siliceous aggregate (quartz used as surrogate) were implemented in GEMS in accordance with reaction rates reported in the literature.

The results show that the temporal evolution of the chemical conditions, in particular pH, in the waste packages is strongly affected by a number of boundary conditions and processes: A) The initial pH is determined by the composition of the mixtures used to make the solidifying concrete. B) The degradation of the organic materials is a key process, which is determined by the type and quantity of organic waste materials, in particular the inventory of readily degrading organics with a low molecular weight and slowly degrading, polymeric organic materials. The degradation of the organics results in the formation of gaseous compounds, in particular $CO_2$ (and its bases), which gives rise to carbonation of hydrated cement. C) Silica is released by the dissolution of siliceous aggregates in highly alkaline cement pore water, which reacts with calcium silicate hydrate (C-S-H) phases, thus producing C-S-H phases with a low Ca/Si ratio. D) Formation of zeolites reduces pH by the uptake of alkalis and water into the structure.

The evolution of pH with time has a major effect on metal corrosion and thus on $H_2$ production. The effect of the chemical processes on the evolution of waste sorts is discussed in this study.

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# LOW-pH CEMENTS BASED ON BLENDS OF MgO AND HYDROMAGNESITE

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Most of the alternative low $CO_2$-cements that have been proposed are based on calcium silicates and aluminates. Their main calcium source is limestone, even though the amounts required may be somewhat lower than for Portland cement clinker.

MgO can be used to make a variety of hydraulic binders as well as binders that harden by carbonation. Potential raw materials are Magnesium silicates or Mg-containing brines, which could be carbonated and partially calcined afterwards to obtain mixture of MgO and basic magnesium carbonates [1]. If the final composition of the hardened binder were sufficiently rich in carbonate the $CO_2$ sequestered by it could fully compensate for the $CO_2$ emitted by the production of the energy needed to drive the manufacturing process, we could talk of a truly carbon-neutral binder. We could even envisage carbon-negative binders for which there would be net consumption of $CO_2$ during manufacture and use. Besides their ability to bind $CO_2$, such binders have a low pH (around 10-11), which could be of potential interest regarding waste encapsulation.

The current study aimed at increasing the initial carbonate content of such binders in order to enhance their effectiveness as a means of reducing $CO_2$ emissions. The hydration of reactive periclase (MgO) in the presence of hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) was investigated by a variety of physical and chemical techniques. Isothermal calorimetry, X-ray powder diffraction, thermal analysis, vibrational spectroscopy (infrared and Raman spectroscopy) and thermodynamic modelling were applied to assess the hydration mechanism.

Isothermal calorimetry showed that partial replacement of the MgO with hydromagnesite accelerated the hydration of the pure MgO at early ages (i.e. for about the first half day). The MgO-hydromagnesite blends always produced a significant amount of an unknown hydrate with a thermal decomposition peak centered on about 100°C as determined by thermogravimetry. This hydrate, which was not observed in a previous study [2], formed quickly – it was already present by one day of hydration and did not increase significantly after that. We hypothesise that this peak represents an amorphous or very poorly-crystalline phase that leads to cohesive binding in these blends. The other main difference between the hydrated MgO-hydromagnesite pastes and the pure MgO paste is the observation of very broad X-ray diffraction peaks for brucite whenever hydromagnesite is present. Furthermore, reflections of a dypingite-like phase ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) were identified by X-ray diffraction. The formation of artinite, which was calculated to be the thermodynamic stable phase, could not be confirmed, even if a few % of pure artinite were added as seeds to the mix.

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# LEACHING OF U(VI) AND Cm(III) DOPED CALCIUM (ALUMINUM) SILICATE HYDRATE GEL (C-(A)-S-H) AND TOBERMORITE IN SALINE BRINES

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To evaluate the retention potential of concrete inside a nuclear waste repository for actinides under saline and hyperalkaline conditions, leaching experiments with actinide doped cementitious phases were performed in repository-relevant brines. Therefore, U(VI) and Cm(III) doped calcium silicate hydrate (C-S-H) phases with different calcium-to-silicon (C/S) ratios (1.0−2.0) were synthesized directly in presence of either U(VI) or Cm(III) and characterized by time-resolved laser-induced luminescence spectroscopy (TRLFS), infrared (IR) spectroscopy, powder X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM). The time-dependent release of Ca, Si, U or Cm from CSH phases into brines that contained either 2.5 M NaCl, 2.5 M NaCl/0.02 M $Na_2SO_4$, 2.5 M NaCl/0.02 M $NaHCO_3$ or 0.02 M $NaHCO_3$ for U(VI) doped CSH phases or 2.5 M NaCl/0.02 M $NaHCO_3$ or 0.02 M $NaHCO_3$ for Cm(III) doped CSH phases was monitored in batch leaching experiments for 30 to 60 days. Subsequently, leaching induced changes of the C-S-H structure and of the U(VI) or Cm(III) coordination environment were investigated with TRLFS, IR spectroscopy and XRD.

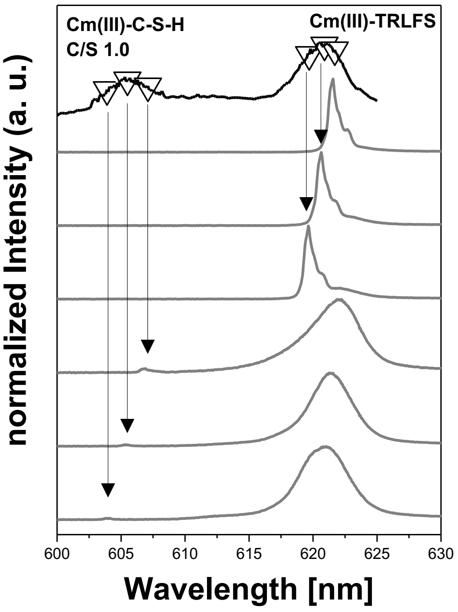

Fig. 1 Site-selective TRLFS spectra of Cm(III) incorporated into a C-S-H phase with a C/S ratio of 1.0.

Results indicated that the U(VI) retention by C-S-H phases is maintained in the presence of NaCl rich solutions due to the formation of uranophane [1]. The presence of carbonate in saline leaching solutions increased the U(VI) mobility due to formation of $Ca_2UO_2(CO_3)_3(aq)$ at moderate alkaline pH values [1]. Furthermore, an influence of the secondary $CaCO_3$ phases calcite, vaterite and aragonite was detected. Calcite contributed to the U(VI) retention which was shown with TRLFS [1]. The binding study of Cm(III) incorporated into C-S-H gel revealed at least two Cm(III) species: (i) Cm(III) substituted against $Ca^{2+}$ from the C-S-H interlayer and (ii) Cm(III) incorporated in the polyhedral CaO plane of the C-S-H structure. Additionally, a luminescence line narrowing effect was observed indicating variations of the local surrounding of Cm(III) in C-S-H gel. Leaching experiments showed that Cm(III) is not mobilized by carbonate but becomes partially incorporated into secondary $CaCO_3$ phases. Recently, we started to investigate the Al and U(VI) incorporation into C-S-H phases at different Al/Si ratios (0.025−0.2) and synthesis temperatures (25°C or 200°C). The obtained phases were investigated with $^{27}$Al NMR, TRLFS, XRD and Raman microscopy. First results indicated an influence of the Al starting material and synthesis temperature on the Al incorporation.

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# STRUCTURE OF SYNTHETIC CALCIUM SILICATE HYDRATE IN PRESENCE OF ALUMINUM AND ALKALIS

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Due to the large volume of Portland cement produced annually worldwide, cement manufacture contributes to 7% of the global anthropogenic $CO_2$ emission; a large fraction of $CO_2$ emissions occurs due to the de-carbonation of limestone during cement production. Thus, the partial replacement of clinker by limestone and supplementary cementitious materials (SCMs) such as blast furnace slags, fly ash, or calcined clays has a high potential to reduce $CO_2$ emissions related to cement manufacturing. These SCMs react chemically during cement hydration and contribute mainly to the amount and composition of calcium silicate hydrates (C-S-H). Because of the high silica and aluminum content in such SCMs, the composition and structure of the C-S-H phases is modified in ways which are not yet understood in detail, C-S-H in these systems has a lower Ca/Si ratio than C-S-H in ordinary Portland cement and higher aluminum content. The aim of this study is to identify aluminum binding sites in C-S-H and determine the relations between Al/Si ratio within the C-S-H and the occupancies of the different Al sites.

C-A-S-H with different Ca/Si and Al/Si samples were synthesized starting from CaO, $SiO_2$ and $CaO{\cdot}Al_2O_3$. The effect of the Al/Si on the structure of C-S-H was investigated by thermal gravimetric analysis (TGA), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR); the aluminum in solution was quantified by ion chromatography. The aluminum uptake in C-S-H was found to increase with dissolved aluminum concentrations. At intermediate Ca/Si ratios, the presence of up to 1 M NaOH increased the aluminum uptake in C-S-H from Al/Si $\approx$ 0.05 in the absence of NaOH to Al/Si $\approx$ 0.15 in the presence of NaOH, as the higher pH suppressed $AH_3$ and stratlingite formation. At low Ca/Si ratios the formation of zeolites in addition to C-A-S-H was observed, while at high Ca/Si katoite and portlandite formation was observed in addition the C-A-S-H.