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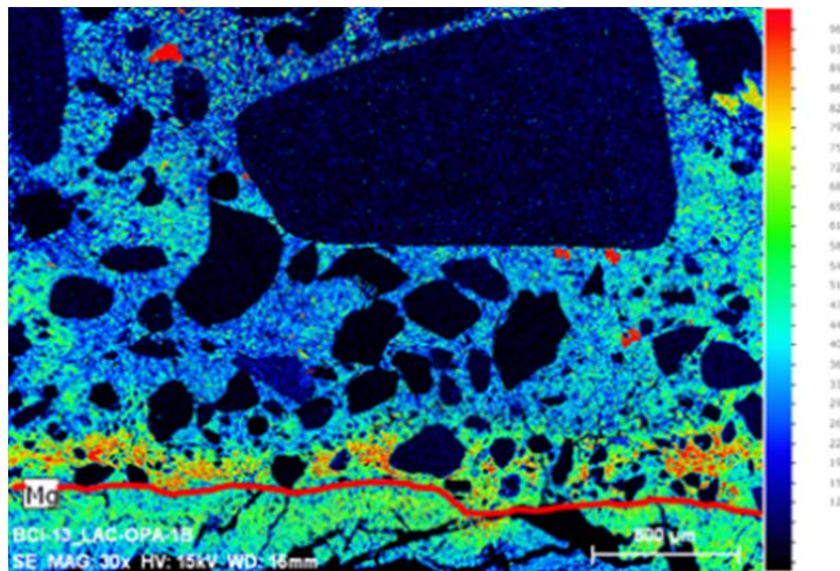
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Book of abstracts

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Keynotes

Reactive transport modeling of cement durability, a dual interaction with waste constituents and the environment

De Windt, L., Corvisier, J., Lagneau, V.

MINES ParisTech, PSL Research University, Centre de Géosciences, Fontainebleau, France

Corresponding author: laurent.dewindt@mines-paristech.fr

Disposals of hazardous industrial and nuclear waste rely upon cement-based matrices and their polyvalent chemical potential for waste immobilization. Their physical barrier capability against leaching and contaminant migration is also beneficial in subsurface disposals and, to a lesser extent, in underground facilities. In the latter, concrete is also used for reinforcement and seals. In agro-food industries and sewage systems, concrete facilities are dedicated to the production, storage and treatment of liquid organic wastes. In all types of waste disposal, several deterioration mechanisms (hydrolysis, sulfate attack, carbonation) of cement-based materials may take place while interacting with the environment. On the other hand, waste constituents may alter cement-based materials by physico-chemical mechanisms (e.g. organic acid attack), gas generation (metal corrosion) or swelling solid phases.

The impressive development of cement thermodynamic science and data over the last decade defines the baseline for a mechanistic modeling of cement durability. We will briefly develop how reactive transport modeling (RTM) complements this approach by coupling water and solutes transport and considering reaction-induced porosity, diffusivity and permeability changes. Furthermore, we will point out that RTM is applicable to the other engineered materials (clay, glass, steel) and the natural environment (soil and unsaturated zone, host rock), allowing for additional coupling of cement durability with the reactivity of such non-cement materials. Therefore, RTM is capable of great generality and flexibility with regard to user-designated composition, temperature, or technical configurations. However, complexity and strong coupling imply that relevant results can only be achieved by combining targeted experiments and analogue (archeological, natural) studies with modeling.

The requirement for RTM is currently growing. We will briefly report the developments under progress in the RTM community that can be of interest for waste/cement interactions. Then, we will present two RTM applications (code HYTEC) on cement durability in which coupling plays a key role and/or a new type of coupling has been implemented. The first one deals with cement biodegradation in organic waste storage. It is shown that coupling enhances or fully inhibits deterioration depending on the nature of organic acids, and that a swelling Ca-organic salt induces cracking. Attempt of coupling geomechanical processes is discussed. The second example concerns the interaction between OPC material and clayey host rock in underground radioactive waste disposals. Our previous RTM studies are revisited, in particular modeling of clogging, paying attention to the effects of voids and cracks, temperature and the gas phase. The latter requires a multicomponent multiphase approach, recently implemented in HYTEC.

Thermodynamic modelling of C-S-H alkali binding

Nonat, A.

CNRS-Université de Bourgogne et Franche-Comté, ICB, UMR 6303, Dijon, France

Corresponding author: andre.nonat@u-bourgogne.fr

Thermodynamic modelling of the hydration of cementitious materials is becoming more and more a useful tool for long term durability predictions and for the hydration of new cement blends [1] and their interaction with waste. To be relevant, these predictions should be established on the basis of a reliable thermodynamic model able to describe the composition of C-S-H in hydrated cement paste, the major component, which is known to vary with the composition of the blend and especially the uptake of alumina. Indeed, C-S-H composition, generally expressed in terms of CaO/SiO_2 and H_2O/SiO_2 stoichiometric ratios (respectively noted C/S and H/S), changes with the composition of the solution with which it is equilibrated. In addition, C-S-H is able to incorporate aluminium if this element is present in solution, to produce what is generally named as C-A-S-H. These variations in composition are accompanied by an evolution of the structure of C-S-H, especially in the silicate connectivity characterized by the chain length and the surface charge (see for example [2] and references therein).

As far as modelling is concerned, two different approaches are able to describe, with a good agreement with the experimental data, the solubility and the variation of composition and the structure of C-S-H as well. The first approach considers solid solutions between three end-members: a tobermorite-like one (infinite silicate chain length), a dimeric one and a pentameric tobermorite-like one, with full interlayer Ca^{2+} occupancy [3]. A drawback is that it is necessary to create a new end-member when another element is introduced such as Al or alkalis. The second approach also considers the solubility of three different phases as suggested earlier [4] and is based on the layered structure of C-S-H. It allows the consideration of surface reactions describing the variation of the Si content by the bridging of dimeric silicates. The variation of the calcium content is described as surface complexation with silanol groups. In addition, the deprotonation of the silanols with the increase of pH can be described as well [5]. The interactions with other cations and anions can be described by surface complexation, or simply by surface charge balance. We show that this last mechanism is generally enough to explain the alkali binding in C-S-H in model systems and in normal and low pH cement pastes.

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Characterisation of grouts, new and old

Provis, J.L.

University of Sheffield, Department of Materials Science and Engineering, Sheffield, United Kingdom

Corresponding author**:** j.provis@sheffield.ac.uk

In understanding how a cementitious grout will interact with both the waste it contains, and the package and geological barriers which in turn surround the grout, characterisation on multiple length scales is essential. This presentation will report recent advances in understanding grout performance from the fresh state (hydration and flow characteristics) to the hardened state (chemical, nanostructural and microstructural evolution), and the resulting implications for transport of fluids and ions in a repository context. The core focus of the presentation will be on high volume blast furnace slag-Portland cement blends, but with consideration of the potential roles which may be played by cements of alternative chemistry in treating various legacy wastes and future arising's.

Pozzolanic reactivity of calcined clays and their impact on the C-S-H structure in portland cement blends

Skibsted, J.

Aarhus University, Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus C, Denmark

Corresponding author: jskib@chem.au.dk

The use of calcined clays as supplementary cementitious materials (SCM's) may provide a valuable contribution to the reduction in CO_2 emissions associated with cement production since calcined clays can be produced at significantly lower temperatures and do not involve a decarbonation reaction. The dehydroxylated form of the principal 1:1 clay kaolinite, metakaolin, represents a model compound for an alumino-silicate rich SCM which has been widely studied in terms of its structure and reactivity. Less attention has been paid to thermal activation of the 2:1 clay, montmorillonite, although this mineral can be found in large deposits all over the world. This presentation focusses on the pozzolanic reactivities of thermally treated kaolinite, montmorillonite and an interstratified illite-smectite clay and on their impact on the structure and composition of the C-A-S-H phase formed in Portland cement – calcined clay blends. The thermally treated clays and the Portland cement – calcined clay blends are characterized primarily using solid-state ^{27}Al and ^{29}Si NMR techniques, which give equal information on amorphous as well as crystalline components in complex cement mixtures. The pozzolanic reactivities in the cement blends are investigated for a fixed replacement level (30 wt.%), and in the case of metakaolin for increasing levels ranging from 5 to 30 wt.% replacement. The latter studies show that the incorporation of aluminum in the C-S-H phase increases with increasing metakaolin content, whereas it is independent of the hydration time [1]. Furthermore, increasing metakaolin contents result in longer average alumino-silicate chain lengths, reflecting a decalcification of the C-S-H phase.

The pozzolanic reactivity of a pure montmorillonite is investigated as a function of the calcination temperature. For maximum reactivity it is found that the resulting C-S-H phase contains silicate chains with the highest aluminum incorporation [2]. This reflects that the aluminate species at this activation temperature are more easily dissolved and thereby available for C-A-S-H formation. This indication is further supported by dissolution experiments on calcined kaolinite and montmorillonite samples.

During dehydroxylation (600 – 900 °C) of the interstratified illite/smectite (70/30) clay, the Q^3-type SiO_4 sites become disordered and octahedral AlO_6 sites transform into tetrahedral sites, resulting in an amorphous material with substantial pozzolanic properties, as demonstrated by reactivity tests and hydration studies of the Portland cement – calcined clay blend [3]. At higher temperatures (above 950 °C), inert Q^4-type phases crystallize which radically reduce the reactivity. At optimum calcination temperature (900 °C), the amorphous material contains highly dissolvable elemental species as seen from complementary ICP-OES analysis.

Overall, calcined clays have been found to significantly impact the C-S-H structure in hydrated Portland cement – calcined clay blends by increasing its Al/Si ratio and decreasing its Ca/Si ratio, in agreement with thermodynamic considerations.

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Topic 1: Cement Chemistry and Microstructure

Effect of magnesium on the stability of C-S-H

Bernard, E.[1], Dauzères, A.[2], Le Goff, F.[1], Pochard, I.[3], Lothenbach, B.[1]

[1] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*
[2] *IRSN, Fontenay aux Roses, France*
[3] *Université de Bourgogne et Franche-Comté, Dijon, France*

Corresponding author: ellina.bernard@empa.ch

Magnesium silicate hydrates (M-S-H) may form in the interaction zone between low-pH cement and clays. Low-pH cements are mainly composed of calcium silicate hydrate gels (C-S-H), with a Ca/Si between 0.7-1.2 [1]. Low-pH cements have been observed to deteriorate in contact with clays rock, i.e. decalcification of C-S-H, leaching, carbonation and magnesium enrichment accompanied by the formation of M-S-H [2]. C-S-H and M-S-H are structurally different. In addition, C-S-H is observed to be stable at pH >10.5, while M-S-H is formed at lower pH values (8.5-10) [3,4].

Batch experiments with magnesium oxide and magnesium chloride additions to C-S-H were carried out to investigate the effects of both magnesium and of pH on the stability of C-S-H. At lower pH values (8 in the presence of $MgCl_2$) the decalcification of C-S-H and formation of M-S-H was observed by FTIR and XRD, while at higher pH values (10.5 in the presence of MgO) C-S-H remained stable and magnesium precipitated as brucite ($Mg(OH)_2$).

In addition, the destabilisation of C-S-H was also studied in interface experiments, where synthetic C-S-H and M-S-H samples, prepared from CaO, MgO and SiO_2 at water to solid ratio of 45 and aged for up to 1 year, were pressed into discs to create a well-defined interface. C-S-H is in direct contact with a magnesium-rich environment which enables us to reproduce the condition in field experiments and to better understand the processes during M-S-H formation (c.f. Figure 1). In the interface experiment the formation of M-S-H was observed within the C-S-H, thus at pH values around 10.5. SEM/EDS data indicate a decalcification of the C-S-H disk coupled with the opening of cracks while a front of magnesium precipitated at the surface. No brucite is observed by FTIR.
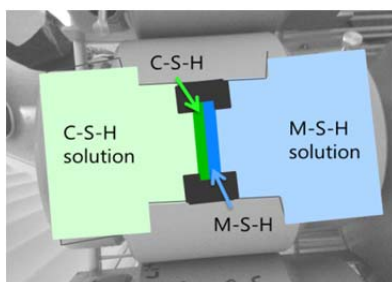
Figure 1: Scheme of the interface experiment in diffusion cell.

The dissolution of C-S-H and precipitation of M-S-H occurred within 3 months. This experiment shows the same phenomena as observed in field studies and thus allows studying the actual deterioration phenomena under well controlled conditions. The results emphasize that M-S-H form directly where originally C-S-H was present at pH values around 10.

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Degradation of real scale cemented simulated waste forms over 35 years in salt solutions

Borkel, C., Schlieker, M., Kienzler, B., Metz, V.

Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Karlsruhe, Germany

Corresponding author: christoph.borkel@kit.edu

Degradation of cemented waste forms in concentrated brines is of importance when assessing the long-term safety of low/intermediate level waste (L/ILW) disposal in rock salt. In certain bedrocks of metamorphic sediments and argillaceous rocks, considered for L/ILW repositories in Germany, porewaters are also saline. Mechanistic understanding of the fate of cemented waste forms in brines is therefore essential for safety assessments.

This study reports new results from leaching and degradation experiments which were performed over several decades to test the behaviour of real scale, simulated, cemented waste forms with respect to chemical resistance and radionuclide mobilization. Twenty six monoliths (masses from 186 kg to 364 kg) were investigated containing up to 10 wt.% simulated ILW from reprocessing (mainly $NaNO_3$). The monoliths were immersed in concentrated NaCl- and in a $MgCl_2$–rich brine. Solution compositions were analysed in course of the experiments [1] and after termination in 2013 drill cores were extracted and subjected to detailed solid phase analysis which are discussed here.

The monoliths were manufactured at water to cement (w/c) ratios from 0.24 l/kg to 0.5 l/kg. Therefore, the studied solids varied significantly in their initial porosity. In the $MgCl_2$–rich brine higher initial porosity (w/c=0.5 l/kg) comprises a higher reactive surface area and eases water penetration. Observed degradation was fast so that the monoliths fully corroded within about 15 years in the stagnant solution. The main identified detrimental process is the exchange of Mg from solution with Ca in the cement, leading to the formation of highly concentrated $CaCl_2$-rich solution. The monoliths lost physical coherence to a large extent and the remaining solid contains heterogeneously disseminated Friedel's salt, brucite, gypsum, Mg-oxychloride and halite as secondary phases, identified by XRD, SEM and TG. Lower initial porosity inhibited the degradation process in $MgCl_2$-rich solution, i.e. at w/c ratio 0.43 l/kg hydrated monoliths degraded relatively slow. At even lower initial porosity (w/c ratio 0.24-0.34 l/kg) the monoliths barely degraded in $MgCl_2$ brine. Solid phase characterization, as well as depth resolved quantification of Cl^- ingress and NO_3^- (waste component) release proved a halt of degradation. Moreover, the composition of the brine remained similar to its initial composition. We identified a thin layer at the external surface in which cement phases were dissolved and secondary phases precipitated. Analytical observations indicated a closure of pore space and an isolation of the interior parts. Hence, at low w/c ratios the detrimental effect of $MgCl_2$ brine was found to be relatively weak for the monoliths.

In the case of NaCl brine results differed strikingly. In all systems leach solutions and solid phases reached thermodynamic equilibrium within less than ~20 years. We observed neither a clogging effect at low initial porosity, nor an influence of the w/c ratio on the degradation kinetics. Mobilisation of NO_3^- to a depth of 10 cm from the surface indicated stronger deterioration at the surface. Up to this depth also constant Cl^- content of 4 wt.% was found in the solid which at greater depth decreased, indicating a diffusive transport of Cl^-.

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Influence of lithium and borate ions on the hydration of calcium sulfoaluminate cement at early age

Cau Dit Coumes, C.[1)], Champenois, J.B.[1)], Dhoury, M.[1)], Mercier, C.[2)], Damidot, D.[3)]

[1)] *CEA, DEN/DTCD/SPDE, Bagnols-sur-Cèze, France*
[2)] *Université de Valenciennes et du Hainaut Cambrésis, LMCPA, Maubeuge, France*
[3)] *Ecole des Mines de Douai, Douai, France*

Corresponding author: celine.cau-dit-coumes@cea.fr

In pressurized water reactors, a solution of boric acid, the pH of which is controlled by the addition of lithium hydroxide, is injected in the primary circuit. Boron acts as a neutron moderator and helps controlling the fission reactions. The treatment of this solution produces waste with significant contents of lithium and borate ions. Its stabilization/solidification with calcium silicate cement is complicated by the strong retarding effect of borate ions on cement hydration. Belite calcium sulfoaluminate (CSA) cements with high ye'elimite content might be more appropriate: their hydration is less retarded and they form by hydration large amounts of AFm and/or AFt phases which can incorporate borate ions into their structure [1, 2]. This presentation is focussed on the processes explaining the retardation effect of borate ions, counterbalanced by the acceleration effect of lithium ions, on CSA cement hydration.

A panel of techniques was used to investigate the early age hydration of CSA cements comprising 0 or 10% gypsum as a function of the lithium and borate concentrations in the mixing solution. The evolution of the electrical conductivity and/or heat flow of cement suspensions and pastes was monitored with ongoing hydration. The pore solution of cement pastes was also extracted using pressure and analysed by ICP-AES. In addition, the phase assemblage was characterized after fixed periods of time by X-ray diffraction, thermogravimetry and MAS-NMR spectroscopy (^{7}Li, ^{11}B, ^{27}Al).

Lithium salts (LiOH, LiNO$_3$) were shown to accelerate CSA hydration by decreasing the duration of the period of low thermal activity. This effect resulted from Li$^+$ cations rather than from their counter-ions, and was noticed even with small additions of lithium (2.5 µmol Li/g of clinker). It increased with the lithium concentration up to 30 µmol/g of clinker, and then reached a plateau. Lithium ions likely precipitated as Li-substituted aluminium hydroxide. The acceleration could result from two processes: *(i)* faster precipitation of Li-substituted Al(OH)$_3$ than Al(OH)$_3$, and *(ii)* formation of particles with increased specific surface area, which provided more surface area for heterogeneous nucleation of the other hydrates.

On the contrary, sodium borate retarded CSA cement hydration by increasing the duration of the period of low thermal activity. Ulexite, a poorly crystallized mineral containing sodium and borates, transiently precipitated at early age. As long as ulexite was present, dissolution of ye'elimite was strongly slowed down.

When sodium borate and lithium hydroxide were simultaneously introduced in the mixing solution, these two mechanisms were superimposed. With a gypsum-free cement, a third process was additionally observed: lithium ions promoted the initial precipitation of a borated AFm phase, which was later converted into a borated AFt phase when hydration accelerated.

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Thermal alteration of cementitious material in TRU radioactive waste disposal

Hayashi, D.[1)], Negishi, K.[2)], Owada, H.[1)], Fujii, N.[1)]

[1)] *Radioactive Waste Management Funding and Research Center, Tokyo, Japan*
[2)] *Taiheiyo Consultant Co., Chiba, Japan*

Corresponding author: d-hayashi@rwmc.or.jp

In the study of geological disposal of TRU (Trans-Uranium) radioactive waste in Japan, the temperature in the facility of the engineered barrier system (EBS) is kept below 80°C in order to mitigate the thermal alteration of cementitious material caused by heat generation of the waste [1]. This thermal alteration of cementitious material results from the crystallization (become to tobermorite and/or jennite) of calcium silicate hydrate (C-S-H). Previous research has suggested that the crystallization of C-S-H can occur at 80°C or less [e.g., 2]. Such crystallization in the cementitious material can affect nuclide migration and the mechanical stability of the EBS. On the positive side, this crystallization lowers the pH of the cement leachate, which may reduce the alteration of the other material such as bentonite by the hyperalkaline plume effect.

This study investigates the possibility that C-S-H may crystalize in the cementitious material of the EBS and the conditions for such crystallization, through an analysis of C-S-H in 80-years-old aged concrete and testing of crystallization of synthetic C-S-H and OPC. Major findings are as follows: crystallization of C-S-H can occur in the concrete, the Ca/Si ratio (C/S) of C-S-H is decreased by the effect of the aggregate, and C-S-H crystallizes when C/S becomes 0.83.

The EPMA results of C/S distribution of aged concrete are shown in Figure. 1 The average C/S value of the cement paste part of aged concrete was close to 0.83, which is the composition of tobermorite. The cement paste in contact with aggregate has a lower C/S than the paste that is farther away from the aggregate. It is therefore presumed that the supply of dissolved Si from aggregate to C-S-H caused the C/S to decrease. The influence of aggregate was confirmed by testing of crystallization.
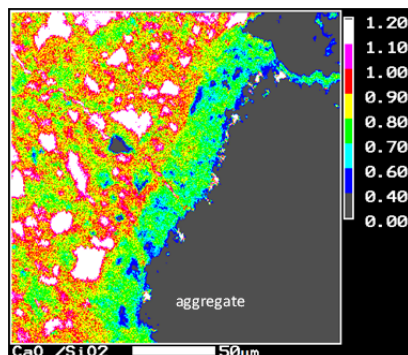
Figure 1: Ca/Si distribution of aged concrete by EPMA.

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C-S-H phase dissolution models: Implications of recent data for low calcium-silicon ratio systems

Heath, T. G.[1], Swanton, S. W. [1], Clacher, A.[2]

[1] *Amec Foster Wheeler, Harwell Campus, Didcot, United Kingdom*
[2] *Amec Foster Wheeler, Warrington, United Kingdom*

Corresponding author: tim.heath@amec.com

A dynamic leaching study [1] has recently been completed of the dissolution of low calcium to silicon ratio (C/S) calcium-silicate-hydrate (C-S-H) systems with initial C/S ranging from 0.2 to 0.6. Some of the key results from this study include:

- similar behaviour for all gels studied during early leaching stages, giving an equilibrated pH of ~9.9 and a solution phase C/S of ~0.29
- C-S-H gels with C/S>0.29 evolve, on leaching, towards a congruent dissolution point with a solid C/S close to 0.84 (consistent with tobermorite) and pH ~10.8
- C-S-H gels with C/S<0.29 become increasingly silica-rich on leaching but maintaining an alkaline pH>9.5 down to at least C/S = 0.07
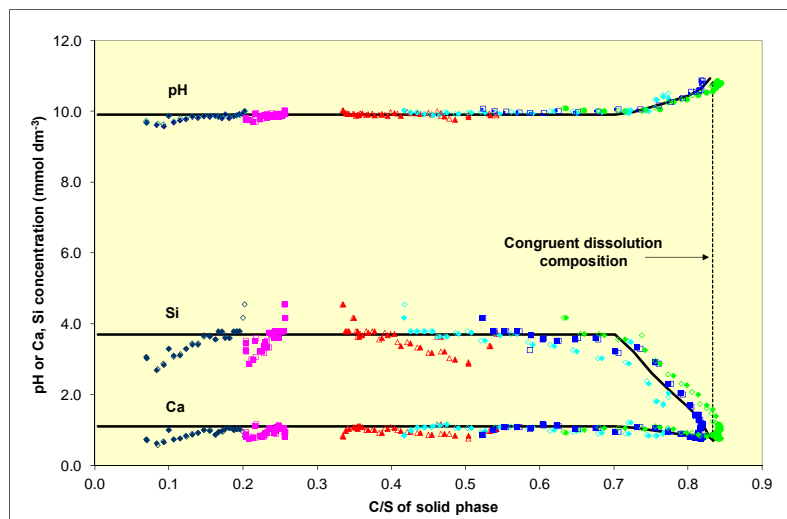
Figure 1: Ideal solid solution model fit (solid line) to experimental data for leached C-S-H gels.

Chemical modeling has shown that above C/S of 0.7, the dissolution data are well described by an ideal solid solution model for the C-S-H phases, based on end members with C/S of 0.67 and 0.83. At C/S<0.67 the data are consistent with equilibration of the aqueous phase with amorphous silica and a C-S-H phase of constant composition. The implications of the new data for C-S-H modelling across the full C/S range are investigated. This work was funded by Radioactive Waste Management as part of its research and development programme.

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Modelling the effect of particle size distributions on early age hydration kinetics of C₃S - fly ash blends

Joseph, S.[1], Bishnoi, S.[2], Van Balen, K.[1], Cizer, Ő.[1]

[1] *KU Leuven, Dept. Civil Engineering, Belgium*
[2] *IIT Delhi, Dept. Civil Engineering, India*

Corresponding author: shiju.joseph@bwk.kuleuven.be

Alite (C_3S) is the major source of portlandite that takes part in the pozzolanic reaction of fly ash especially in the early ages as belite hardly reacts at this period. The effect of particle size distribution of alite and fly ash on the hydration kinetics is studied. Blends composed of alite of three different fineness and fly ash of three different fineness are investigated to understand the hydration kinetics. Isothermal calorimetry and thermogravimetric analysis are used to distinguish the degree of alite hydration from the overall degree of hydration. The filler effect is identified from the results of an alite-quartz system to determine the heat release from the hydration of the pozzolanic reaction of fly ash. A two-step growth mechanism, densified volumetric growth (DVG) model with varying outer growth of C-S-H and densification is used to fit the results. The DVG model is simulated in a modelling platform developed in C++ using object-oriented algorithms to simulate different reaction mechanisms with high speed without the need to truncate the particle size distribution. This study is able to model the effect of particle size distribution on the early age hydration kinetics of blends made of a combination of C_3S and fly ash.

Parameterization of multi-site solid-solution models of C-S-H with alkali and aluminium contents

Kulik, D.A.[1], Lothenbach, B.[2], Miron, G.D.[3]

[1] *Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland*
[2] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*
[3] *ETH Zurich, Institute of Geochemistry and Petrology, Zürich, Switzerland*

Corresponding author: dmitrii.kulik@psi.ch

Our CASHNK multi-site (sublattice) solid solution model aims to describe the effect of aluminium and alkali on C-S-H solubility and structure. It is based on a defect-tobermorite structure, in which three sites (interlayer IC, bridging tetrahedra BT, and additional calcium unit CU) with substitutions of Ca, K, Na, Si, Al moieties or vacancies can be identified [1]. All end members were generated by permutation of moieties on their respective structural sites. Such apparently complex solid solution models with many end-members and many site interaction parameters, easily computed with the GEM software, can reproduce stability and water content of C-S-H, as well as its structural properties such as MCL (mean chain length). The aim of our work was to obtain a consistent thermodynamic data set for the CASHNK model by stepwise multi-parameter optimization for sub-models against selected C-S-H solubility datasets and known trends in MCL or in Al distribution between structural sites as functions of Ca/Si ratio in C-S-H. Such a demanding parameterization effort would not be possible without a dedicated software tool GEMSFITS [2], developed as part of in-house GEM software (http://gems.web.psi.ch).

We started with a sub-model for the co-precipitated C-S-H, which could reproduce both the solubility and MCL (obtained from ^{29}Si MAS NMR data) only after including the MCL data into the least-square objective function for fitting 11 parameters (G^o_{298} values of 8 end members and 3 symmetric site interaction parameters) simultaneously. Optimized values of these parameters were fixed in fitting of other sub-models extended with K, Na, and Al-containing end members. For CSHK and CSHN sub-models (4 more end members and 2 more interaction parameters each), reasonable fits to the solubility data were obtained. The MCL reduction by added alkali could again be reproduced only after including the MCL data into the fitting process.

For the CASH sub-model (19 more end members and 6 more interaction parameters), the major difficulty in parameterization process was that a large part of the available solubility data, where dissolved Al concentrations fall at or below detection limits, had to be discarded. Because the Al data also show a strong dependence on the reaction time in the experiments, the fitting was limited to datasets for ca. 4 weeks equilibration time. Although reported trends in Al distribution among IC, BT and CU sites are somewhat equivocal [1], they are necessary to "teach" the model to yield the realistic Al solid speciation. More experimental and spectroscopic data are needed to resolve these issues and to fit the remaining CASHK and CASHN sub-models.

Our progress in stepwise parameterization of the structurally consistent, extendable multi-site CASHNK model shows a clear pathway for adding more components of relevance for waste-cement interactions (e.g. U, Zn, Sr) if their structural sites in C-S-H can be identified in spectroscopic and atomistic studies, and experimental uptake isotherms in C-S-H are available.

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Investigating the corrosion of aluminum metal in cement-based matrices using electrochemical impedance spectroscopy

Lahalle, H.[1)], Cau Dit Coumes, C.[1)], Lambertin, D.[1)], Cannes, C.[2)], Delpech, S.[2)], Gauffinet, S.[3)]

[1)] *CEA, DEN/DTCD/SPDE, Bagnols-sur-Cèze, France*
[2)] *CNRS, Université Paris-Sud 11, Institut de Physique Nucléaire, Orsay, France*
[3)] *Université de Bourgogne et Franche-Comté, ICB, UMR 6303, Laboratoire Interdisciplinaire Carnot de Bourgogne, Faculté des Sciences Mirande, Dijon, France*

Corresponding author: hugo.lahalle@cea.fr

Metallic aluminum can be found in legacy nuclear waste arising from the reprocessing of spent fuel designed for natural uranium graphite gas reactors. Prior to disposal, this waste shall be conditioned in a stable, monolithic and confined form. In a strongly alkaline medium, such as that encountered in conventional cementitious materials based on Portland cement, aluminum metal is corroded, with continued production of dihydrogen. In order to develop a mineral matrix having enhanced compatibility with aluminum, an experimental study was previously carried out to measure the dihydrogen production resulting from corrosion of aluminum metal rods encapsulated in different cement pastes [1]. The best results were achieved with magnesium phosphate cement, which released very little dihydrogen over the duration of the study. This was explained by the pore solution pH of the binder, close to 8, which fell within the passivation domain of aluminum metal.

This presentation provides deeper characterization of the interface between metallic aluminium and the cement pastes as a function of time using two electrochemical techniques: *(i)* measurement of the open circuit potential and *(ii)* recording of the electrochemical impedance spectrum of an aluminium electrode directly embedded in the cement matrix. Electrochemical Impedance Spectroscopy (EIS) avoids indeed any perturbation of the metal/paste interface if the measurement is carried out at the open circuit potential. In the Portland cement paste, the electrochemical data confirmed the corrosion of aluminum, whereas this latter tended towards a passive state in the magnesium phosphate binder. The beneficial addition of lithium nitrate, which acted as a corrosion inhibitor, was pointed out for both cements (Figure 1). The EIS diagrams were analysed using equivalent electrical circuits to get more information on the corrosion mechanism. Combining electrical circuit components with kinetic constants related to the different steps of a reaction pathway allowed rates of corrosion to be calculated. The resulting production of dihydrogen fitted well with that measured experimentally.
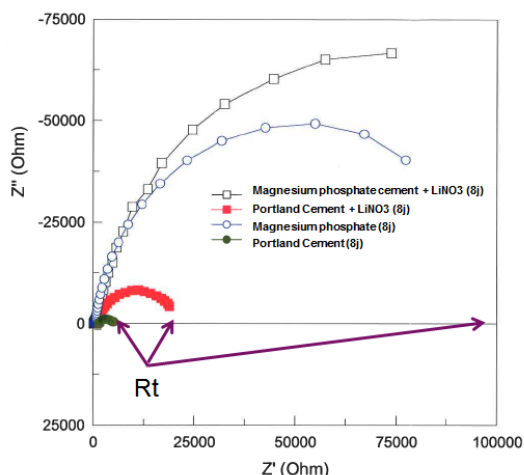
Figure 1: Impedance spectra in Nyquist representation recorded on an aluminum electrode embedded in a Portland or magnesium phosphate cement paste as a function of its lithium nitrate concentration.

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Investigation of the hydration process of a wollastonite-based calcium phosphate cement

Laniesse, P.[1], Cau Dit Coumes, C.[1], Bourchy, A.[1], Antonucci, P.[1], Mesbah, A.[2],
Le Saout, G.[3]

[1] *CEA, DEN/DTCD/SPDE, Bagnols-sur-Cèze, France*
[2] *CEA/CNRS/UM/ENSCM, ICSM, UMR 5257, Bagnols-sur-Cèze, France*
[3] *Ecole des Mines d'Alès, Centre des Matériaux des Mines d'Alès, Alès, France*

Corresponding author: priscillia.laniesse@cea.fr

Portland cement is extensively used for the conditioning of low- or intermediate-level radioactive wastes. However, its high alkalinity is a serious obstacle in the case of acidic wastes. This presentation aims at investigating a wollastonite-based phosphate binder which might show an enhanced chemical compatibility with acidic wastes, as compared to usual calcium silicate cements.

The binder was a two-component system, consisting of wollastonite and of a phosphoric acid-based solution. The weight ratio of the mixing solution to the cement powder was fixed to 1.25, resulting in a P/Ca molar ratio of 0.94. A specific cell [1] was used to monitor simultaneously the evolution of the shear storage modulus, electrical conductivity and temperature of the cement paste with ongoing hydration. In addition, the phase assemblage was characterized after fixed periods of time by X-ray diffraction, thermogravimetry analysis and Raman spectroscopy. The pore solution was also extracted using pressure and analysed by ICP-AES.

Hydration was shown to occur in two main steps. In addition to amorphous silica, dissolution of wollastonite successively yielded monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2 \cdot H_2O$) and brushite ($CaHPO_4 \cdot 2H_2O$). Gibbsite, present as an impurity in the wollastonite powder, dissolved initially because of the low pH of the mixing solution (pH 1), but later re-precipitated when the pH increased (pH 4). This phase evolution was well reproduced by thermodynamic modelling using the Chess database enriched with phosphate minerals and aqueous species (Figure 1).
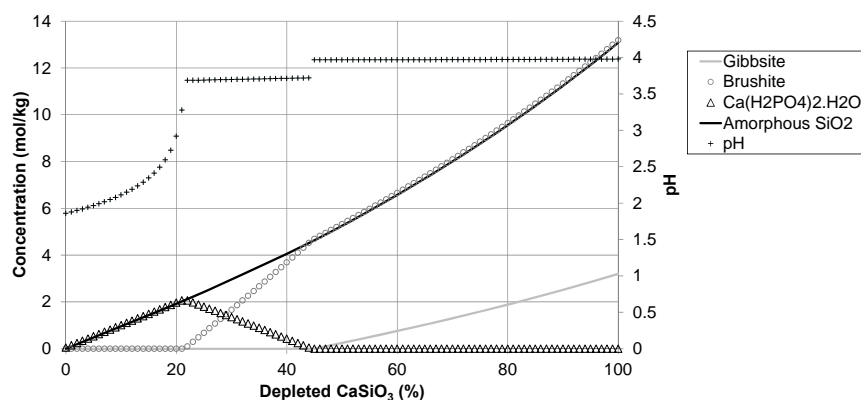
Figure 1: Thermodynamic modelling of the phase evolution of a wollastonite-based calcium phosphate cement with ongoing hydration.

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Internally consistent thermodynamic dataset for aqueous species in the system Ca-Mg-Na-K-Al-Si-O-H-C-Cl

Miron, G. D.[1, 3)], Wagner, T.[2)], Kulik, D. A.[3)], Lothenbach, B.[4)], Heinrich, C. A.[1)]

[1)] *ETH Zurich, Institute of Geochemistry and Petrology, Zürich, Switzerland*
[2)] *University of Helsinki, Department of Geosciences and Geography, Helsinki, Finland*
[3)] *Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland*
[4)] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*

Corresponding author: dan.miron@psi.ch

Results of chemical speciation modeling cannot be better than the quality of the underlying thermodynamic database. With this in mind, the standard Gibbs energies $G^o_{1,298}$ at 1 bar 25 C of aqueous ions and complexes were simultaneously refined against a large set of critically evaluated experimental data on mineral solubility, covering the entire Ca-Mg-Na-K-Al-Si-O-H-C-Cl system over wide ranges in temperature and pressure. Thermodynamic properties of solubility-controlling minerals were adopted from the dataset of Holland and Powell (2002; Thermocalc dataset ds55) [1], assumed to be fully internally consistent and non-adjustable. Results from new high-precision conductance and potentiometric experiments on electrolyte association were used to derive more reliable and accurate equilibrium constants for weak complexation and to constrain the properties of complexes which are insensitive to the solubility data. The global optimization of $G^o_{1,298}$ values of aqueous species was performed with the GEMSFITS code [2] in such a way that the speciation equilibria for ion pairs and complexes were always maintained by constraining the freely adjustable parameters via the independently derived reaction equilibrium constants [3].

For the cement-relevant extension of the initial system (Na-K-Al-Si-O-H-Cl) with Ca, Mg, and C, the solubility of CO_2 in pure H_2O and in electrolyte solutions, as well as the stability of Ca, Mg, chloride, hydroxide and carbonate/bicarbonate species were revised firstly. Most thermodynamic properties and HKF EoS [4] parameters for these species were derived from correlations, and some were found to reside on the incorrectly interpreted experimental data. For instance, the stability of $CaOH^+$ calculated from the previously reported parameters [4] results in a large overestimation of the calcite $CaCO_3$ solubility at elevated temperatures and pressures. Hence, the properties of $CaOH^+$ were revised in this study against portlandite solubility experiments. This led to a good agreement between calculated and measured calcite solubility, in pure H_2O and in electrolyte solutions. For aqueous species such as $CaSiO_3^0$ and $MgSiO_3^0$ there were little to no reported standard properties and HKF parameters. Such species become important in cementitious systems at high pH, and can be major species Ca-Mg-Si buffered systems at elevated temperatures. The anchor thermodynamic data for $CaSiO_3^0$ species, retrieved from the CSH solubility at ambient conditions, have proven to be useful for determining the HKF parameters along with wollastonite solubility experiments at elevated temperatures and pressures.

Our study indicates that more research is needed for a better identification of the presence of complexes such as $CaSiO_3^0$ and $MgSiO_3^0$ and/or and higher-order associated species, and for determining their thermodynamic properties. Using the developed strategy, the thermodynamic dataset can be extended with more major, trace and ore elements. In future, the optimization process can be repeated when the new solubility/speciation data and/or the improved equation of states for multicomponent aqueous solutions become available.

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Confirmation of phase formation within Portland/slag cement using thermodynamic modelling and experimental techniques

Prentice, D.[1)], Bernal, S.A.[1)], Bankhead, M.[2)], Hayes, M.[2)], Provis, J.L.[1)]

[1)] *University of Sheffield, Immobilisation Science Laboratory, Department of Materials Science and Engineering, Sheffield, United Kingdom*
[2)] *National Nuclear Laboratory, Warrington, United Kingdom*

Corresponding author: dprentice1@sheffield.ac.uk

Portland cements (PC) blended with slag (BFS) are used extensively for encapsulation of nuclear wastes in the UK, offering advantageous properties such as reduced operational cost, relatively high waste loading, and retention of radionuclides [1]. In the context of nuclear waste disposal, these cements are designed for a service life of hundreds to thousands of years. Therefore, it is imperative to develop tools to predict the long-term phase assemblages of a waste package, and thus its potential performance. Thermodynamic modelling can be used to predict how modification of the cement system will affect the nature of the hydration products, as can be seen in Figure 1. For the purpose of this work, the GEMS software environment and the CEMDATA14 database have been selected to describe the hydration products, using the CNASH_ss solid solution model [2].
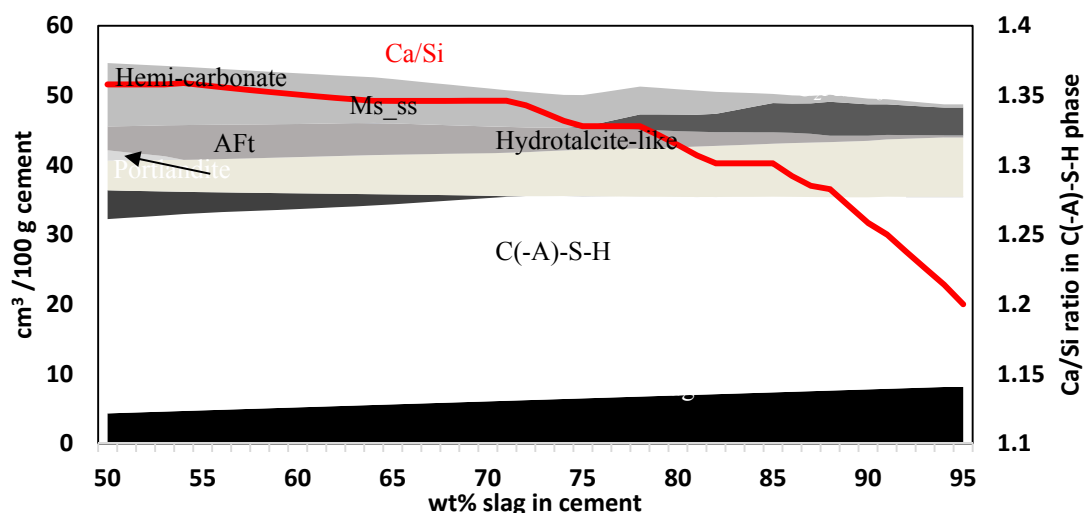
Figure 1: Simulation of the phase assemblage in PC/BFS cement blends with varying quantities of slag, assuming 100% hydration of PC, 75% hydration of slag, and w/s = 0.5.

Confirmation of the nature of the hydration products is key to determine whether the modelling work is accurate. Techniques such as XRD analysis, degree of hydration testing and NMR spectroscopy have been used to identify whether the phases have been predicted correctly, with a particular focus on the slag-rich blends used for nuclear waste immobilization in the UK.

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Crystal structure of magnesium silicate hydrates (M-S-H): The relation with 2:1 Mg-Si phyllosilicates

Roosz, C.[1,2], Grangeon, S.[2], Blanc, P.[2], Montouillout, V.[3], Lothenbach, B.[4], Henocq, P.[1], Giffaut, E.[1], Vieillard, P.[5], Gaboreau, S.[2]

[1] *Andra, Chatenay-Malabry, France*
[2] *BRGM, Orléans, France*
[3] *CNRS, CEMHTI, UPR 3079, Orléans, France*
[4] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*
[5] *CNRS, IC2MP, UMR 7285, Equipe HydrASA, Poitiers, France*

Corresponding author**:** c.roosz@brgm.fr

Two magnesium silicate hydrates (M-S-H) with structural magnesium/silicon ratios of 0.57 ± 0.08 and 1.07 ± 0.13 were synthesized at room temperature, with one year of synthesis duration. Their structure was clarified by considering results from X-ray diffraction, TEM, 29Si MAS NMR spectroscopy, TGA, and EPMA. A modelling approach appropriate to defective minerals was used because usual XRD refinement techniques cannot be used in the case of turbostratic samples, where coherency between successive layers is lost. M-S-H with Mg/Si ratio of ~0.6 appears to be structurally close to nanocrystalline turbostratic 2:1 Mg-Si phyllosilicates. The increase of the Mg/Si ratio from 0.6 to 1.2 occurs by increasing the occurrence of defects in the silicate plan. The layer-to-layer distance evolves from 9.46 Å to 14 Å under air-dried and ethylene glycol conditions, respectively. Crystallites have a mean size of 1.5 nm in the **ab** plane, and 2.4 nm along **c***.

Beyond theses structural considerations, a set of thermodynamic properties are proposed for these phases, based on a dedicated set of experimental measurement.

Traditional Portland cement and MgO-based cement: A promising combination?

Tonelli, M.[1], Ridi, F.[1], Borsacchi, S.[2], Martini, F.[2], Calucci, L.[2], Fratini, E.[1], Geppi, M.[3], Baglioni, P.[1]

[1] *University of Florence, Department of Chemistry "Ugo Schiff" & CSGI, Sesto Fiorentino (FI), Italy*
[2] *Consiglio Nazionale delle Ricerche − CNR U.O.S di Pisa, Istituto di Chimica dei Composti OrganoMetallici, Pisa, Italy*
[3] *University of Pisa, Department of Chemistry and Industrial Chemistry, Pisa, Italy*

Corresponding author: tonelli@csgi.unifi.it
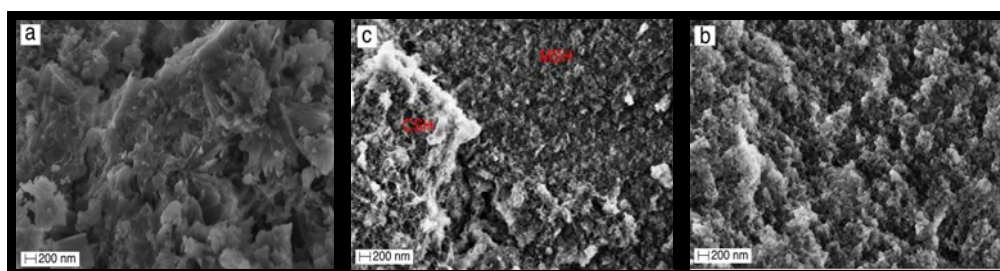
Figure 1: SEM images of CaO-based cement (a), mixed pastes with MgO- and CaO-based cements (b) and MgO-based cement (c).

Cement formulations based on reactive periclase (MgO) [1,2] constitute a promising emerging technology toward eco-sustainable binders, with reduced CO_2 emissions as compared to the traditional CaO-based cements, which have been demonstrated useful in the field of radioactive waste containment [3]. The aim of the present study was to investigate the hydration reaction and the microstructure development of pastes prepared by mixing Portland cement and a MgO/SiO_2 blend. Different percentages of CaO- and MgO-based binders were evaluated to explore the possibility of preparing pastes that could in principle combine the optimal mechanical properties of calcium-based cement with the ecological features of MgO-based cement. The hydration kinetics of the mixtures were investigated by means of Differential Scanning Calorimetry (DSC). Concurrently, the pastes were characterized by means of a multi-scale approach and the formation of hydrated phases was studied by Thermogravimetric Analysis (TG), Fourier Transform IR spectroscopy (FTIR) and X-ray Diffraction (XRD. The structural properties of all samples were investigated by solid state ^{29}Si-NMR. Finally, the morphology of the pastes has been studied by means of Scanning Electron Microscopy(SEM). The results showed that in the mixed pastes both calcium silicate hydrate (C-S-H) and M-S-H binder gel phases form, but, as evidenced in Figure 1, their domains remain segregate in different regions. Moreover, interestingly, the kinetics of hydration in the mixed samples is dominated by MgO/SiO_2 hydration in the first period, while the diffusional stage is mostly dependent on the Portland cement presence.

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The effect of nanoclays additives on the morphologies and hydration of MgO-based cement

Tonelli, M., Ridi, F., Baglioni, P.

University of Florence, Department of Chemistry "Ugo Schiff" & CSGI, Sesto Fiorentino (FI), Italy

Corresponding author: tonelli@csgi.unifi.it

Magnesium based cements are attracting increasing interest as eco-compatible cements. Differently from traditional Portland cements, they can be produced with minimum CO_2 emissions and are perfectly suited for radioactive waste encapsulation application, because of the low pH involved in their hydration process. In spite of the potential importance of this new class of cements, the knowledge of the structural features of magnesium silicate hydrate (M-S-H) binder phase and their dependence on reaction conditions is still quite limited. Recently, the research interest in MgO-based cement has significantly grown but only a few additives have been used so far with this new kind of cement [1]. In traditional CaO-based cement many organic and inorganic additives are commonly used to modulate cement performances to specific application [2-5]. In this work we tested the effect of adding different phosphate-based additives and tubular aluminosilicate nanoclays to MgO-based cement. These compounds have been chosen for their compatibility to magnesium silicate hydrate binder gel phase. Moreover, the 1D geometry of the nanoclays is ideal for reinforcing purpose. Highly reactive MgO and SiO_2 were mixed at ambient temperature and pressure conditions. The effect of adding phosphate-based and nanoclays additives was studied by means of a multi-technique approach. The hydration reaction was investigated by means of Differential Scanning Calorimetry (DSC), while the combination of Thermogravimetric Analysis (TG), Fourier Transform IR spectroscopy (FTIR) and X-ray Diffraction (XRD) allowed the characterization of the hydrated phases formed during the reaction. Moreover the morphology of the pastes has been studied by means of Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The mechanical properties were also analysed by means of micro-hardness testing and AFM-nanoindentation.

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Kinetics parameters for assessing the pH evolution of low-pH concrete

Vehmas, T. J., Leivo, M. T., Holt, E. E.

VTT Technical Research Centre of Finland, Espoo, Finland

Corresponding author: tapio.vehmas@vtt.fi

Ordinary Portland Cement (OPC) based materials play a major role in spent nuclear fuel repository systems. Even in the KBS-3V Engineered Barrier System[1] (EBS), where bentonite act as a main barrier material and concrete acts only as a structural component for rock support and tunnel closure, OPC based materials are used in large amounts. OPC based materials have naturally high pH which endangers the stability of the bentonite buffer. Low pH mix designs have been developed that utilizes large amounts of pozzolanic materials to ensure the safety of the bentonite buffer.

Measuring the pH development of the bentonite/low-pH OPC materials is difficult to study experimentally due to the extremely long service life (up to 100 000 years) of the EBS and thus modelling is required to evaluate degradation scenarios. The quality of the modelling is dependent on the parameters that describe the kinetic and thermodynamic behaviour of the modelled system. We have defined kinetic parameters for various pozzolanic materials by utilizing the Arrhenius equation[2]. According to the results, a frequency factor (A) was related to the surface area of the pozzolanic materials and the activation energy (E_a) was related solely to the pozzolanic reaction. By differentiating the parameters related to chemical reaction and material related parameters, pH development of OPC materials can be transparently and reliable modelled. In the first step, activation energy of portlandite to produce calcium-silicate hydrates was studied. Activation energy for calcium-silicate-hydrates transformation will be also determined.

The frequency factor has been measured for granulated silica fume and nanosilica slurry.

The studied system differs from traditional low-pH concrete. In concrete, physical and chemical factors might have a significant effect on the pozzolanic reactivity. Transport properties of the low-pH concrete potentially alter the reaction kinetics significantly. Also the chemical environment of OPC differs greatly from pure equilibrium compositions of calcium-silicate-hydrates. These two factors are being incorporated into kinetic models by variable parameters that describe the effect of chemical environment and transport properties of low-pH concrete. The results are being used by Posiva Oy in the safety case evaluation of cementitious materials prior to operation of the ONKALO facility. Part of this work is being supported by the European Commission within the CEBAMA project (H2020, 2015-19).

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Thermal stability of hydrated calcium sulfoaluminate cements

Winnefeld, F., Marhoffer, M., Kaufmann, J., Lothenbach, B.

Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland

Corresponding author: frank.winnefeld@empa.ch

Calcium sulfoaluminate cements (CSA), which contain ye'elimite as major clinker phase, are regarded as a promising low-CO_2 alternative to Portland cements [1,2]. They are also proposed as suitable material for waste encapsulation due to their relatively low pH ($\approx$ 11-12.8), their low porosity and permeability and the ability of their main hydration products ettringite and AFm phases to bind cations and anions [3,4].

Elevated temperatures, which occur either during early hydration or in underground nuclear waste repositories, may lead to changes in the hydrate assemblage [5], which can alter the binding capacity of hydrated CSA cement. Thus, the temperature stability of the phase assemblage of hydrated CSA pastes of varying compositions (different CSA clinkers, different ratio CSA clinker/anhydrite, was investigated between 20 and 110°C mainly by means of X-ray diffraction and thermogravimetry and compared to the calculated stable phase assemblage using thermodynamic modelling. Figure 1 shows as an example the temperature dependence of the phase assemblage of a hydrated CSA clinker blended with anhydrite at a molar ratio anhydrite/ye'elimite of 1. CAH_{10} and ettringite are the main crystalline phases at 20°C. Strätlingite, which is present at 50°C, did not form at 85°C. Ettringite is stable until 85°C, and decomposes at higher temperatures. At 110°C only monosulfate, siliceous hydrogarnet and anhydrite (not shown in the XRD pattern) persist.

The experimental data is in good agreement with the stable hydrate assemblages calculated by thermodynamic modelling [5].
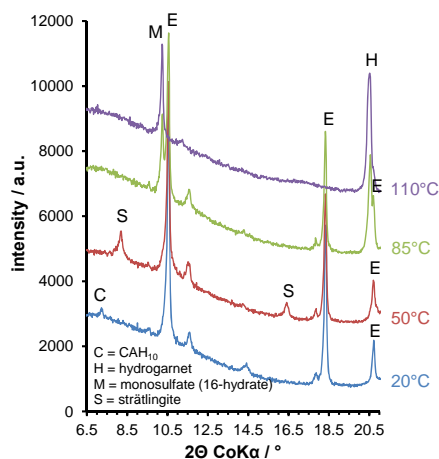
Figure 1: XRD patterns of a CSA cement hydrated for 28 d at different temperatures (w/c 0.72).

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Topic 2: Cement/Rock/Soil Interfaces and Transport

Interaction processes at the concrete-bentonite interface after 13 years of Febex-plug operation: Part I concrete alteration

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

[1] *IETcc-CSIC, Madrid, Spain*
[2] *UAM, Madrid, Spain*
[3] *CIEMAT, Madrid, Spain*

Corresponding authors: *Alonso M.C. and Garcia-Calvo J.L.*, email: mcalonso@ietcc.csic.es jolgac@ietcc.csic.es

A high concern exists on the interaction of engineering barriers in the high-level waste storage concept. Concrete and bentonite are two main components that will interact during the service life of the storage facility. A lot of work has been dedicated to the action of alkaline concrete waters towards the bentonite and low pH cements have been developed to mitigate this damage. However, less attention has been paid to the action of bentonite waters towards the concrete interface.

The paper is focussed on the identification of cement paste alteration due to long-term interaction of concrete with bentonite waters. Concrete samples from dismantling of the concrete plug at the FEBEX gallery of the Grimsel Test Site (www.grimsel.com) are used to identify the aging at the near region due to the contact with bentonite-saturated waters. The plug was fabricated using the shotcrete technology. The type of cement used was a CEM II A-L 32.5R.

The concrete plug has been sealing a granitic gallery filled with bentonite during 13 years. Interaction has taken place with ground waters of the Grimsel site and influence of the bentonite pore water should be considered at the bentonite interface zone. The alteration of concrete is analysed up to few centimetres from the contact with bentonite and compared with zones isolated from bentonite interface. Microstructural changes in cement paste has been analysed through XRD, TG, SEM-EDX.

Results show that a clear alteration of the interface side of the concrete is observed. CSH is significantly altered, and porlandite removed from the first cm. Formation of expansive phases as ettringite and thaumasite is detected inducing microcracking. At longer distance chlorides have also penetrated and formation of Friedel salt is also observed.

Overview on the Horizon2020 CEBAMA project

Altmaier, M.[1)], Duro, L.[2)], Montoya, V.[1)], Kienzler, B.[1)], Perrone, J.[3)], Holt, E.[4)], Claret, F.[5)], Mäder, U.K.[6)], Grambow, B.[7)], Idiart, A.[2)]

[1)] *KIT-INE, Germany,* [2)]*Amphos[21], Spain,* [3)]*Amphos[21] France, France,* [4)]*VTT, Finland,* [5)]*BRGM, France,* [6)]*Universität Bern, Switzerland,* [7)]*ARMINES, France.*

Corresponding author: marcus.altmaier@kit.edu

Cebama is a research and innovation action granted by the European Atomic Energy Community in support of the implementation of the first-of-the-kind geological repositories. The 4-year project, started 1st of June 2015, is carried out by a consortium of 27 partners consisting of large Research Institutions, Universities, one TSO (Technical and Scientific Support Organizations), and one SME (small medium enterprise) from 9 EURATOM Signatory States, Switzerland and Japan. National Waste Management Organizations support Cebama by co-developing the work plan, participating in the End-User Group, granting co-funding to some beneficiaries, and providing for knowledge and information transfer.

The overall strategic objective of Cebama is to support the implementation of geological disposal by significantly improving the knowledge base for the Safety Case for European repository concepts. Scientific/technical research in Cebama is largely independent of specific disposal concepts and addresses different types of host rocks, as well as bentonite. Cebama is not focusing on one specific cementitious material, but aims at studying a variety of important cement-based materials in order to provide insight on general processes and phenomena which can then be easily transferred to different applications and projects. Specific objectives of Cebama are summarized as follows:

- ➢ Perform experimental studies to understand the interface processes between cement-based materials and the host rocks (crystalline rock, Boom Clay, Opalinus Clay (OPA), Callovo-Oxfordian (COX), Toarcian mudstone) or bentonite backfill and assess the impact on physical (transport) properties.
- ➢ Study radionuclide retention processes in high pH concrete environments. Radionuclides which have high priority from the scientific and applied perspective are selected.
- ➢ Improve validity of numerical models to predict changes in transport processes as a result of chemical degradation. Support advanced data interpretation and process modelling, covering mainly issues responsible for the changes in transport properties.

Work in Cebama is organized in 3 scientific/technical work packages (WP): WP1 – Experiments on interface processes and the impact on physical properties *(lead: E. Holt, F. Claret, U. Mäder*; WP2 – Radionuclide retention (*B. Grambow*); WP3 – Interpretation & Modelling (*A. Idiart*). In addition, WP4 is on Documentation, Knowledge Management, Dissemination and Training (*J. Perrone*) and WP5 on Management (*M. Altmaier, V. Montoya*).

Cebama is offering the opportunity of external groups to join the project within the status of Associated Groups (AG). AGs will participate in Cebama at their own costs with specific scientific/technical contributions or particular information exchange functions. The AGs will be invited to the Annual Project Workshops and receive access to the public deliverables and scientific technical information obtained in the project (contact: marcus.altmaier@kit.edu).

Information on Cebama and on upcoming Cebama project events is available at the project website at www.cebama.eu.

Experiments on a cement-clay interface and the impact on physical properties: The Dutch context

Bykov, D. M.[1)], Sabău, A.[1)], Konings, R. J. M.[1)], Kloosterman, J. L.[1)], Meeussen, J.C.L.[2)]

[1)] *Delft University of Technology, Delft, Netherlands*
[2)] *Nuclear Research and Consultancy Group, Petten, Netherlands*

Corresponding author: d.bykov@tudelft.nl

In the Netherlands the feasibility of the disposal concept in Boom clay is being studied within OPERA research programme [1]. Recently, several types of cements have been considered in relation to the Dutch case depending on their different functions: Portland fly ash unreinforced cement as a base for concrete gallery lining of a waste repository (mechanical support function); foam concrete as a backfill material; and rheoplastic concrete (RPC) and self-compacting concrete (SCC) as part of the waste package to fulfil the waste containment function [2].

In the conditions of a repository concrete and clay will be in direct contact. Chemical interactions at the interface between high pH cementitious materials and clays may change the porosity and the pore structure, and affect the engineered barrier system saturation, diffusive transport of water and radionuclides, macro and trace elements, and the mechanical behavior of the EBS. Therefore, investigations of the processes at the interface are of high importance for the geological storage of radioactive waste. Recent studies [3] have shown that the composition of the pore water in the Netherlands differs significantly from that in Belgium, where Boom clay has also been studied as a host rock for the geological repository.

Our research is focused on the concretes with the backfill and the waste containment functions and the Dutch Boom clay. The cementitious materials chosen for the investigations are essentially relevant to the Dutch disposal concept: CEM-III/B 42.5 LH HS (concrete); CEM-I (foamed concrete); CEM-III/B 42.5 LH HS (foamed concrete). Unoxidized Boom clay samples originate from Rupel formation and are excavated from the depth 68-88 m. We are aiming at quantification of the relevant alteration processes and their impact on physical properties, especially on the diffusive and advective transport characteristics for pore water and the dissolved species. The expected outcome of these experiments includes transport parameters and related microstructural characteristics. We are going to present the first results of the corresponding migration experiments and the neutron imaging study of water transport across the cement-clay interface.

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Interaction processes at the concrete-bentonite interface after 13 years of FEBEX-plug operation: Part II bentonite contact

Cuevas, J.[1], Ruiz, A.I.[1], Fernández, R.[1], Torres, E.[2], Alonso, M.C.[3], García-Calvo, J.L.[3] Aparicio, A.[1], Turrero, M.J.[2]

[1] *UAM, Madrid, Spain*
[2] *CIEMAT, Madrid, Spain*
[3] *IETcc-CSIC, Madrid, Spain*

Corresponding author: Jaime.Cuevas@uam.es

The Deep Geological Repository (DGR) concept requires concrete in several functions as the installation of plugs for the isolation of part of the bentonite buffer-nuclear waste canister system galleries. Concrete is a potential source of an alkaline front affecting the mineralogy of the clay buffer [1]. Some authors, [2] showed the relative absence of representative studies in real clay/concrete interfaces taking into account the volumes and chemistry of pore-waters migrating through the porosities of the involved materials and the impacts on the concrete mineralogy.

This paper describes the mineralogical and physical-chemical characterization of a concrete (CEM II A-L 32.5R type)/FEBEX bentonite 13 years interface obtained during the dismantling of FEBEX gallery of the Grimsel Test Site (www.grimsel.com) during 2015. XRD, TG, BET surface, $\delta^{13}C$ and $\delta^{18}O$ isotopes, and soluble ions-exchangeable cations (bentonite) were determined in a concrete (~10 cm)/-bentonite (~5 cm) longitudinal section. In addition, a vacuum dried polished section (Figure 1) was examined by SEM-EDX.
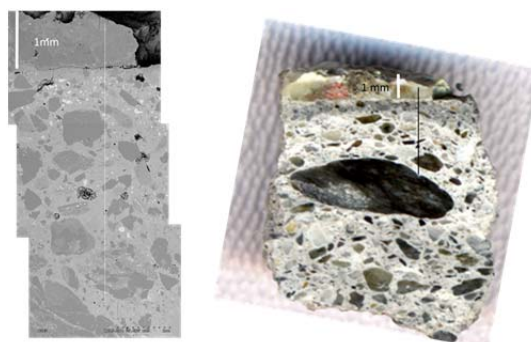
Figure 1: SEM-EDX (BSE) and Air dried aspect of bentonite (upper side)/concrete interface.

Bentonite mineralogy and most physical-chemical properties remained virtually unaltered. In contrast, concrete showed carbonate depletion and ettringite precipitation near the interface in a cm scale. Ca and Al are concentrated in the concrete and depleted in bentonite at < 0.5 mm thickness in which Mg was concentrated. This results indicate very low bentonite alteration compared to the apparent high reactivity detected in the concrete material (Part-I).

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The Long-Term Cement Studies (LCS) at the Grimsel Test Site: 6 years of in-situ cement-granite interactions

Giroud, N.[1)], Martin, A.[1)], Mårtensson, P.[2)], Norris, S.[3)], Sasamoto, H.[4)], Vuorio, M.[5)]

[1)] *Nagra, Wettingen, Switzerland*
[2)] *SKB, Stockholm, Sweden*
[3)] *RWM, Harwell Oxford, United Kingdom*
[4)] *JAEA, Tokai, Ibaraki, Japan*
[5)] *Posiva Oy, Eurajoki, Finland*

Corresponding author: niels.giroud@nagra.ch

The LCS Experiment at the Grimsel Test Site (GTS) aims at increasing the understanding of the high pH cement interaction effects in the repository near field and geosphere, so that modelling can make confident, robust and safety-relevant assessments of future system behaviour. Safety relevant processes include in particular clogging of flow paths by secondary minerals resulting in a lowered hydraulic conductivity, or armouring of dispersive pathways and rock matrix, reducing radionuclide retardation.

The project is an international partner project combining an in-situ experiment at GTS, with laboratory experiments (see for example [1]), the study of the natural and industrial analogues (Maqarin, Jordan, and Tournemire, France), and the work of several modelling teams. The analogues and laboratory experiments help building confidence in the reactive transport modelling and improving the thermodynamic databases. The GTS in-situ experiment consists of an OPC cement sample emplaced in 2009 in a borehole at the intersection with a discrete fracture system. Two boreholes, located at 0.56 and 1.12 m from the emplacement borehole allowed monitoring of the high pH plume and the modifications of hydrochemistry during artificial groundwater injection into the source borehole. Tracer and hydraulic tests performed before and at regular interval after the emplacement of the cement source showed a transmissivity reduction with time.

Modelling of the flow field around the three experiment boreholes and reactive transport around the cement source (see for example [2]) and along the fracture (see [3]) aim at simulating the observed hydraulic and/or hydrochemical data and to predict the interactions between the high pH source and the granite. In 2015, the cement elements were removed and the emplacement borehole overcored for analysis. This paper presents the first post-mortem analysis results, which will be used to confirm or to help improving the modelling predictions.

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Chemical and hydraulic behaviour of cement-based sealing materials in rock salt - laboratory investigations and modelling activities

Jantschik, K., Moog, H.C.

Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) GmbH, Braunschweig, Germany

Corresponding author: kyra.jantschik@grs.de

For the safe disposal of heat-emitting radioactive waste in Germany the disposal in deep geological formations is regarded as a possible option. The former German Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety requires the isolation of the radioactive waste from the biosphere and the permanent safe enclosure of the waste in the containment providing rock zone (September 2010).

Rock salt is one possible host rock formation for the disposal of radioactive waste. The geological barrier is disturbed by mining activities, providing potential pathways for the migration of radionuclides. In order to ensure the safe enclosure of the waste, drifts and shafts have to be sealed with plugs consisting of adequate construction materials. The sealing capability of these plugs depends on the structurally engineered properties of the material itself and on the long-term interaction between the plug and the host rock and the potentially inflowing brine.

GRS is investigating two types of sealing materials: salt concrete, which consists of crushed salt, blast-furnace cement and NaCl-brine and sorelconcrete, which consist of crushed salt, magnesium oxide and $MgCl_2$-brine. Different tests are executed for investigating diffusive and advective transport in both concretes in contact to NaCl-saturated respectively Mg-rich brines. Additional tests are performed for investigating the transport at the contact zone between concrete and rock salt. Changes of solution composition, dissolution and precipitation of concrete phases and changes of permeability are recorded.

Preliminary results show, that salt concrete is stable against NaCl-brine and corrodes in contact to Mg-rich brines by dissolution of the C-S-H phases (Calcium-silicate-hydrates). Sorelconcrete shows an opposed corrosion behaviour and is consequently stable against Mg-rich brines and corrodes in contact to NaCl-brines. In this case the 3-1-8 phases ($3\ Mg(OH)_2 \cdot MgCl_2 \cdot 8\ H_2O$) dissipate and consequently porosity increases.

Because of the requirement, that radioactive waste has to be isolated from the biosphere for a long time, it is necessary to predict the chemical-hydraulic material behaviour of the sealing materials and the resulting reactive mass transport of radionuclides following brine intrusion by numerical modelling. This work aims to adapt reactive mass transport models to laboratory results described within this abstract.

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Cement-Opalinus Clay interaction: Comparison of modelling results with experimental data

Jenni, A., Mäder, U.K.

University of Bern, RWI, Institute of Geological Sciences, Bern, Switzerland

Corresponding author: andreas.jenni@geo.unibe.ch

Cementitious materials will be emplaced in deep geological waste repositories, regardless of host rocks considered. The enormous material contrasts between cement and any type of host rock leads to chemical and mineralogical interaction, mainly driven by chemical gradients and subsequent diffusion in pore water. Relevant host rock properties like swelling pressure in case of clay rocks, permeability, or specific retention might be altered.

Reactive transport modelling helps to understand the related mechanisms, which interact and leave behind complex traces in interface samples. Modelling cement – clay rock interaction is extremely demanding:

- Clay rocks contain a pore fraction influenced by the negatively charged layer surfaces of clay minerals (Donnan porosity). This pore fraction, typically around half of total pore volume (Opalinus Clay), has a solute composition different from the charge-balanced intergranular porosity. Porosity clogging is expected to occur mainly within intergranular porosity, whereas solute transport continues in the Donnan porosity, although transport properties herein are substantially different. Conventional model approaches treat the Donnan porosity as immobile cations undergoing cation exchange reactions.
- Several studies indicate that interactions start right after concrete emplacement, and slow down relatively soon thereafter. The entire cement hydration at the interface, interacting with the clay rock, has to be modelled. Therefore,
- the model needs to cover porosity evolutions ranging from 0.7 in a fresh cement paste, down to zero at a clogged interface. Furthermore, immense spatial gradients occur in porosity, pH, and solute concentrations.
- Many cement hydrates form process – relevant solid solutions, of which one exclusively observed at cement – clay interfaces has only recently thermodynamically characterised and implemented in a numerical simulation (MSH) [1].

The model approach presented here meets these demands. The set-up of the Mt. Terri CI experiment, a concrete – Opalinus Clay interface, was simulated from right after casting the concrete into a drill hole. The model results reproduce chemical zonations measured by SEM EDX after 3 and 5 y, and meet mineralogical gradients observed by various methods [2]. The numerical results allow for isolating the major interacting mechanisms:

- Decalcification of cement, Ca increase on clay exchanger
- S diffusion from clay into cement, and further away from interface until pH is again high enough for precipitation of S containing hydrates
- Mg diffusion from clay to the interface, precipitation of mainly MSH
- C diffusion from clay into cement, followed by carbonation of cement hydrates

All these mechanisms influence porosity at different locations. The model outcome can give an estimation of porosity evolution with time, and emphasise the change in transport properties.

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Reactive transport modelling of cement/clay interactions

Kosakowski, G.

Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland

Corresponding author: georg.kosakowski@psi.ch

Reactive transport models are commonly used to investigate the long-term evolution of clay/cement interfaces. In such systems the mineralogical changes near the interface are driven by chemical gradients in the pore waters. Diffusive transport of solutes in the pore space is the dominating transport mechanism due to the low hydraulic permeability of the media. Mineralogical changes induce changes in the pore space which will feed back on the media transport properties. Due to the diffusion limited transport of reactants and the relatively slow precipitation/dissolution kinetics of clay minerals, the geochemical evolution near such interfaces is experimentally not easily accessible.

This work presents reactive transport calculations aimed at reproducing experimental results from the Cement-Clay Interaction (CI) Experiment at the Mont Terri Underground Laboratory in St. Ursanne (Switzerland). The CI Experiment is aimed at the "long-term" investigation of interfaces between several concretes and Opalinus Clay under natural conditions. The dataset [3] offers the possibility to test, validate and further develop modelling concepts which were previously used to for investigating long/term cement/clay interactions [1,2].

The simulations were conducted with the code OpenGeoSys-GEM and aim at using a consistent geochemical and conceptual model for concretes, bentonite and the Opalinus Clay. The updated thermodynamic model utilizes the PSI/Nagra thermodynamic database (https://www.psi.ch/les/database) in combination with the latest version of the cement specific database CEMDATA 14.01 (http://www.empa.ch/plugin/template/empa/*/62204/---/l=1) and additional mineral phases for clays and zeolites, which are taken from the Thermoddem database (http://thermoddem.bgr.fr).

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Impact of temperature on microstructure and transport properties of OPC paste / argilite interface

Lalan, P.[1,2], Dauzères, A.[1], De Windt, L.[2], Bartier, D.[3], Sammaljärvi, J.[4], Techer, I.[5], Detilleux, V.[6]

[1] *Institute of Radiation Protection and Nuclear Safety (IRSN), Fontenay-aux-Roses, France*
[2] *MINES ParisTech, PSL Research University, Centre de Géosciences, Fontainebleau, France*
[3] *CNRS UMR 7566, Université de Lorraine, Vandœuvre-lès-Nancy, France*
[4] *University of Helsinki, Laboratory of Radiochemistry HYRL, Helsinki, Finland*
[5] *Université Nîmes, EA 7352 CHROME, Nîmes, France*
[6] *Bel V, Anderlecht, Belgium*

Corresponding author: philippines.lalan@irsn.fr

In several countries the recommended option for long term management of intermediate-level long-lived or high-level radioactive wastes is deep geological disposal. In France, a thick argillaceous layer (argillite) of Callovo-Oxfordian age was chosen as host rock. Use of cementitious materials for radioactive waste containers, facility vaults and sealing could be disturbed by the nearby argillite. In fact, argillite and cementitious materials have contrasting chemical properties triggering perturbations in each material around their contact. Moreover, presence of the radioactive waste will increase temperature at these interfaces until 70 °C and the impact of this temperature remains poorly characterised.

The present study focused on the argillite / OPC hardened cement paste evolution at 70 °C in term of mineralogy, microstructure and transport properties. 2, 6, and 12 month experiments in dedicated diffusion cells were carried out at 70 °C. Cement paste was poured directly on the argillite surface. Multiple analyses were used to characterise samples: XRD, SEM-EDS, µ-tomography and ^{14}C-PMMA autoradiography for solid samples; ICP-OES, chromatography, pH-metry and TOC-metry for aqueous samples. Ahead, work was done on the characterisation of the sound cement paste at 70 °C and showed ettringite total dissolution without precipitation of other sulphated phase. Precipitation of C-S-H, Tobermorite, C-(A)-S-H and calcite occurred at the interface, forming a brittle area after 2 months. Decalcification and carbonation of the cement paste were also observed. Mineralogical evolution led to an opening of the macroporosity in the cement paste linked to portlandite dissolution. Nevertheless, precipitation processes caused a fall of the total connected porosity within both materials in the altered zone. Analyses confirmed that these phenomena impacted diffusion properties especially by decreasing effective coefficient diffusion. These lab results showed many similarities with those of a companion in situ experiment of the same cement/argillite interface performed during 1 year in the Tournemire URL but gave a better access to alteration kinetics.

Furthermore, reactive transport modelling with HYTEC was performed in order to test the ability of the model to reproduce the experimental data with the aim of doing predictive modelling at larger time scale. The temperature of 70 °C raised the issue of acquiring a relevant set of thermodynamic constants and activation energies of Arrhenius law for chemical reaction rate and dissolved species diffusion. A special emphasis was put on the alteration depths and on evolution understanding of the diffusion properties within the materials around their contact.

Cemtex project: Understand the physico-chemical evolution of cementitious material in clayey environment at 70°C

Lalan, P.[1,2], Dauzères, A.[1], de Windt, L.[2], Bartier, D.[3], Sammaljärvi, J.[4], Techer, I.[5]

[1] *Institute of Radiation Protection and Nuclear Safety (IRSN), Fontenay-aux-Roses, France*
[2] *MINES ParisTech, PSL Research University, Centre de Géosciences, Fontainebleau, France*
[3] *CNRS UMR 7566, Université de Lorraine, Vandœuvre-lès-Nancy, France*
[4] *University of Helsinki, Laboratory of Radiochemistry HYRL, Helsinki, Finland*
[5] *Université Nîmes, EA 7352 CHROME, Nîmes, France*

Corresponding author: alexandre.dauzeres@irsn.fr

In the future radioactive waste geological disposal, the multibarrier system will induce interactions between natural (argillite) and industrial geo-materials (bentonite swelling clay, concrete). Studies have been led on representative systems putting in contact cementitious and clayey materials, both in laboratory or under in situ conditions. The temperatures of these experiments, ranging from 20 to 50°C, are representative of the ones found in the intermediate long-lived waste disposal cells. However, temperature may reach 70°C at the materials interface of the high-level waste disposal cells. Nevertheless, the effects of high temperatures on the concrete/swelling clay or cement/argillite interactions have never been studied. Such higher temperatures may likely alter the reactive pathways evidenced at lower temperature and potentially accelerate the disturbance propagation.

The CEMTEX project (CEMent Temperature EXperiment) aims to fill the lack of knowledge about the geochemical and micro-structural evolutions of these contacts under representative thermo-hydraulic conditions (i.e. 70 °C and full water saturation), which should provide input for future studies on the durability of cementitious materials. In this framework, six in situ experiments have been emplaced in IRSN's underground research laboratory of Tournemire (France): three with a low-pH formulation (ternary mix of silica fume, fly ashes, Portland cement) and three with an Ordinary Portland Cement. Interfaces evolutions were investigated by a set of characterization devices: XRD, SEM-EDS, TEM, TGA, FTIR, μtomography, auto-radiography.

The results of the OPC/ argillite interaction after 1 year show classical decalcification of cement and its carbonation as well as illitisation of clay-type phases. A C-S-H ribbon appears at the interface between the two materials. A layer grows between the C-S-H ribbon and the cementitious material. This layer behaves as a diffusive barrier and contains phillipsite-type zeolites. Ettringite precipitation occurs in the cement in retreat from the interface. The carbonation is diffuse in the in situ test while it forms a thin layer at the interface in the cell experiments. The disturbance thickness is about 1 mm in the cement paste and about 0.5-1 mm in the argillite. The influence of these mineralogical changes on the microstructure evolution exhibits a macroporosity opening clearly linked to the portlandite crystals dissolution. But the total porosity decreases (initial 32-35%, final 25-28%) due mainly to the calcite precipitation.

To conclude, the temperature increasing seems to have a positive effect on the evolution of the transport properties of cementitious material in clayey environment.

Opalinus claystone - low alkali (LAC) concrete interaction: Mineralogical investigations and identification of a Mg-rich phase

Lerouge, C.[1)], Gaboreau, S.[1)], Grangeon, S.[1)], Roosz, S.[2)], Jenni, A.[3)], Mäder, U.K.[3)], Claret, F.[1)], Cloet, V.[4)]

[1)] *BRGM, Orléans, France*
[2)] *Andra, Chatenay-Malabry, France*
[3)] *University of Bern, RWI, Institute of Geological Sciences, Bern, Switzerland*
[4)] *Nagra, Wettingen, Switzerland*

Corresponding author: c.lerouge@brgm.fr

A five-years-old interface between a low alkali concrete (LAC, CEM III/B containing 66% slag and 10% nanosilica) and Opalinus (OPA) claystone from CI drillhole (Mont Terri Underground Rock Laboratory – Jenni et al., 2014) was studied for its textural properties, mineralogy and chemistry, in order to investigate the alkaline perturbation.

After five years, the reactivity between LAC concrete and Opalinus claystone is found to be limited to a ~1 mm–thick layer with a porous (~75% porosity) white crust developed on the concrete side. Quantitative mineralogical mapping of the white crust (electron microprobe - EPMA), combined with infrared and Raman spectroscopies on material separated from the cement matrix, provides evidence for a Mg-rich and phyllosilicate-like phase, which could have talc-like structure (Roosz et al., 2015) accounting for ~25 % of the matrix, associated with the presence of ~11% of calcite. EPMA profiles of Al, Ca, Mg and Si performed through the white crust provide evidence for about homogeneous composition. The chemical formula of the Mg-rich phase was found to be $Ca_{0.6}Fe_{0.1}Mg_{1.6}Al_{1.2}Si_{3.45}O_{10}(OH)_2$ by spot EPMA analyses.

Textural, mineralogical and chemical modifications due to the chemical gradient in the OPA clay at contact with the LAC concrete are limited. Mineralogy of OPA clay remains largely unmodified. The cation exchange capacity (CEC) values measured in OPA clayrocks at contact with the LAC concrete range between 153 and 175 meq kg^{-1}, close to the reference value of 170 ± 10 meq kg^{-1} (Pearson et al., 2003). The cation occupancies in the CEC change at the interface with LAC cement, marked mainly by an increase of Mg and a decrease of Na. EPMA mapping of major elements in Opalinus claystone side also provided evidence of a Mg-enriched 300-400 µm-thick band. Leaching tests performed on OPA clay with deionised water and at different solid to water ratios strongly suggest that Cl and SO_4 have conservative behaviour, with concentrations measured at 2 cm from the interface being close to concentrations of preserved OPA pore waters (SO_4: 0.45 ± 0.15 mmol 100 g^{-1}; Cl: 0.75 ± 0.21 mmol 100 g^{-1}), and increasing towards the interface with the concrete. The SO_4 to Cl ratios also increase towards the interface, suggesting that the increasing anion concentrations are not related to porosity variations.

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Interaction of cement with rock forming minerals

Lothenbach, B.[1)], Bernard, E.[1)], Mäder, U.[2)], Savage, D.[3)]

[1)] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*
[2)] *University of Bern, RWI, Institute of Geological Sciences, Bern, Switzerland*
[3)] *Savage Earth Associates Limited, Bournemouth, United Kingdom*

Corresponding author: barbara.lothenbach@empa.ch

In Portland cements (PC) high alkali concentrations and correspondingly pH values of 13.5 or even higher are encountered [1]. In contact with the environment, however, Portland cements slowly degrade and the pH becomes lower. In a first step the alkalis are leached and the pH is lowered to ≈12.5. In a second step, portlandite is destabilised, while the concentration of other ions is expected to remain more or less constant [2]. In a third stage, decalcification of C-S-H and destabilisation AFm phases and of ettringite can be expected while the pH drops to 11 or even lower. The solution composition changes drastically with a strong increase of aluminium, silicon and sulfate concentrations. The composition of such leached Portland cements is similar to the composition of "low-pH" cements, which have been developed in the last years for radioactive waste disposal. Such low-pH cements consist of binary mixtures of Portland cement (PC) and silica fume (SF), or of ternary mixtures containing also blastfurnace slag or fly ash. Reported pH values of the interstitial solution of such low-pH cements are between 11 and 12. Decalcified C-S-H and ettringite are the main hydrates present, while portlandite and sometimes also AFm-phases are destabilised [3], comparable with the composition of leached Portland cements in step III.

The pH drops not only with leaching and time, but also spatially if the cement solution starts to interact with the surrounding rock, leading to a lower pH values, the removal of calcium due to the formation of C-S-H gel and an increase in silicon and aluminium concentrations through dissolution of aluminosilicate minerals in the rock [4]. Such alterations are typically associated with the growth of zeolites rather than C-S-H gels/minerals. Little focus has up to now be aimed to investigate the effect of less "aggressive' solutions representing more leached Portland cements in stage III or low pH cements, i.e. solutions dominated by the leaching of C-S-H gels and ettringite at pH values near 11.

The present paper presents experimental data from batch experiments carried out at 20, 50 and 80 °C where the evolution of the solution and the formation of hydrates in the presence of albite, ettringite and C-S-H have been studied up to 2 years. At 50 and 80°C, C-S-H, ettringite and partially albite were destabilised while zeolite P(Ca) ($CaAl_2SiO_2O_8 \cdot 4H_2O$) and natrolite ($Na_2Al_2Si_3O_{10} \cdot 2H_2O$) were formed as observed by XRD, TGA and IR. At 20°C no new phases had formed within 2 years and ettringite and albite were still present.

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Predicting long term interactions between concrete and boom clay with a reactive transport model

Meeussen, J. C. L.[1], Koenen, M. [2], Griffioen, J.[2]

[1] *Nuclear Research and Consultancy Group, Petten, The Netherlands*
[2] *TNO, Geological Survey, Utrecht , The Netherlands*

Corresponding author: meeussen@nrg.eu

Cementitious materials are a main bulk construction material of radioactive waste repositories. Such materials have a high alkalinity that potentially interacts with surrounding rock-soil material with which it is in contact. These interaction processes could have an effect on the chemistry and the long-term integrity of the cementitious materials or lead to chemical changes in the surrounding soil-rock material. An increase in local pH values, which is likely to happen, may have significant consequences for local chemical conditions and processes such as sorption and precipitation, as the pH is a driving factor in soil chemical processes.

Interaction between cementitious materials and surrounding rock – soil materials takes place via diffusive transport of dissolved ions in pore solutions of both materials. At the same time these dissolved ions interact by adsorption/desorption and precipitation/dissolution with the solid phases of both matrices. Proper estimation of resulting net diffusion rates requires sufficient understanding of the chemical interaction processes within the cementitious materials as well as in the Boom clay. Modelling requires sufficiently detailed thermodynamic models for both the concrete and the clay matrix in combination with diffusion model.

In this work we show the results for a reactive transport model for cement and clay that makes use of available thermodynamic databases for cement [1] and soil [2] and was set up within the ORCHESTRA [3] model. The model predictions show the extent of the chemical changes in cement and clay as a function of time. We evaluate the sensitivity of the calculated results for a number of important input parameters as well as for alternative versions of the concrete and clay chemical sub-models.

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Mineralogical changes by the interaction of bentonite and cement

Negishi, K.[1], Sakamoto, H.[1], Hayashi, D.[2], Fujii, N.[2], Owada, H.[2], Nitani, H.[3]

[1] *Taiheiyo Consultant Co., Chiba, Japan*
[2] *Radioactive Waste Management Funding and Research Center, Tokyo, Japan*
[3] *High Energy Accelerator Research Organization, Tsukuba-shi, Ibaraki, Japan*

Corresponding author: Kumi_Negishi@taiheiyo-c.co.jp

The proposed transuranic (TRU) waste disposal facility in Japan uses a cementitious material as a structural or filling material and bentonitic material, e.g. bentonite and/or bentonite-sand as a buffer material. There is a concern that the component minerals of bentonite will not be stable under highly alkaline conditions arisen from leaching of cementitious materials. An additional concern is that its performance will alter in the long term. For the estimation of the long-term alteration of the engineered barriers, it is very important to evaluate the change of mineralogical compositions that occur during the cement-bentonite interaction. We focused on an experimental study of the change of the minerals at the cement-bentonite interface. A test piece prepared by contacting a hardened cement paste and compacted bentonite was immersed in the simulated fresh-reducing-high pH (FRHP) groundwater [1] for 76 months. Samples collected from the cement-bentonite interface were analysed using several methods, such as XRD, EPMA and XAFS. The XAFS analysis was assumed to be an efficient technique for studying the poorly crystalline C-S-H, in order to provide information about the local structure around the specific element (in this case Ca). The XAFS measurement allowed for evaluation of the variation of the quantity of the C-S-H in the bentonite. No significant difference was observed in the EXAFS spectra of C-S-H with different a Ca/Si ratio. The local structural conditions around Ca in the C-S-H were similar regardless of the different of Ca/Si ratio.
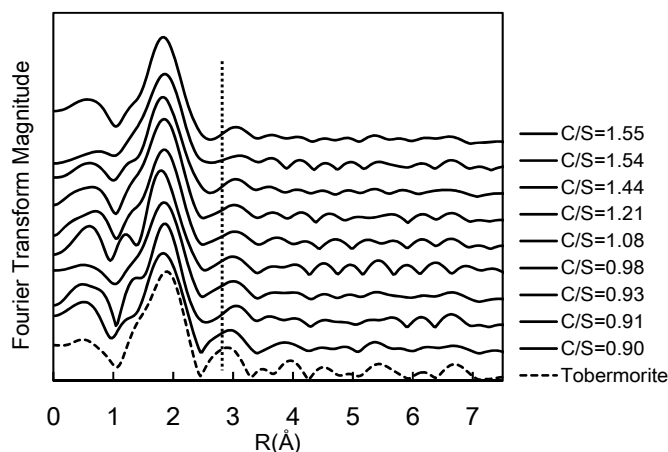
Figure 1: Radial structure function of C-S-H.

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Overview of RWMC's R&D regarding cement leaching - as a source term of the long-term alteration of EBS system

Owada, H., Fujii, N., Hayashi, D.

Radioactive Waste Management Funding and Research Center, Tokyo, Japan

Corresponding author: owada@rwmc.or.jp

Both bentonitic and cementitious materials are planned to be used as engineered barrier materials in the geological disposal of high-level vitrified waste and also so called TRU waste in Japan. Bentonitic material will be placed around the waste packages as buffer material and a large amount of cementitious material are set as filler, structure, support and grout [1]. Cementitious material supplies the alkaline solution with high calcium concentration by the reaction with ground water. This alkaline water will be the cause of the chemical and physical alteration of bentonitic material and surrounding rock. Alkalinity and the supply vary in cement leachate according to the chemical and physical properties of cementitious material such as mineral composition, diffusion coefficient and water permeability. Therefore, alteration of cementitious material will be a cause of the change of the influences on the bentonitic material and bedrock.

RWMC already reported the alteration model of various kinds of cement [2]. In this research, RWMC focused on (1) the thermal alteration and (2) changes of diffusivity by the cement alteration as the change of chemical and physical properties to evaluate the long-term performance of EBS. In addition, RWMC observed the change of the mineral composition around the interface between cement and bentonite to estimate the influences of cement leachate. In this report, the overview of RWMC's R&D regarding the influences of cement alteration (Figure.1) will be presented.
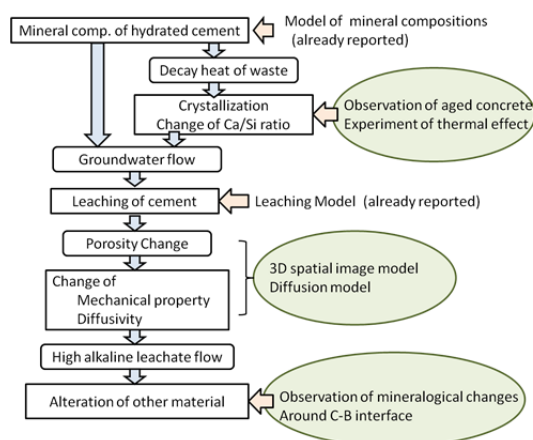
Figure 1: Structure of RWMC's R&D regarding cement alteration.

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Reactive transport modeling of water-cement-rock interaction in fractured granite at Grimsel

Saaltink, M. W.[1,3], Soler J. M.[2,3]

[1] *UPC, Barcelona, Catalonia, Spain*
[2] *IDAEA-CSIC, Barcelona, Catalonia, Spain*
[3] *Associated Unit: Hydrogeology Group (UPC-CSIC)*

Corresponding author: josep.soler@idaea.csic.es

Within the framework of the GTS-LCS project (Grimsel Test Site – Long-Term Cement Studies), an in-situ experiment lasting about 5 years was started in 2009 to study water-cement-rock interactions in fractured granite. A solid cement source (OPC) was installed in a borehole intersecting a water conducting fracture. Two other boreholes at about 0.56 m (observation) and 1.12 m (extraction) from the emplacement borehole were used to monitor the evolution of water composition in the fracture. Prior to the experiment, a tracer test was performed to characterize the initial flow and transport properties of the rock around the experimental boreholes. The flow and reactive transport calculations have been performed using the Retraso-CodeBright code [1]. Solute transport is assumed to be controlled by diffusion in the cement and by advection-dispersion in the rock fracture.

Initially, the flow model calculated from the results of the pre-emplacement tracer test [2], assuming a homogeneous fracture, was used to model reactive transport after emplacement of the cement. Since the small grid size from the flow model led to excessive computational times, the domain was divided into (a) a 1D radial model for the emplacement borehole and a small volume of rock around it, and (b) a 2D model for the rest of the domain. The results from (a) were used as input for (b). First results from reactive transport modeling underestimated the increase in pH observed in the observation and extraction boreholes, indicating a need to further reduce grid size and dispersivity. With this approach, the calculated solute concentrations and pH in the boreholes approximated more closely the measured values.

The model results show dissolution of portlandite and C-S-H in a thin (mm) external layer of the cement (emplacement borehole). In the rock fracture there is dissolution of the primary silicates (except phlogopite) and precipitation of C-S-H, C-A-S-H and calcite. Fracture porosity is reduced in a belt around the 3 boreholes, converging at the extraction borehole (due to the magnitude of the extraction flow rate). The decrease in porosity, due mainly to the precipitation of calcite, is stronger right next to the extraction borehole, due to the more favourable mixing conditions between Grimsel groundwater and cement porewater. The changing water injection rate conditions in the emplacement borehole lead to changes in the flow field and in the position of the mineral reaction fronts.

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Porosity changes during cement-clay interactions and their effect on transport

Shafizadeh, A.[1], Gimmi, T.[1,2], Van Loon, L.[1], Churakov, S.V.[1], Kaestner, A.[3], Lehmann, E.[3], Mäder, U.K.[2]

[1] *Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland*
[2] *University of Bern, RWI, Institute of Geological Sciences, Bern, Switzerland*
[3] *Paul Scherrer Institut, Laboratory for Neutron Scattering and Imaging, Villigen PSI, Switzerland*

Corresponding author: thomas.gimmi@psi.ch

Cement and concrete are important materials in the design of underground disposal sites for nuclear waste. They are designated to reinforce tunnels and drifts as well as to protect and isolate the waste as part of the engineered barrier system. Cement and concrete will come into direct contact with bentonite clay (intended as backfill) or Opalinus Clay (a potential host rock). The geochemical contrast between cement and clay pore waters promotes geochemical reactions that may alter the pore structure of the cement-clay interface. This alteration can lead to modifications of local transport parameters, which then influence further processes considered in the repository's performance assessment. So far, little is known about the exact extent and the time dependence of porosity changes and their feedback on further transport.

Here we report on experimental investigations of such interactions and the quantification of transport across model cement-clay interfaces. Small plugs (5 mm diameter, 5 mm length) of ordinary Portland cement (OPC, 14 years old) and Na montmorillonite (NaM) were brought into contact. Neutron imaging [1] allowed monitoring the development of zones with increasing (OPC) and with decreasing (NaM) porosity over about two years. The diffusion properties at the interface were determined in separate neutron imaging experiments, using D_2O as a tracer. The geochemical reactions led to a clear reduction of the diffusive flux across the interface within several months (Fig. 1), but not to complete clogging. The results will be used to better constrain reactive transport models for predicting the long-term evolution of cement-clay interfaces.
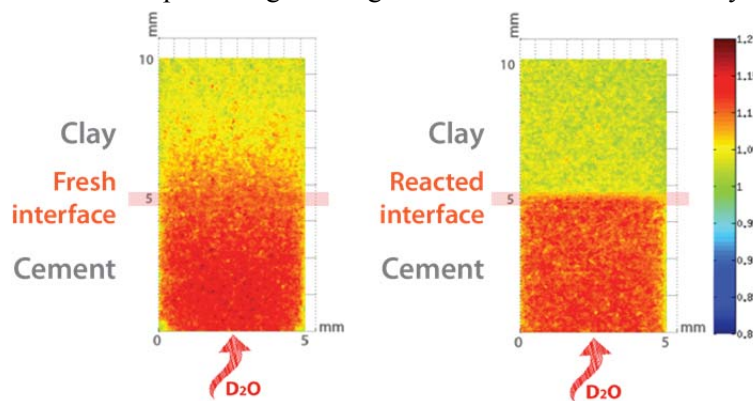
Figure 1: D_2O distribution derived from neutron imaging after diffusion from the cement side across fresh (left) and reacted (right) interface samples. Red indicates high D_2O contents.

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Characterization of the concrete/bentonite interfaces from scale-model column experiments: Significance for upscaling

Torres, E.[1)], Turrero, M.J.[1)], Fernández, R.[2)], Ruiz, A.I.[2)], Cuevas, J.[2)]

[1)] *CIEMAT, Madrid, Spain*
[2)] *UAM, Madrid, Spain*

Corresponding author: elena.torres@ciemat.es

During post-closure and operational phases of a Deep Geological Repository (DGR), unsaturated conditions will prevail throughout the bentonite barrier. Along these stages, concrete and bentonite are expected to be affected by coupled processes such as heating, re-saturation and geochemical processes involving reactions between bentonite and cement pore fluids.

A series of six identical scale-model experiments was planned to simulate the evolution of the concrete degradation processes that occurred in the concrete/bentonite interface through a sequential dismantling and analysis. This paper compiles the results obtained from the characterization of five of the six scale-model tests after 196, 347, 568, 1610 and 2550 days of operation. The experimental setup was designed after the *in situ* FEBEX test and the FEBEX mock-up experiment [1,2]. Both, the experimental design and the duration of the experiments make up an added value to previous work, since they imply a more realistic approach to the conditions expected in a repository during the re-saturation process and to further spatial upscaling interpretation. A 30-mm concrete slab (CEM I SR) was placed over a 70 mm FEBEX compacted bentonite column in a hermetic cylindrical cell, subjected to thermal and hydraulic gradients similar to the ones expected in the repository. After dismantling, concrete and bentonite samples were analysed by means of XRD, FTIR spectroscopy and SEM-EDS. In bentonite sections, chemical analysis for cation exchange capacity and soluble salts were performed.

Sequential dismantling allowed a progressive decalcification and carbonate depletion in the concrete slabs to be observed. Precipitation of Friedel's salt and sulfate-rich phases (ettringite, gypsum) increased with the duration of the tests, mainly inside the pores near the concrete/bentonite interface. In the last test dismantled, ettringite was gradually depleted in favour of gypsum and alumino-ferrite phases, which seems to point to the dissolution of ettringite to yield gypsum and C-(A)-S-H phases.

Mineralogical and physico-chemical changes in bentonite were restricted to few mm from the interface. Precipitation of newly-formed phases, such as calcite or C-(A)-S-H gels, was detected at the interface. Formation of these secondary phases seems to be related to the decrease in BET-SSA and total porosity, which could result in a certain clogging effect on bentonite.

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Reactive transport modelling of an in-situ cement leaching experiment

Wilson, J. C.[1], Watson, C.E.[2], Savage, D.[3], Norris, S.[4]

[1] *Quintessa Ltd., Warrington, United Kingdom*
[2] *Quintessa Ltd., Henley-on-Thames, United Kingdom*
[3] *Savage Earth Associates Ltd., Bournemouth, United Kingdom*
[4] *Radioactive Waste Management Limited, Harwell, United Kingdom*

Corresponding author: jameswilson@quintessa.org

As part of the international Long-term Cement Studies (LCS) project, modelling of an *in-situ* experiment at the Grimsel underground laboratory has been undertaken. In the experiment, a pre-hardened (Portland) cement source was inserted into a borehole drilled into granitic rock, which intersects a fracture. Two other boreholes were drilled to intersect the same fracture, at distances of approximately 0.5 and 1 m from the emplacement borehole. Fully-coupled reactive transport models have been developed to simulate the leaching of the cement source to create a high pH plume in the fracture. Modelling of the experiment was undertaken at the same time as the experiment was being conducted, thereby providing 'blind' predictions of cement-groundwater interaction.

A 2D model including where the borehole and fracture intersects was constructed using a circular geometry. A number of model cases were developed to explore the implications of variation in model assumptions and input parameters, in particular: model discretisation, the presence/absence of a gap between cement and rock, the inclusion/exclusion of alkalis leached from the cement; and flow geometry. The models predict leaching of Portlandite and C-S-H gel in particular, with the formation of gismondine (a representative zeolite mineral, which may be considered a proxy for C-A-S-H, Figure 1). Different model assumptions, in particular the approach taken to discretisation and the presence or absence of a gap next to the emplaced cement, resulted in some variation in the spatial (1 - 3 mm) and temporal (1 – 3 years) extent of cement leaching and alteration.
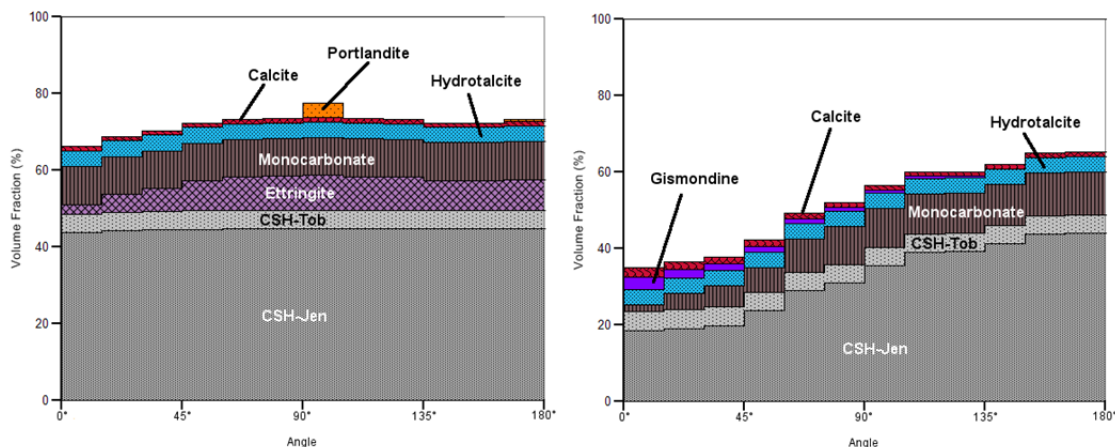
Figure 1: Volume fraction plots for outer 1 mm of cement in the base case simulation after 0.5 years (left) and 5 years (right). The plots are 'folded out' sections of the cylindrical grid; the angle is measured from high to low head across the fracture.

Reactive transport models of long-term cement degradation processes in a radioactive waste disposal system

Wilson, J.C.[1], Benbow, S.[2], Metcalfe, R.[2]

[1] *Quintessa Ltd., Warrington, United Kingdom*
[2] *Quintessa Ltd., Henley-on-Thames, United Kingdom*

Corresponding author: jameswilson@quintessa.org

The current candidate backfill material for use in intermediate-level waste vaults in a UK Geological Disposal Facility (GDF) in a higher-strength rock is the cement-based NRVB that was developed in the 1990s. A large body of work on NRVB has been undertaken concerning both the properties of freshly-cured material and its leaching characteristics. More recently, studies have considered the potential for different modes of cement alteration to occur depending on groundwater chemistry. In particular, 1-D reactive-transport models have been constructed to simulate a block of cement (1 m thick) that is in contact with different illustrative groundwater compositions using the Quintessa software 'CABARET'. The models include the following processes: mineral dissolution-precipitation reactions (kinetic treatment); aqueous speciation; diffusive and advective solute transport; and porosity evolution. A number of illustrative groundwaters were considered in models of NRVB evolution to represent possible UK-relevant geological environments, including: a reference Higher Strength Rock (HSR) groundwater, an alternative 'dilute' HSR water composition, an HSR 'brine' composition and a Low Strength Sedimentary Rock (LSSR) (claystone) porewater. A number of variant cases were produced to explore the effect of model assumptions and uncertainties on the calculated evolution.

The results show a range of potential cement alteration pathways, depending upon groundwater composition. In lower ionic-strength groundwaters, leaching and carbonation predominate along with the formation of Mg-rich minerals (Figure 1); whereas water compositions with higher chloride and sulphate concentrations resulted in external sulphate attack (ettringite and thaumasite formation), magnesium attack and chloride attack (Friedel's salt formation). The different types of cement alteration have different implications for the evolution of cement porewater pH. For example, Friedel's salt formation resulted in a pH increase (up to ~13), whereas magnesium attack resulting in brucite or Mg-rich silicate mineral precipitation results in a pH decrease to ~9.5-10.
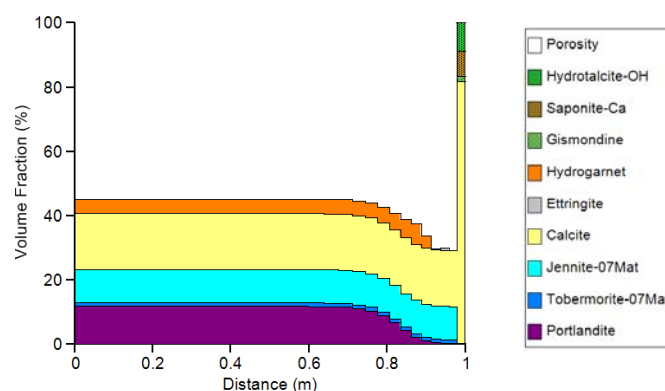
Figure 1: Volume fraction plot for reactive transport simulation of NRVB reacting with an illustrative 'dilute' HSR groundwater after 531 years (x-axis shows distance from the inside edge of a 1 m thick backfill at 0 m, to the outer edge of cement in contact with groundwater at 1 m).

Analytical estimation on alkaline alteration of bedrock wall

<u>Yamamoto, T.</u>, Oyama, T.

Central Research Institute of Electric Power Industry, Chiba-ken, Japan

Corresponding author: t-yama@criepi.denken.or.jp

Chemical properties of bedrock exposed to concrete were slightly changed during five years contact. The void water of bedrock in 20 cm depth from the concrete contacted surface showed diffusion effects of Ca from concrete with raising pH up to about 10. There was a large difference in pH and the concentration of alkaline ions between the pore water of concrete and void water of bedrock. The former showed much higher pH and higher concentrations of alkaline ions. Though the diffusion of alkaline ions occurred, the consumption of OH$^-$ is the factor causing raising pH, which occurred at the concrete contacted surface area of the bedrock with forming calcium silicate compounds at the surface of volcanic glass in the bedrock. During the formation of C-S-H products in the pore space of the bedrock, the porosity was reduced. There are needs to estimate the stability of secondary products, i.e. C-S-H, and the mechanical property of altered bed rock for the long-term evaluation of the natural barrier at the radioactive waste disposal site.

a) Backscattered electron image (BEI)

b) Ca concentration at same area as BEI data
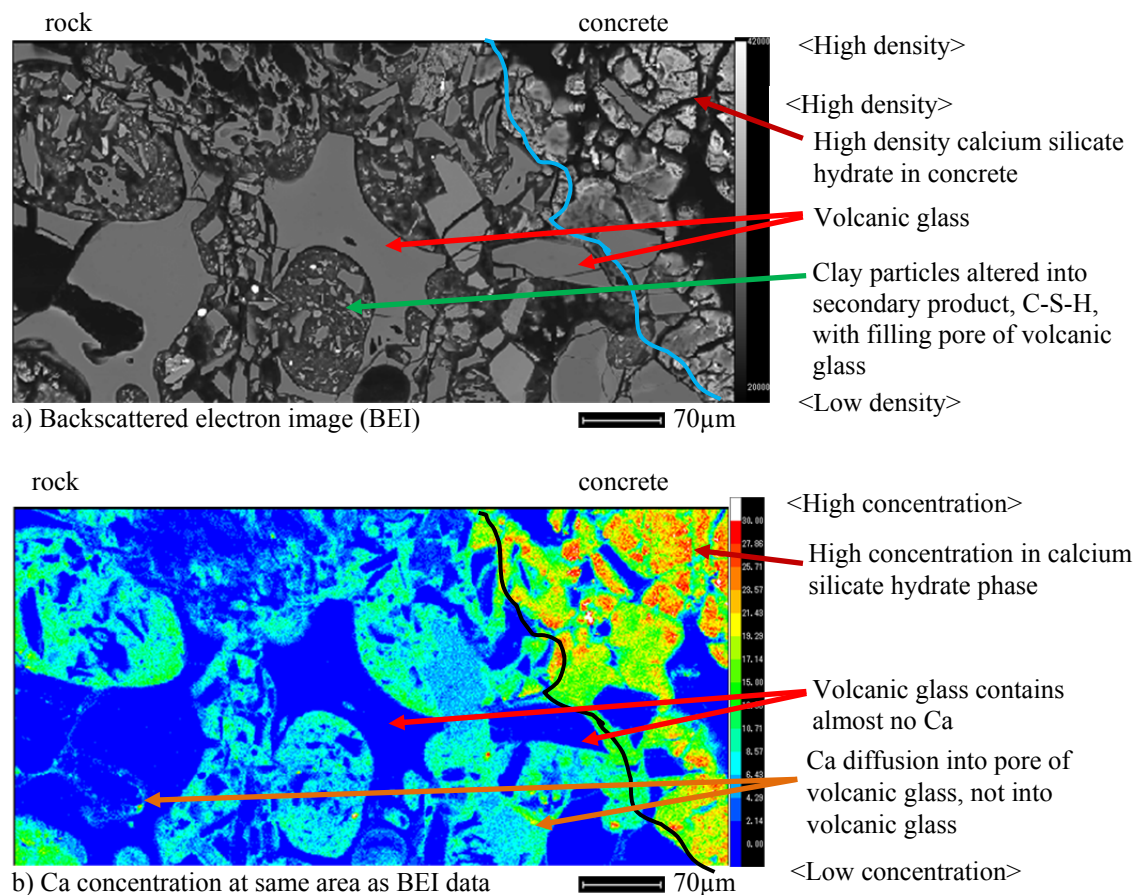
Figure 1: Morphological observation and Ca concentration distribution at interaction surface.

Topic 3: Interaction of Cement with Waste Constituents

Influence of gamma radiations on cement hydrates

Acher, L.[1], Haas, J.[1], Dannoux-Papin, A.[1], Frizon, F.[1], Dunstetter, F.[2],
De Noirfontaine, M-A.[2]

[1] *CEA, DEN/DTCD/SPDE/LP2C, Bagnols-sur-Cèze, France*
[2] *CNRS UMR 7642-CEA-Ecole Polytechnique, Laboratoire des Solides Irradiés, Palaiseau, France*

Corresponding author: loren.acher@cea.fr

Water radiolysis is one of the consequences of the interaction between cement and low and intermediate level nuclear waste. It leads to production of radiolysis gases such as dihydrogen, flammable. So, it is essential to quantify and minimize the H_2 production induced by radiation. Based on previous studies on the behaviour of cements and concretes placed under γ-radiation, it is assumed that water radiolysis mostly occurs in pore solution [1]. However the influence of structural water (ie OH^- in case of $Ca(OH)_2$) and crystallization molecular water (i.e. H_2O in case of $CaSO_4 \cdot 2H_2O$) on H_2 radiolytic yield is not yet well understood.

The aim of this work is to uncouple the role of each hydrate on radiolytic gas production under γ-radiation, without transport limitation relative to cement based materials. Hydrates were first synthesized from the experimental protocol detailed by Matschei [2] and stored at different relative humidity. Their purity and hydration state were respectively determined by XRD and TGA. Since the moisture equilibrium was reached, the samples were sealed under argon in ampoules and placed under γ-irradiations with a dose rate of 600 Gy/h up to 1MGy. The stability of hydrates after irradiation was checked by TGA and XRD. Radiolytic gas products were also analyzed and quantified by GC.
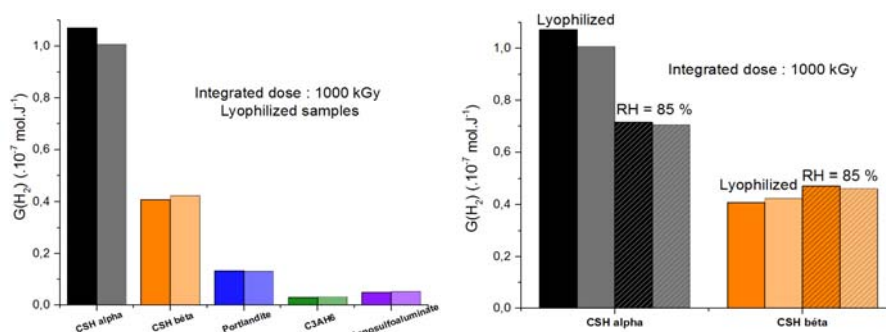
Figure 1: G(H₂) values obtained for different cement hydrates at 1000 kGy.

The radiolytic yield in H_2, $G(H_2)$ expressed as mol J^{-1}, represents the amount of H_2 produced per energy unit deposited in the system. Gas measurements show that the nature of the hydrate and the storage humidity play an important role on the gas production, hence $G(H_2)$ values (Figure 1). Experiments are still in progress to determine the contribution of bound water to gas production.

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Interaction of radionuclides with C-S-H phases in the presence of organic additives

Androniuk, I.[1)], Landesman, C.[1)], Kalinichev, A.G.[1)], Henocq, P.[2)]

[1)] *Laboratoire Subatech (UMR 6457), Ecole des Mines de Nantes, Nantes, France.*
[2)] *Andra, Châtenay-Malabry, France.*

Corresponding author: iuliia.androniuk@subatech.in2p3.fr

Cementitious materials are extensively used in the design and construction of radioactive waste repositories. Organic additives are a specific component of concrete improving its strength, resistance, durability, workability, etc. Even though the amount of such admixtures is small (0.1-2.0% wt.), the residual presence of organics in the pore water can influence the radionuclide mobility through complexation and competition for sorption sites at the surface of cement hydrates. Quantitative and qualitative understanding of the molecular mechanisms controlling such interactions is the primary objective of this study.

This study is performed on Calcium Silicate Hydrates (C-S-H) as model of the cementitious matrix. The investigated system has three components: (i) synthetic pure C-S-H phases with different Ca/Si ratios (0.83, 1.0, 1.4); (ii) gluconate as a simple well-understood model of organic additive stable in highly alkaline solutions; (iii) U(VI) as radionuclide of interest. Previous studies were focused mostly on the influence of admixtures on hydration processes [1-2], while much less efforts were made to understand their postproduction effects for radioactive waste storage applications [3-5]. Data on binary systems (C-S-H/gluconate, HCP/gluconate [4], C-S-H/U(VI) [6]) can provide basis for the study of complex ternary system (C-S-H/gluconate/U(VI)). In this work, experimental data on sorption and desorption kinetics and isotherms for gluconate and U(VI) on C-S-H in a relevant range of Ca/Si ratios were collected. There is a noticeable effect of Ca/Si ratio on the gluconate sorption on C-S-H, with stronger sorption at higher Ca/Si ratios. Gluconate labelled with ^{14}C was used in order to improve the sensitivity of analytical detection techniques (LSC) at particularly low concentrations (10^{-8} - 10^{-5} mol/l).

In parallel, atomistic models for C-S-H surfaces and interfaces are developed for classical molecular dynamics (MD) simulations. Following the previously developed approaches [7], unconstrained MD simulations are performed to determine the differences in the solution structure and dynamics as a function of composition in the bulk phase and at the C-S-H surface. Constrained MD simulations for selected cases are being performed to determine the adsorption free energy profiles via the potential of mean force calculations and to estimate the complexation constants. In close coordination with experimental work, the modelling efforts are characterising the same binary systems and are further expanded to the ternary system. Gluconate is a good starting model for the investigation of molecular mechanisms of cement-organic-radionuclide interactions. More complex systems involving model polycarboxylate superplasticiser (PCE) will be studied at the next step.

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The effect of gamma irradiation on crystalline and non-crystalline geopolymer matrices

Arbel-Haddad, M.[1], Bar-Nes, G.[1], Borojovich, J.C.E.[1], Lambertin, D.[2], Dannoux-Papin, A.[2], Frizon, F.[2]

[1] *NRCN, Beer-Sheva, Israel*
[2] *CEA, DEN/DTCD/SPDE, Laboratoire de Physico-Chimie des Matériaux Cimentaire, Bagnols-sur-Cèze, France*

Corresponding author: arbel.haddad@gmail.com

Geopolymers are relatively new materials considered to be possible candidates for radioactive waste immobilization due to the combination of metal binding properties with chemical stability and improved mechanical properties. These materials are prepared by alkaline activation of alumino-silicate materials, either natural materials such as clays, or industrials by-products such as coal fly ash or slag. The effect of ionizing radiation on the stability and the performance of these matrices have scarcely been reported. Recent publications showed that gamma-ray irradiation induces a densification of the material due to microstructural modifications in geopolymer and improves the mechanical strength [2-3].

In this study we compared the influence of gamma irradiation on metakaolin based geopolymers of different compositions: either high-silica content, resulting in an amorphous microstructure or low-silica content yielding a partially crystalline product. Sodium nitrate which is a major component in many nuclear waste streams was introduced into the geopolymeric mix in order to assess the influence of the immobilized waste on both structure and radiation stability of these materials. The various samples were irradiated (^{60}Co source, 5 MGy) for 6 months under inert conditions.

XRD measurement with PDF (Pair distribution function) analyses show some increase in the crystallinity due to the addition of sodium nitrate for the low silica formulation. However no clear evidence of structural changes due to irradiation was found for all four formulations.

FTIR data reveal that the nitrate ions have undergone partial radiolysis to yield nitrite ions. Leaching tests were performed to the nitrate bearing geopolymers, according to the ANSI/ANS-16.1-1986 procedure [3]. While the retention of nitrite and nitrate ions by the high-silica amorphous geopolymer was poor, the low-silica crystalline formulation retained the same ions with higher efficiency. The mechanism of this preferential retention will be discussed in the present paper.

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Modelling of cementitious backfill interactions with vitrified ILW

Baston, G.M.N, Heath, T.G., Hunter, F.M.I.

Amec Foster Wheeler, Harwell Campus, Didcot, United Kingdom

Corresponding author: tim.heath@amec.com

New types of wasteform and waste package are being considered for the geological disposal of intermediate-level waste (ILW) in the UK. This includes vitrified ILW. For disposal of such ILW in a geological disposal facility (GDF), a range of concepts are under consideration, including options with a high-pH cementitious backfill such as the Nirex Reference Vault Backfill (NRVB) or disposal in areas that may be backfilled with a cement-based backfill that buffers to a lower pH (typically <11). To assess the suitability of these potential new wasteforms for disposal, it is necessary to understand their impacts on the long-term evolution of the backfill. A detailed thermodynamic modelling study was undertaken, using data selected from the PSI/Nagra and CEMDATA databases to help understand the effects of these wastes and their potential impacts on the performance of the backfill. This included the ability of the backfill to maintain alkaline conditions, and consideration of the potential impacts on the sorption capacity, porosity, and gas permeability.
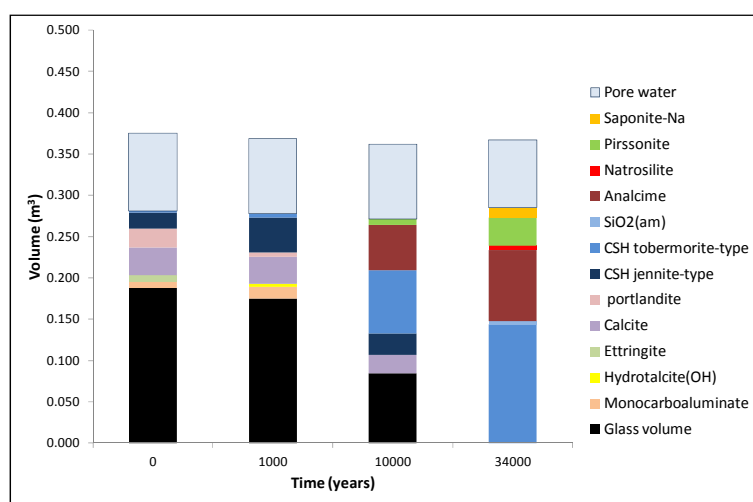
Figure 1: Predicted changes in backfill mineralogy due to clinoptilolite glass interaction with NRVB within a closed system.

Significant model findings for vitrified ILW interactions with the backfill include its effect on pH buffering. The buffering capacity at pH ~12.5 is predicted to decrease, but the pH buffering capacity at lower pH values increases, due to incorporation of silicon from the glass into C-S-H phases of low calcium-silicon ratio. The sorption capacity safety function of the backfill is unlikely to be impaired by interactions with vitrified ILW. Indeed it may be increased, due to the additional C-S-H phase formation.

Reactions of iron floc wastes when encapsulated using a blend of fly ash and cement

Blackham, R.[2], Cann, G.[1], Caruthers, K.[1], Dixon H.[1], Godfrey, I. H.[1], Gravett, C.[1], Harris, R.[1], Stothers, J.[2]

[1] *National Nuclear Laboratory, Workington, United Kingdom*
[2] *Sellafield Limited, Sellafield, United Kingdom*

Corresponding author: hugh.godfrey@nnl.co.uk

At the Sellafield Site in the UK actinide containing liquid effluent is treated by co-precipitating the active species with iron to produce an iron floc. After concentration by ultrafiltration the iron floc is encapsulated in 500 L drums using an in-drum-mixing process. This process involves pre-treating the waste with calcium hydroxide, then encapsulating the waste using a PFA/CEM I blend, and finally capping again using a PFA/CEM I grout. This process has been used successfully for over twenty years generating many thousands of drums of encapsulated waste.

During the initial development work poor wasteform stability was encountered and this was overcome by pre-treating the iron floc with calcium hydroxide before encapsulation. The proposed cause of this instability was given as being due to the reaction between the iron in the floc and the calcium in the cement forming a calcium ferrite phase, which resulted in shrinkage. It was thought that the pre-treatment with calcium hydroxide caused this reaction to occur before encapsulation. Acceptable formulation envelopes, waste loadings, and plant operating parameters, etc. were subsequently developed using trials which demonstrated that providing that the process was operated within the limits of these trials acceptable products would be generated. Changes to these limits were supported by additional encapsulation trials. However, whilst this approach has been successful to date, due to upstream changes in processes the feeds to the waste stream will become much more variable in the future. This means that better understanding of the chemistry of the interaction of the floc with the cement is required to minimise the need for trial work that requires the manufacture of expensive simulants.

This paper describes the literature that has been reviewed to develop a better understating of how the iron reacts with the cement during pre-treatment and subsequent encapsulation, and a new model for the reaction of the iron floc with the calcium hydroxide and subsequently the cement generated. This model proposes that without the addition of extra calcium in the pre-treatment reaction the iron removes calcium from the cement system meaning that there is insufficient calcium remaining to produce enough C-S-H to form a quality wasteform. It also suggests that pre-treatment is not necessary and all that is required is that sufficient calcium is present from both the cement powders and the calcium hydroxide to form enough C-S-H. Hence rather than wait for the pre-treatment reaction to occur the calcium hydroxide can be added with the cement powders. Subsequently small-scale inactive trials were carried out to confirm the proposed model. Some of these results are presented and these include XRD, TGA, and SEM analyses as well as strength development and dimensional stability measurements over ninety days.

The understanding developed in this work has allowed the current waste treatment process to be optimised and in the future will increase the flexibility of the encapsulation process allowing it to be more responsive to changes in the waste feed that currently could not be achieved without extensive trial work.

Redox chemistry and solubility of uranium in alkaline to hyperalkaline NaCl/KCl systems

Cevirim, N., Yalcintas, E., Gaona, X., Altmaier, M., Geckeis, H.

Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Karlsruhe, Germany

Corresponding author: nese.cevirim@kit.edu

For the long-term performance assessment of nuclear waste repositories, the prediction of the possible mobilization of radionuclides from the repository to the biosphere is of high importance. Uranium is the main element in the nuclear fuel cycle and, consequently, contributes with the largest inventory to the radioactive waste. U(VI) is the most stable oxidation state of uranium under anoxic and oxidising conditions, whereas U(IV) prevails in strongly reducing environments. U(VI) shows an amphoteric behaviour and precipitates as $UO_3 \cdot H_2O(cr)$ 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. Na, K and Ca are abundant cations in different types of groundwaters, but can also be found in relatively high concentrations in cementitious systems as those considered for the stabilization of radioactive waste and for construction purposes in deep underground repositories. Although the pH-independent chemical reaction $UO_2(am,hyd) + 2\,H_2O(l) \Leftrightarrow U(OH)_4(aq)$ is expected to control the solubility of uranium under hyperalkaline reducing conditions, the known stabilization of higher oxidation states provided by high [OH^-] and the recent description of $U(OH)_5^-$ and $U(OH)_6^{2-}$ at pH > 12 [1] pose relevant uncertainties deserving dedicated experimental efforts. In contrast to Ca- and Na-uranates, little is known on the solubility of K–U(VI)–OH phases expectedly controlling the solubility of U(VI) in the early stages of cement degradation. All experiments were performed in Ar gloveboxes at T = 22 ± 2 °C. The redox chemistry of uranium was investigated in 0.1 M NaCl–NaOH and 0.1 M KCl–KOH solutions with 8 ≤ pH_m ≤ 12.8. Strongly reducing conditions (pH + 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), Sn(II) + Fe_3O_4, Sn(II) + TiO_2) reducing systems. Uranium concentration, pH_m and E_h values were monitored at regular time intervals and systematized on Pourbaix diagrams calculated using thermodynamic data reported elsewhere [2-4]. XPS was used to determine the oxidation state of uranium in the solid phase. The reduction of U(VI) to U(IV) is affected by strong kinetics, although a pH-independent solubility behaviour is confirmed in all systems in the long-term. These observations are in good agreement thermodynamic calculations, and thus disregard the formation of anionic U(IV) hydrolysis species within the investigated pH_m conditions. The solubility of $K_2U_2O_7 \cdot xH_2O(s)$ was investigated in 0.1–4.0 M KCl–KOH solutions with 8 ≤ pH_m ≤ 14.5. Uranium concentration and pH_m values were monitored at regular time intervals until attaining thermodynamic equilibrium. Experimental solubility data show a pH-independent behaviour up to pH_m ≈ 10, whereas an increase of the solubility with a well-defined slope of +1 (log [U] *vs.* pH_m) is observed at pH_m ≥ 10. The combination of solid phase characterisation and slope analysis clearly indicate the predominance of $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$ in the aqueous phase, respectively. Preliminary thermodynamic and activity models (SIT, Pitzer) for the system UO_2^{2+}–H^+–K^+–OH^-–Cl^-–$H_2O(l)$ are derived based on the proposed chemical model and the newly generated experimental solubility data.

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Chemical behavior of nuclear waste glass in contact with hardened OPC paste in a mock-up test: Characterization of the glass-cement interface

Ferrand, K.[1], Mercado, S.[2], Angeli, F.[3], Liu, S.[1], Elia, A.[1], Lemmens, K.[1]

[1] *Belgian Nuclear Research Institute, Mol, Belgium*
[2] *CRITT Matériaux Alsace, Schiltigheim, France*
[3] *CEA, DTCD/SECM/LCLT, Bagnols-sur-Cèze, France*

Corresponding authors: kferrand@sckcen.be, klemmens@sckcen.be

The current Belgian reference design for geological disposal of vitrified High-Level Waste (HLW) and Spent Fuel foresees the use of *Supercontainers*. In this design, the canisters with the waste form will be enclosed by a 30 mm thick carbon steel overpack and an ordinary Portland cement (OPC) buffer. This design will thus provide a highly alkaline chemical environment. To evaluate the stability of the waste forms in such an environment, a research programme was started at the Belgian Nuclear Research Centre (SCK•CEN). Most studies on vitrified HLW were parametric, and allow the determination of the various processes involved and the proposal of a mechanistic glass dissolution model [1-2]. Apart from this, experiments were done to validate the model in more realistic conditions. For this purpose, mock-up test cells were filled with a layer of glass powder, in contact with a plug of hardened OPC paste (Figure 1), and saturated with a synthetic young cement water at pH 13.5 (room temperature). The set-up allowed for monitoring the solution concentrations and pH as a function of time and space, to follow glass dissolution and diffusion of species. At the end of the experiment, the cells were dismantled to study the glass-concrete interface by SEM-EDX analyses. The results of this characterization are presented and discussed.
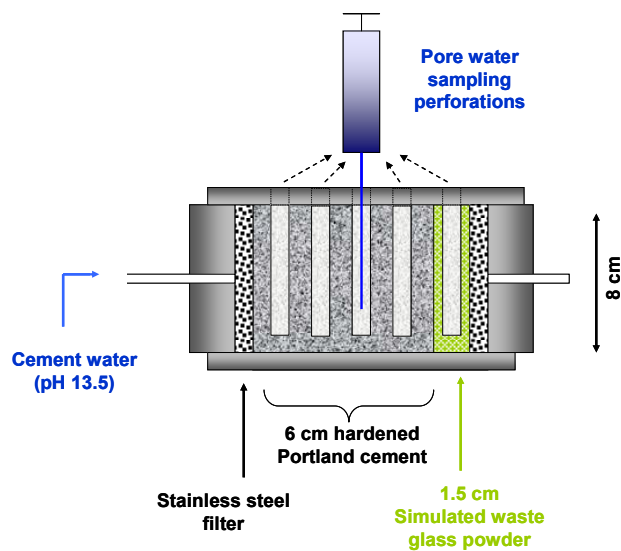
Figure 1: Cross section of mock-up cell.

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Solubility and sorption of beryllium in cementitious systems

Gaona, X., Böttle, M., Rabung, Th., Altmaier, M.

Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Karlsruhe, Germany

Corresponding author: xavier.gaona@kit.edu

Beryllium is a chemotoxic element expected in certain waste forms to be disposed of in repositories for radioactive waste disposal. The amphoteric behaviour of Be is widely accepted in the literature [1-2], 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 conditions is very scarce [3-4]. In spite of the lack of dedicated studies assessing the uptake of Be by cementitious materials, a weaker sorption is conservatively predicted based on the formation of negatively charged species in the aqueous phase [5]. In the context of the EU collaborative project on Cement Based Materials (CEBAMA; www.cebama.eu), one of the research activities on-going at KIT–INE focuses on the aquatic chemistry of Be under alkaline to hyperalkaline conditions. In a second stage of the project, the uptake of Be by cement and C–S–H phases with different Ca:Si ratios will be also investigated. The main objectives are the development of comprehensive thermodynamic and activity models for the system $Be^{2+}–Na^+–K^+–Ca^{2+}–H^+–Cl^-–OH^-–H_2O(l)$, the determination of robust solubility upper limits for source term estimations and, further, the quantitative assessment of the uptake of Be by cementitious materials.

Solubility experiments with $Be(OH)_2(s)$ are performed from undersaturation conditions in Ar-gloveboxes at T = 22°C in dilute to concentrated NaCl, KCl and $CaCl_2$ solutions (I $\leq$ 3.0 M). Experiments focussed on the pH_m range 10–14 (with $pH_m = -\log_{10} m_{H^+}$), although complementary experiments were conducted under acidic conditions to properly characterize $\log_{10} *K°_{s,0}\{Be(OH)_2(s)\}$. Total concentration of Be in the aqueous phase is quantified by ICP–MS after ultrafiltration with 10 kD filters. Solid phases in selected solubility experiments are characterized by XRD, SEM–EDS, XPS and quantitative chemical analysis after attaining thermodynamic equilibrium, which is assumed after obtaining constant pH_m and m_{Be} measurements. The Specific Ion Interaction Theory (SIT) is considered to account for ion interaction processes. Preliminary results on the solubility and aqueous speciation of Be under hyperalkaline conditions will be presented and discussed.

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The potential role of superplasticizers on radionuclides mobilization

García, D.[1,2], Grivé, M.[1], Duro, L.[1], Brassinnes, S.[3], De Pablo, J.[2]

[1] *Amphos21 Consulting S.L, Barcelona, Spain*
[2] *CTM Centre Tecnològic, Manresa, Spain*
[3] *Belgian Agency for Radioactive Waste and Enriched Fissile materials (ONDRAF/NIRAS), Brussels, Belgium*

Corresponding author: david.garcia@amphos21.com

Polymeric superplasticizers (SPs) are a type of organic chemical admixtures used by manufacturers to improve concrete workability. Their main effect is to reduce the volume of water required to add to the system [1]. Organic substances may influence the behaviour of radionuclides [2, 3], so that the understanding on the nature and strength of the interactions between radionuclides and organic admixtures present in the concrete formulations deserves devoted studies. This work aims at investigating to which extent the presence of SPs affects radionuclide behaviour in concrete environments.

The effect of a polycarboxylic ether (PCE) based SP (i.e. glenium® 27) on the mobility of Ni and U has been investigated in this work through solubility and sorption studies. Solubility experiments were performed in different media (concrete synthetic porewater without SPs, concrete synthetic porewater containing glenium® 27, leachates of concrete samples without SPs, leachates of concrete samples containing glenium® 27). Sorption studies presented here were performed with cementitious materials such as concrete and hardened cement paste (HCP) with and without SPs. All experiments (solubility and sorption) were run under $N_2(g)$ atmosphere. At given time intervals, aliquots of the samples were collected and filtered through 0.45 μm Nylon filters, acidified and analysed for Ni and U concentration in the liquid phase by ICP-MS. Solid phases were analysed by XRD and SEM-EDX (Figure 1).
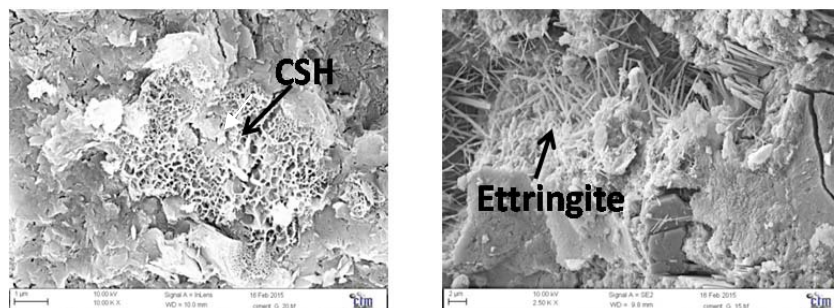
Figure 1: SEM images obtained from HCP. Flaky-fibre CSH could be identified in the left image and ettringite needles in the right image.

By and large, our results indicate that the level of SPs dosage commonly used in cement formulations (TOC ~ $5.5 \cdot 10^{-5}$ mol·l^{-1}) is too low to noticeably affect the retention behaviour of a trace radionuclide like Ni or U. Nevertheless, increased "free" SPs concentrations, up to 10^{-3} mol·l^{-1} may cause an important enhancement of the solubility of Ni at hyperalkaline conditions.

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Porosity and leaching chemistry of cementitious (cast stone) materials containing high-salt wastestreams

Garrabrants, A. C., Branch, J. L., DeLapp, R. C., Brown, K. G., Kosson, D. S.

Vanderbilt University, Nashville, USA

Corresponding author: a.garrabrants@vanderbilt.edu

Cementitious materials used in traditional industrial waste management are often selected due to their low cost of materials relative to their ability to either fix constituents of potential concern (COPCs) within a solid mineral structure, or to retain COPCs in a discontinuous porous matrix. However, traditional solidification/stabilization (S/S) designs are not optimal if wastestreams contain high levels of soluble salts, such as the secondary wastes from disposal of low-activity waste at United States Department of Energy (US DOE) sites. For these wastes, the preferred cementitious mixes, referred to as "cast stone" materials (CSMs) are based on a binder with high slag cement and coal combustion fly ash content (e.g., 46 wt.% each) with little Portland cement (8 wt%). Basic characterization of CSMs indicate pore structure, chemical and physical properties, and leaching behaviour unlike other S/S materials or commercial mortars.

Microconcrete with fly ash   Cast stone
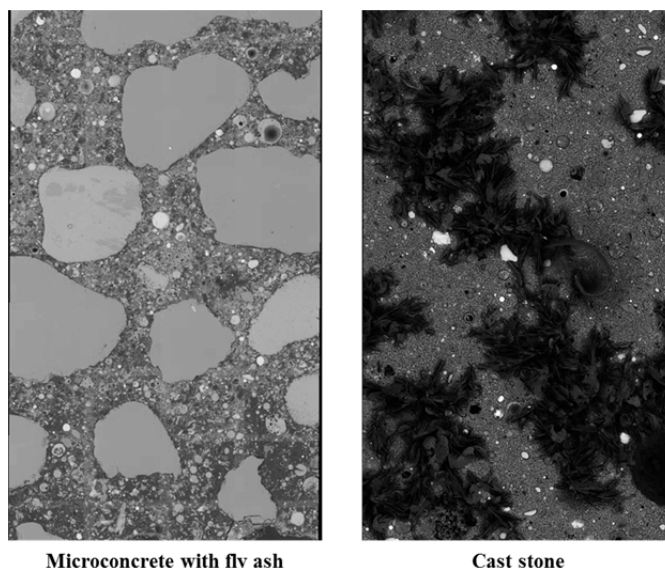
Figure 1: Comparison of SEM images (1 mm x 1.6 mm) showing structure of commercial microconcrete (left) and high-salt loading cast stone (right).

This presentation provides an overview of studies focusing on determining the properties of CSMs with regard to microstructure, moisture retention and leaching behaviour. Release of COPCs was evaluated following the Leaching Environmental Assessment Framework (LEAF; Kosson et al., 2012) using US Environmental Protection Agency (US EPA) leaching tests analogous to Comité Européen de Normalisation (CEN) methods. Batch leaching tests were used to measure liquid-solid partitioning of COPCs relative to the release-controlling factors of pH and liquid-solid ratio in the test environment. The relationship between relative humidity (RH) and pore saturation was estimated via gravimetric experiments under controlled RH conditions. Image analysis from scanning electron microscopy was used to estimate porosity and to provide insight on waste/cement interactions. Throughout, the porosity of the CSMs was an overarching parameter that significantly influences the environmental behaviour of these materials. Approaches for estimating the porosity CSMs, where "veins" of soluble salts may be solubilized by water contact, will be reviewed.

Radium mobility under alkaline conditions in low-level long-lived radioactive waste disposal

Grandia, F.[1], Missana, T.[2], Olmeda, J.[1], García-Gutiérrez, M.[2], Colàs, E.[1], Grivé, M.[1]

[1] *Amphos21 Consulting S.L., Barcelona, Spain*
[2] *CIEMAT, Department of Environment, Madrid, Spain*

Corresponding author: mireia.grive@amphos21.com

Andra is developing concepts and methodologies for a large variety of radioactive wastes including those with "very-low-level" and "low-level, long-lived" residues. Among them, radium-bearing waste from industrial activities is of high relevance, due to its substantial volume and potential environmental risk. The repository solution of radium-bearing waste must ensure the safety and radiation protection of the staff working on the site, of neighbouring population and of the environment. Radium-bearing residues are long-lived (the half-life of ^{226}Ra is 1600 years) and require specific long-term management solutions to prevent any migration or transfer of radioactive substances and to protect the environment against contamination risks. The waste units are designed to be protected by cementitious backfill. The mobility of radium under alkaline conditions will be highly dependent on the stability of Ra-barite, which is the main primary radium solid source term, and, in the case of its dissolution, on Ra sorption on cementitious materials. The work presented here combines experimental studies in laboratory and supporting numerical modelling for the sake of the prediction of the long-term stability of radium in the repository facilities. From the solubility and sorption data obtained in the devoted experiments, numerical simulations of radium solubility will be performed to explain the experimental data by using ThermoChimie (v.9) as thermodynamic database [1].

This work shows a set of experiments that have been developed to quantify (1) the stability of Ra-barite under cementitious conditions, and (2) the sorption of Ra on cementitious phases. Both Ra-barite and cement have been synthesized and characterized before each experiment. The final Ra/Ba ratio was 2×10^{-7}, in the range of the Ra-barite wastes. Stability experiments have been conducted with both barite and Ra-barite samples in order to compare Ra and Ba behaviour. Cement samples (CEM V) with a water-cement ratio of 0.4 were cured during 28 days, and were subsequently ground and sieved with a size < 63 µm. 10 g of the powder material were contacted with 1 L of degassed Milli-Q water to obtain the water in equilibrium with cement to be used in sorption tests.

Experimental results indicate that Ra sorption in both fresh and degraded CEM V materials is linear in the concentration ranges studied ([Ra] from 10^{-10} to 10^{-8} M). Non-significant influence of the solid/liquid ratio is observed (in the range 5 to 50 g/L). Mean log K_d (ml/g) values are in the range of 2 to 3. In general, it can be observed that adsorption on the degraded material is higher than on the fresh one. Sorption of Ba shows similar behaviour as Ra.

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Corrosion assessments of reactive metallic waste in grouted packages and effect on ILW containers

Hayes, M.[1], Palethorpe, J.S.[2], Anderson, W.D.[2], Jackson, J.M.[3]

[1] *National Nuclear Laboratory, Warrington, United Kingdom*
[2] *National Nuclear Laboratory, Workington, United Kingdom*
[3] *National Nuclear Laboratory, Preston, United Kingdom*

Corresponding author: martin.hayes@nnl.co.uk

In the UK the most common treatment process for intermediate level Waste (ILW) is to encapsulate it in a cementitious matrix. Unfortunately many cemented wasteforms still contain chemically reactive metals such as uranium, Magnox and aluminium that will undergo corrosion within the cement matrix. These reactions result in the release of gas (notably hydrogen) and a corrosion product that is more voluminous than the parent metal, with the possible consequence that the cement matrix becomes stressed and may ultimately crack, with the transfer of expansive forces to the ILW container, which may cause deformation of the package over time. As a result, the paper describes a series of corrosion assessments in which experimentally derived corrosion rates for reactive metals in the environments covering the key phases of waste storage have been used to predict the degree of corrosion in grouted waste packages over the timescales of interim storage and operational phase of a Geological Disposal Facility. In addition, the paper also details preliminary studies to directly measure the expansive forces generated from uranium corrosion in relation to the amount corroded. The paper describes how the results can inform finite element modelling studies of the waste package in order to predict waste loadings that can be safely packaged over prolonged timescales and also inform strategies regarding wasteform management.

A sorption model for radionuclides in cement-based materials – correlations with solubility and electrokinetic properties

Henocq, P.

Andra, Châtenay-Malabry, France.

Corresponding author: pierre.henocq@andra.fr

Cement-based materials such as concrete will be highly used in the context of Intermediate Level Long Lived Waste (IL-LLW) disposal in a deep geological repository. Concrete represents the first barrier against the migration to the far field. Interactions between the radionuclides and the cementitious matrix are therefore required and basically defined using distribution ratios (R_d). As the cementitious materials are not thermodynamically stable in contact with the host-rock, the retention properties of the radionuclides are generally determined for four degradation states according to the pH evolution in the cementitious pore water as follows: (i) state I (12.5<pH<13.5), (ii) state 2 (pH=12.5), (iii) state 3 (10<pH<12.5), and (iv) state 4 (pH<10).

The R_d approach is limited to specific conditions and the effect of perturbations cannot be predicted. A mechanistic approach is then considered for identifying the mechanisms taking place and for reducing the uncertainties on the retention parameters. The surface complexation model is a well-developed concept to describe the sorption process [1-3]. Specially, C-S-H and their surface properties (surface complexation constants) were mainly assessed from zeta potential measurements in various salt and pH conditions [4,5]. Nevertheless, the large number of experimental parameters can lead to different interpretations and sorption models. Consequently, this paper presents a surface complexation model, based on the CD-Music method in PHREEQC v3.2.2, for interpreting zeta potential measurements, coupled with sorption measurements. The methodology takes into account updated thermodynamic data recently obtained on C-S-H as well as advanced measurements of their specific surface area. The objective is a mechanistic description of the radionuclide sorption on C-S-H in correlation with their solubility, electrokinetic and specific surface area properties.

This approach is applied to interpret experimental data on radionuclides of interest on C-S-H and cement pastes in relation with the degradation states. Simulations to predict R_d values in specific conditions are performed to complete the lack of knowledge on some radionuclides. In addition, this sorption model is applied for determining the porewater/mineral equilibrium of various cement-based materials for a global characterization of the cementitious system i.e. species in solution, adsorbed species and precipitated species. In particular, that leads to assess the role of the species coming from cement and their competitive effect regarding the radionuclide retention. Further works will investigate the impact of perturbations related to specific radwastes such as high concentrated solutions and the presence of organic molecules.

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Preparation of alkali-tolerant prussian-blue analogue as Cs immobilizer for the cement-solidification of radioactively contaminated municipal solid waste incinerator fly ash

Ichikawa, T.[1, 2)], Yamada, K.[2)], Osako, M.[2)]

[1)] *Hokkaido University, Sapporo, Japan*
[2)] *National Institute for Environmental Studies, Tsukuba, Japan*

Corresponding author: tsuneki@eng.hokudai.ac.jp

The Fukushima Daiichi nuclear reactor accident induced by the East Japan earthquake and tsunami on March 11, 2011 released approximately 1.8×10^{16} Bq of ^{134}Cs and 1.5×10^{16} Bq of ^{137}Cs, which contaminated plants, soils, houses and so on around the reactor site. The demolished houses, plants and other wastes were collected in incineration facilities as municipal solid wastes, and incinerated for volume reduction. Since Cs in the wastes was volatile at high temperature, a significant amount of radioactive Cs was concentrated in the municipal solid waste incinerator fly ash (MSWI FA) as water-soluble CsCl. Special care has therefore been taken for preventing the leaching of radioactive cesium from the ash during the long-term isolated storage.

One of the simplest methods for preventing the leaching of radioactive Cs is to cement-solidify MSWI FA with a Cs immobilizer. However, the presence of large amounts of water-soluble chlorides and $Ca(OH)_2$ in MSWI FA makes it difficult to apply conventional Cs adsorbents to MSWI FA. About one third of MSWI FA is composed of alkaline and alkaline earth chlorides, so that the leachate contains significant amount of alkali metal and alkaline earth ions. MSWI FA also contains a significant amount of $Ca(OH)_2$ that is added for neutralizing HCl in the flue gas. The leachate is therefore an alkaline solution of pH < 12.7.
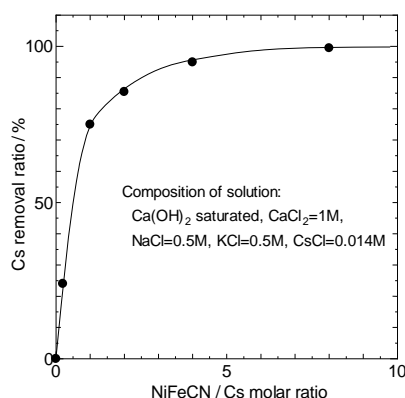
Figure 1: Cs adsorption efficiency of NiFeCN in leachate solution.

Although zeolites and clay minerals are well known Cs adsorbents, they cannot be used for MSWI FA because their selectivity coefficients for K^+ and Cs^+ are not much different and the K^+/Cs^+ molar ratio in MSWI FA is more than 10^4. Prussian blue (iron ferrocyanide) and its analogues are known to absorb Cs^+ selectively without much interference from K^+ ions. However, under an alkaline environment, it decomposes into ferrocyanide and metal hydroxides. We found that nickel ferrocyanide (NiFeCN) or nickel hexacyanoferrate(II) grown on the interface between concentrated nickel and ferrocyanide solutions is an excellent Cs immobilizer for MSWI FA. It adsorbs Cs^+ in highly alkaline solutions of pH < 13 without much interference from K^+, Na^+ and Ca^{2+}. On the other hand, NiFeCN prepared with a conventional titration method gradually decomposes into ferrocyanide and nickel hydroxide under the alkaline condition. Figure 1 shows the Cs-adsorption efficiency of NiFeCN in a simulated leachate solution. The amount of NiFeCN necessary for adsorbing practically all the Cs in 1000 kg of radioactively contaminated MSWI FA is less than 1 kg even the MSWI FA contains 10 ppm of stable and radioactive Cs^+ ions.

Suppression of the embrittlement of cement-solidified municipal solid waste incinerator fly ash due to volume expansion

Ichikawa, T.[1, 2], Yamada, K.[2], Osako, M.[2], Haga, K.[3]

[1] *Hokkaido University, Sapporo, Japan*
[2] *National Institute for Environmental Studies, Tsukuba, Japan*
[3] *Taiheiyo Consultant, Co. Ltd., Tokyo, Japan*

Corresponding author: tsuneki@eng.hokudai.ac.jp

The solidification/stabilization of municipal solid waste incineration fly ash (MSWI FA), especially from fluidized bed incinerators, with Portland cement and water is difficult, because it contains significant amount of metallic aluminum and $Ca(OH)_2$ in addition to $CaCl_2$, $NaCl$ and KCl, and the addition of water causes the evolution of hydrogen gas by the reaction of contained metallic aluminum and the alkaline solution and results in the formation of porous and brittle solid. We found that the evolution of hydrogen gas is can be suppressed by improving the mixing method and controlling the amount of $CaCl_2$ in the ingredients.

The evolution of hydrogen gas is separated into two chemical processes: the dissolution of the protective oxide layer on aluminum by the alkaline solution, and subsequent reaction of metallic aluminum with the solution. Cement-solidification of MSWI FA is generally achieved with a traditional method by mixing MSWI FA and cement powders with a pan-type mixer, adding water slowly to the mixture while mixing, and mixing the ingredients thoroughly. The protective oxide layer on aluminum is eroded during the mixing process, especially when the amount of water is not enough for reducing the friction between aluminum and other particles. Aluminum with a broken oxide layer then easily reacts with the alkaline solution to generate hydrogen gas.
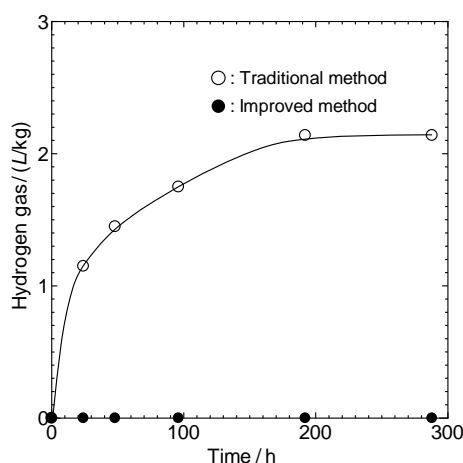
Figure 1: Evolution of hydrogen gas from cement-solidified MSWI FA prepared with traditional and improved mixing methods.

Thorough mixing of MSWI FA and cement powders with a drum-type mixer without water and subsequent addition of a specific amount of water at once scarcely induces the mechanical destruction of the oxide layer during the mixing process, since the amounts of air and water in the dry and wet admixtures, respectively, are enough for reducing the friction. Water soluble $CaCl_2$ externally added and/or contained in MSWI FA itself reduces the alkalinity of the aqueous solution by reacting with hydroxyl ions and therefore prevents the attack of the solution to the oxide layer. As shown in Figure 1, the evolution of hydrogen gas is thus suppressed by improving the mixing procedure and controlling the content of $CaCl_2$.

The volume expansion of cement-solidified Stoker-type MSWI FA probably due to AFt formation was found to be suppressed by wetting the FA before the solidification, though the mechanism of the suppression was not clarified yet.

Effects of phosphate modification on incorporation of caesium nitrate by calcium aluminate cement

Irisawa, K.[1,2], Mcgahan, M. J.[1], Meguro, Y.[2], Kinoshita, H.[1]

[1] *University of Sheffield, Department of Materials Science & Engineering, Sheffield, United Kingdom*
[2] *JAEA, Radioactive Waste Processing and Disposal Department, Tokai, Ibaraki, Japan*

Corresponding author: h.kinoshita@sheffield.ac.uk

Calcium aluminate cement modified with phosphate (CAP) has been studied as one of the alternative cementitious matrices for the encapsulation of nuclear wastes, especially those containing reactive metals [1,2]. Our previous study indicated a potential advantage in phosphate modification of this system for incorporation of $CsNO_3$ [3]. ^{137}Cs is one of the key radioactive nuclides which causes the majority of the radioactivity in the earlier age of nuclear wastes, yet difficult to incorporate into cement systems due to the mobile nature of an alkaline element. The present study investigates the compositional effects on the CAP system, focusing on the effects of phosphate on the incorporation of $CsNO_3$.

The CAP samples were prepared by mixing calcium aluminate cement (CAC) with the aqueous solution of sodium polyphosphate and $CsNO_3$. In order to keep the weight % of $CsNO_3$ constant in the prepared samples, the total weight of the matrix forming reagents (CAC and phosphate) were kept constant, as well as that of water. Only the balance between CAC and phosphate was changed to study the compositional effects. All samples were cured up to 28 days in a sealed container under ambient condition.

In the XRD data, precipitation of $CsNO_3$ was clearly observed in the neat CAC, as previously reported in the slag-Portland cement systems [4], suggesting a limited interaction of $CsNO_3$ with CAC and its hydration products. On the other hand, when the polyphosphate content in the system increased, a limited formation of the conventional crystalline hydration phases of CAC was observed, and the precipitation of $CsNO_3$ in the system also decreased significantly. The SEM/EDX analysis indicated clusters of Cs present with N, confirming the precipitation of $CsNO_3$ in the CAP system, but it also showed that some of Cs is in the amorphous binding phase of the CAP system. Although we do not know, at this stage, exactly how Cs is present in the amorphous phase, the obtained results suggest that a part of Cs is incorporated in the amorphous binding phase, leading to the restricted precipitation of $CsNO_3$. CAP system can be a good candidate matrix for $CsNO_3$ incorporation, worth studying further.

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Investigation of the swelling behavior of cationic exchange resins saturated with Na$^+$ ions in a C$_3$S paste

Lafond, E.[1], <u>Cau Dit Coumes, C.</u>[1], Gauffinet, S.[2], Chartier, D.[1], Le Bescop, P.[3], Stefan, L.[4], Nonat, A.[2]

[1] *CEA, DEN/MAR/DTCD/SPDE, Bagnols-sur-Cèze, France*

[2] *Université de Bourgogne et Franche-Comté, Faculté des Sciences Mirande, Institut Carnot de Bourgogne, Dijon, France*

[3] *CEA, DEN/SAC/DPC/SECR, Gif-sur-Yvette, France*

[4] *AREVA NC/BU-Valorisation, Paris , France*

Corresponding author: emilie.lafond@cea.fr

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 that allows for precipitating and thus confining many radionuclides. However, several particularities of IERs have to be taken into account to design a robust cement-based matrix: (i) their ability to exchange ions with the cementitious medium, which may influence cement hydration [1], (ii) their low mechanical strength, which strongly weakens the strength of the solidified waste forms [2], (iii) their strong dimensional variations which can, under severe conditions, induce swelling and cracking of the matrix [3-4]. In this work, the interactions between cationic resins in the Na$^+$ form and tricalciumsilicate are investigated during the early stages of hydration in order to gain a better understanding of the expansion process. Evolution of the mineralogy, microstructure and interstitial solution composition is compared for samples prepared with C$_3$S and resins initially saturated with and without Na$^+$. Hydration is followed using isothermal microcalorimetry at 25 °C and different devices are used to follow the volumetric change of C$_3$S–waste forms with ongoing hydration (dilatometry method and shrinkage cone method). Experiments are supported by thermodynamic equilibrium modeling in order to predict the evolution of the mineralogy of the C$_3$S paste and of the composition of the IERs with ongoing hydration. The results show that the IERs exhibit a transient swelling of small magnitude due to the decrease in the osmotic pressure of the external solution. This expansion, which occurs just after setting, is sufficient to damage the material which is poorly consolidated for several reasons: low degree of hydration, precipitation of poorly cohesive sodium-bearing C–S–H, and very heterogeneous microstructure with zones of high porosity.

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Investigation of magnesium phosphate cement hydration and its retardation by boric acid

Lahalle, H.[1], Cau Dit Coumes, C.[1], Lambertin, D.[1], Cannes, C.[2], Delpech, S.[2], Gauffinet, S.[3]

[1] *CEA, DEN/DTCD/SPDE, Bagnols-sur-Cèze, France*
[2] *CNRS, Univ. Paris-Sud 11, Institut de Physique Nucléaire, Orsay, France*
[3] *Université de Bourgogne et Franche-Comté, Faculté des Sciences Mirande, Institut Carnot de Bourgogne, Dijon, France*

Corresponding author: sandrine.gauffinet@u-bourgogne.fr

Magnesium phosphate cements (MPCs) are known for fast setting and hardening, good volume stability and excellent bonding to old concrete structures. Their main area of application is thus rapid repair works, but they may also offer prospects for the stabilization / solidification of deleterious waste.

MPCs contain calcined magnesium oxide and a water-soluble acid phosphate, such as potassium dihydrogen phosphate (KH_2PO_4). The main precipitated hydrate is then K-struvite ($MgKPO_4 \cdot 6H_2O$). This presentation aims at giving new insight into the processes involved in its formation. Since cement hydration is very rapid and needs to be retarded for field application, the second objective of this work is to understand how boric acid, a common admixture, retards the precipitation of K-struvite.

MPC was prepared by mixing deadburnt magnesia and KH_2PO_4 in equimolar amounts. Cement pastes comprised MPC, low-CaO fly ash used as a filler (fly ash-to-cement weight ratio of 1), and water (water-to-cement weight ratio of 0.56). Additional experiments were performed on cement suspensions (water-to-cement ratios equal to 10 and 100). The boric acid concentration was fixed at 4.17 mmol L^{-1} for the study. A panel of techniques was used to investigate the early age hydration of MPC. The evolution of the shear modulus, electrical conductivity and heat flow of the cement pastes were monitored with ongoing hydration. In addition, the phase assemblage was characterized after fixed periods of time by X-ray diffraction and thermogravimetry. Complementary experiments on suspensions allowed for determining the evolution of the solution composition with time.

A multi-stage process was evidenced: precipitation of struvite was preceded by the successive formation of newberyite ($MgHPO_4 \cdot 3H_2O$) and $Mg_2KH(PO_4)_2 \cdot 15H_2O$. Boric acid doesn't slow down the initial dissolution of the reactants, but rather retards the precipitation of the products.

Uptake and retention of safety relevant radionuclides in cementitious systems

Lange, S., Deissmann, G., Bosbach, D.

Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research: Nuclear Waste Management and Reactor Safety (IEK-6), Jülich, Germany

Corresponding author: s.lange@fz-juelich.de

Cementitious materials are widely used in nuclear waste management, for example for the solidification of low and intermediate level wastes, or as construction and barrier material in underground and surface repositories. The retention of radionuclides in cement-based materials is controlled by radionuclide solubility phenomena and sorption or incorporation of radionuclides into solids including the formation of solid solutions. Within the frame of the European CEBAMA project, we study the uptake of selected long-lived fission and decay products in cementitious materials, and the radionuclide distribution between and within various cement phases on the micro scale, using advanced micro analytical and spectroscopic tools. The objective of these investigations is to enhance the mechanistic understanding of the uptake and retention of safety relevant radionuclides in cementitious systems and to assess the relevance of chemical alteration processes, such as carbonation, on the solid speciation of radionuclides in aged concrete. In this context, a bottom-up approach is pursued using synthesized cement phases (model phases) on the one hand and hardened cement pastes with different compositions on the other.

Single model phases, namely calcium silicate hydrates (CSH) of different Ca/Si ratios, ettringite, monosulfate (AFm), and hydrogarnet were synthesized in a glove box under argon atmosphere, using well established experimental procedures (e.g. [1-4]). Purity and composition of the phases were confirmed by XRD, TG-DSC and XRF, the microstructure of the products was investigated by SEM. The sorption/uptake kinetics of radium and technetium by the model phases as well as by hardened cement pastes were studied in static batch experiments. The distribution of the radionuclides in and between the cement phases on the microscale was determined using SEM/EDX and TOF/SIMS. Sorption data derived on the model phases were aggregated and compared to the results of the radionuclide uptake experiments on hardened cement pastes. The results of this ongoing study will lead to a better understanding of the uptake and retention mechanisms of safety relevant radionuclides in cementitious barriers and materials and thus contribute to the scientific basis of the safety case for deep geological disposal of nuclear wastes.

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Application of electrical migration: Investigation of increase in barium in simulated wasteforms

MacArthur, A.J.[1], Hashimoto, K.[2], Provis, J.L.[1], Kinoshita, H.[1]

[1] *University of Sheffield, Department of Materials Science & Engineering, Sheffield, United Kingdom*
[2] *Hokkaido University, Lifetime Engineering Laboratory, Faculty of Engineering, Sapporo, Japan*

Corresponding author: h.kinoshita@sheffield.ac.uk

^{137}Cs is a problematic radionuclide in Intermediate Level Waste (ILW) due to its mobility and abundance [1]. Reasonably, there are various studies on encapsulation of Cs and its behaviour in cement matrices. However, few studies have considered the effect of radioactive decay process from ^{137}Cs to ^{137}Ba. The amount of Cs in the system decreases with its decay process, and chemically toxic Ba in the system simultaneously increases. The electrical migration technique can provide us with a unique opportunity to examine this simultaneous decrease in Cs content and increase in Ba content in a hydrated cementitious system. This preliminary research utilises the electrical migration technique to examine the effect of Ba migration into a hardened cementitious system containing caesium in the initial formulation.

A blend of Blast Furnace Slag and Portland Cement (3:1 BFS:PC) with water to binder ratio of 0.34, based on the UK standard for ILW encapsulation, was prepared with or without inclusion of $CsNO_3$. After curing for 28 days under ambient condition in a sealed container, specimens were cut (40x40x5mm) and placed in the migration cell with 750ml of distilled water in both anode and cathode tanks [2]. Ba was introduced as $Ba(OH)_2 \cdot 8H_2O$, dissolved in the distilled water in the anode tank. The migration tests were conducted at room temperature with 25 A m^{-2} of applied current for various durations. For comparison, samples containing $Ba(OH)_2 \cdot 8H_2O$ in the initial formulation was also prepared and tested.

When Ba is externally introduced to the cement matrix from the anode solution, the obtained XRD results indicated that Ba can react with the sulphate content in the cement matrix and forms barite ($BaSO_4$). This was similar to when Ba was internally mixed in the initial formulation. The obtained results also show that the barite formed (when Ba is internally mixed) appears unaffected by electric migration in terms of its dissolution and leaching, whereas portlandite in the system appeared to have dissolved significantly on electrical migration test, suggesting that, once formed, barite is well immobilised in the cement matrix.

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Investigation of EDTA and gluconate migration into cementitious materials using carbon-14-labelled radiotracers

Macé, N., Radwan, J., Page, J., Coreau N., Blin, V.

CEA, DEN/DANS/DPC/SECR, Laboratory of Radionuclides Migration, Measurements and Modelling (L3MR), Gif-sur-Yvette, France

Corresponding author: nathalie.mace@cea.fr

Ethylenediamine-tetraacetic acid (EDTA) and gluconic acid (GLU) are stable under hyper-alkaline conditions and show high affinities for metal complexation (e.g. [1] and [2]). EDTA and GLU are then used as decontamination reagents in radioactive waste reprocessing technology. One possible way to stabilize these specific organic slurries is to use cementitious materials. In such a context, migration of EDTA and GLU under hyper-alkaline conditions is relevant to be determined in order to evaluate the safety and performance of radwaste disposals.

In this study, the migration of EDTA and GLU has been performed using different types of cementitious materials from a hydrated cement paste (HCP) to a steel-fiber-reinforced concrete. HCP samples have been prepared using a CEM V/A cement with a water to cement ratio of 0.44. EDTA and GLU adsorption kinetics have been quantified until 90 days of contact time, as well as adsorption isotherms with increasing initial organic concentration up to $\sim 10^{-2}$ mol/L. Through-diffusion and in-diffusion experiments have been carried out until about 500 days. As reference, tritiated water (HTO) diffusion has also been measured through mortar and concrete samples. For some dedicated samples, EDTA diffusion profiles into the solid have been characterized. This allowed a validation of the model, in addition to the determination of migration parameters (effective diffusion coefficient, D_e, and retardation factor, R) thanks to the interpretation of the upstream and downstream reservoirs concentration evolutions. ^{14}C-EDTA and ^{14}C-GLU have been used as radiotracer and have been measured by liquid scintillation counting technique in these migration experiments.

First adsorption results show a higher affinity of GLU compared to EDTA for HCP. They have been confirmed in terms of retardation onto the diffusion through mortar and concrete following this trend: R(GLU)>R(EDTA)>R(HTO). Each adsorption isotherm displays an adsorption-site saturation effect. However, interaction processes between the HCP and EDTA and GLU were not precisely identified. Some discrepancies remain and will be discussed between model and diffusion behaviours of these organic species through mortar and concrete.

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Uptake of sulfur, selenium and iodine in AFm-phases

Nedyalkova, L.[1], Lothenbach, B.[1], Tits, J.[2], Wieland, E.[2], Mäder, U.K.[3]

[1] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*
[2] *Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland*
[3] *University of Bern, Institute of Geological Sciences, RWI, Bern, Switzerland*

Corresponding author: latina.nedyalkova@empa.ch

Selenium and iodine are usually present in anionic form under the alkaline conditions prevailing in the cementitious near-field of low- and intermediate level nuclear waste (L/ILW) repositories. The negatively charged surfaces of many common near- and far-field minerals can thus only weakly retard the Se and I anionic species. This, combined with the long half-lives of these elements ($t_{1/2} \sim 7 \times 10^4$ a and $\sim 1.57 \times 10^7$ a for ^{79}Se and ^{129}I, respectively), defines them as important dose-determining radionuclides in such repositories [1]. Some positively charged anion exchangers, however, present in the cementitious near-field matrix, such as AFm(Al_2O_3-Fe_2O_3-mono)-phases, have the potential to incorporate Se and I in their structure and may play an important role in the immobilization of these hazardous elements. AFm-phases have a lamellar structure with a positively charged main layer, $[Ca_2(Al,Fe)(OH)_6]^+$, and a negatively charged interlayer, $[X \cdot nH_2O]^-$, where X denotes a singly charged or half of a doubly charged anion.

In order to investigate the incorporation of Se, I and S in AFm-phases, Se(VI)-, Se(IV)-, I(-I)-, S(VI)-, S(IV)- and S(II)-AFm phases were synthesized accounting for a range of possible redox conditions in a cement-based repository in deep geological formations. The AFm-phases were characterized by X-ray diffraction. The X-ray spectra revealed different interlayer distances (hkl 003 and 006) for all of the synthesized products whereas no shift in the main layer (hkl 110) could be observed. This suggests an intercalation of the Se, I and S anions in the AFm interlayers. From a bulk chemical analysis of the liquid phase the pH values and the solubility products were also determined.
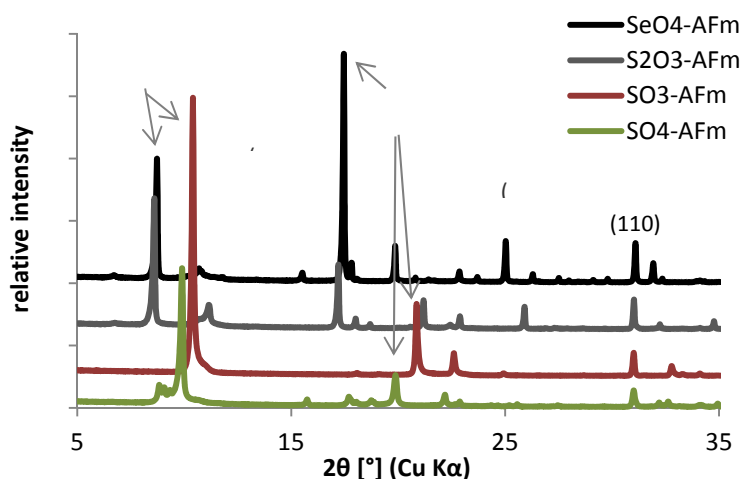
Figure 1: XRD of synthesized AFm-phases.

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Complexing power of hydro-soluble degradation products from γ-irradiated polyvinylchloride: Influence on Eu(OH)$_3$(s) solubility and Eu(III) speciation

Reiller, P.E., Ferry, M., Legand, S.

CEA, DEN/DANS/Department of Physical Chemistry, Gif-sur-Yvette, France

Corresponding author: pascal.reiller@cea.fr

The radio-oxidation of the polymers that would be disposed of within the intermediate and low level (ILL) activity nuclear wastes is producing hydro-soluble degradation products (HDPs), containing shorter chain organic molecules, and an appreciable amount of a not yet identified pool of organic substances. Among these organic pools, the possibility to generate complexing entities is susceptible to lead to the modification of the solubility of the radionuclides within the waste packages. As an example, in the case of ion exchange resins this led to the formation of short-chained organic molecules and of an unknown pool of ligands [1]. Out of the short chained molecules, dicarboxylic acids such as oxalic acid were identified, but none of these short-chained molecules could compete for hydrolysis of actinides(III) and precipitation of solid hydroxides in cementitious systems.

In this study, we evaluate the complexing power of the HDPs from a γ-irradiated polymer (polyvinylchloride PVC, 10 MGy) basic lixiviate (pH 13.3, KOH/NaOH) in two ways: first, through the solubility modification of Eu(OH)$_3$(am) vs. increasing concentration of an HDPs solution at constant pH 13.3 (KOH/NaOH); second, through the influence of increasing amounts of the basic HDP solution on the fluorescence of europium between pH 6 and 11.2. As a large part of the HDP composition remains unknown, all concentrations are referred to the amount of carbon in solution.

Contrary to simple carboxylic or dicarboxylic acids, it appears that HDPs have an appreciable effect on the solubility of Eu(OH)$_3$(am) for concentrations higher than 0.1 mol$_{carbon}$/kg$_{water}$ in the system. The effect is comparable to the iso-saccharinic acid complexing power on the same concentration scale.

It also appears that several complexes can be identified in time-resolved laser-induced fluorescence spectroscopy (TRLIFS) between pH 6 and 11.2. The evolutions of the Eu(III) fluorescence with increasing HDP concentration, and pH, show that at least two species are formed with different spectra and decay times. It is also worthy to notice that HDPs prevent Eu(III) from precipitating under the experimental conditions and for at least three weeks.

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Dissolution and reaction rates of waste materials in cement: Temperature dependence

Snellings, R.[1)], Kazemi-Kamyab, H.[2)], Ferrand, K.[3)]

[1)] *VITO, Mol, Belgium*
[2)] *Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland*
[3)] *SCK-CEN, Mol, Belgium*

Corresponding author: ruben.snellings@vito.be

A growing body of research is showing that the reaction rates of inorganic waste streams in cementitious systems are related to the chemical composition of their constituent glass phases [1,2]. In parallel, it is commonly accepted that there are strong correlations between the chemical composition of a glass and its dissolution rate in alkaline solutions [3].

Combining these two observations, the central hypothesis of the contributed paper is that dissolution of the waste glass phases is, at least initially, the rate controlling step in the reaction of the waste materials and cement. This hypothesis is investigated by comparing the temperature dependence of the reaction of a selection of commonly used supplementary cementitious materials (SCMs), i.e. fly ash, blast-furnace slag and a natural pozzolan.

The reaction of the SCMs was studied in two model systems. In the first system, the dissolution rate of the materials was determined in dilute suspensions at pH 13. Dissolution rates were determined for 20, 30 and 40 °C by reaction in a stirred batch reactor system. In the second model system, the materials were mixed with $Ca(OH)_2$, alkali sulfates and water to simulate the reaction environment in a hydrating cement. Reaction kinetics were determined by measuring the heat flow in an isothermal conduction calorimeter. The reaction was monitored at 20, 30 and 40°C.

The temperature dependence of the dissolution rates was used to extract the activation energies for the dissolution reaction. These were compared to the apparent activation energies obtained for the paste model mixes. The dependence of activation energies on glass composition is discussed and compared to literature data. Finally, the comparison of activation energies is critically assessed in view of the central hypothesis of dissolution as rate-controlling step in the reaction of supplementary cementitious materials.

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Solubility of plutonium under alkaline to hyperalkaline reducing conditions: Redox chemistry and complexation with ISA

Tasi, A.G.[1], Gaona, X.[1], Fellhauer, D.[1], Böttle, M.[1], Rothe, J.[1], Schild, D.[1], Graser, C.-H.[1], Grivé, M.[2], Bruno, J.[2], Källström, K.[3], Altmaier, M.[1], Geckeis, H.[1]

[1] *Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Karlsruhe, Germany*
[2] *Amphos 21 Consulting S.L., Barcelona, Spain*
[3] *SKB, Stockholm, Sweden*

Corresponding authors: agost.tasi@kit.edu; xavier.gaona@kit.edu

Deep geological formations are one of the internationally accepted options for the final disposal of nuclear waste. Strongly reducing conditions are expected in the post-closure period of these facilities due to anoxic corrosion of steel. In the case of low and intermediate level wastes (L/ILW), the preferred concept usually involves the use of cementitious materials for the stabilization of the waste and for construction purposes. The interaction of these materials with groundwater buffers the pH in the alkaline to hyperalkaline range ($10 \leq$ pH ≤ 13.3) over a very long time-scale. The formation of Pu(III) and Pu(IV) species is expected under strongly reducing conditions. The limited knowledge on the thermodynamic data hinders the current NEA–TDB selection, increasing the uncertainties associated to Pu(III) and Pu(IV) aqueous species and solid compounds expected to exert a solubility control under alkaline pH conditions. Cellulose is a significant contributor to the SFR repository, the Final Repository for Short-lived Radioactive Waste in Sweden. Isosaccharinic acid ($C_6H_{12}O_6$, HISA) was identified as the main degradation product of cellulose under hyperalkaline conditions. The formation of stable An(III)– and An(IV)–ISA binary complexes was previously reported, however, the role of Ca and the possible formation of very stable ternary complexes Ca–An(III)/An(IV)–ISA is controversially discussed in the literature. A very limited number of experimental studies was dedicated so far to assess the impact of ISA on Pu solubility under repository-relevant conditions.

All experiments were conducted at $T = 22 \pm 2$ °C in Ar gloveboxes in the controlled area of KIT–INE. Independent undersaturation solubility experiments were prepared using a well-characterized, aged $^{242}PuO_2$(am,hyd) solid phase. Redox conditions were buffered with 2 mM hydroquinone (pe + pH$_m$ = 9.5 ± 1) or SnCl$_2$ (pe + pH$_m$ = 2 ± 1). pH$_m$ was varied from 8 to 13 (I = 0.10 M NaCl–NaOH). [Pu]$_{tot}$ was determined after ultracentrifugation by sector field ICP–MS. Liquid-liquid extraction and capillary electrophoresis (CE) coupled to SF–ICP–MS were used for the redox speciation of Pu in the aqueous phase. Solid phase characterization was performed using XRD, (synchrotron-based) in-situ XRD, XPS and XANES/EXAFS. A second series of solubility experiments was prepared using the same solid phase and experimental boundary conditions, but including 10^{-6} M $\leq$ [ISA] ≤ 0.1 M in the absence or presence of Ca.

XRD, XPS and XANES analyses confirm the nanocrystalline morphology of the PuO$_2$(am,hyd) solid phase used as a starting material. The solubility product of this solid phase was experimentally determined in this work, and is in very good agreement with log$_{10}$ *$K°_{s,0}$ currently selected in the NEA–TDB for PuO$_2$(am,hyd). The solubility of Pu in hydroquinone systems at $8 \leq$ pH$_m \leq 13$ is very low and consistent with a solubility control by PuO$_2$(am,hyd). The predominance of this solid phase under these boundary conditions was confirmed by in-situ XRD, XPS and XANES, and is in good agreement with thermodynamic calculations. XANES analyses confirm the presence of Pu(III) in the solid phases controlling the solubility of Pu in (redox buffered) SnCl$_2$ systems. In spite of this, the solubility of Pu remains very low ($\leq 10^{-10}$ m) at pH$_m \geq 9$. These observations indicate that log$_{10}$ *$K°_{s,0}${Pu(OH)$_3$(s)} currently selected in the NEA–TDB is likely overestimated, and that the Pu(III) redox state needs to be considered for describing experimental studies under strongly reducing alkaline to hyperalkaline conditions. Preliminary results on the impact of ISA on the solubility of Pu under hyperalkaline reducing conditions will be presented and discussed.

Assessing the role of AFm phases in the immobilization of selenium by cement under oxidizing and reducing conditions

Tits, J.[1], Rojo, H.[1,2], Scheinost, A.C.[3], Lothenbach, B.[4], Wieland, E.[1]

[1] *Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland*
[2] *Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Karlsruhe, Germany*
[3] *Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Dresden-Rossendorf, Germany*
[4] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*

Corresponding author: jan.tits@psi.ch

Selenium-79 is an important dose-determining radionuclide in low- and intermediate level (L/ILW) nuclear waste repositories due to its long half-life and its presence in the anionic form resulting in weak retention by many common minerals of the host rock. Under the oxidizing conditions prevailing during operation of the repository, the aqueous redox speciation of Se is dominated by selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}), whereas under the reducing conditions established after closure of the repository, species such as Se(0) and HSe^- will dominate. To assess the long-term mobility of Se in the cementitious near field of a L/ILW repository, batch experiments were performed to measure Se sorption onto different cement minerals under both oxidizing and reducing conditions. Furthermore, X-ray absorption spectroscopy was employed to explore the redox reactivity of sorbed Se species.

Batch sorption studies showed that both SeO_3^{2-} and HSe^- are preferentially retained by AFm phases rather than by calcium silicate hydrates (C-S-H phases) in spite of the much higher specific surface areas of C-S-H phases (~150 m^2/g) [1] compared to AFm phases (~5 m^2/g) [2]. Indeed, at trace loadings, sorption distribution ratios (R_d) were found to range between 500 L kg^{-1} and $2 \cdot 10^4$ L kg^{-1} for both redox states in the case of AFm phases, whereas in the case of C-S-H phases, R_d values ranged from 5 to 10 L kg^{-1}. In addition, in the case of the AFm phases, R_d values appeared to be highly dependent on the type of anion present in the AFm interlayer and thus on the interlayer spacing: measured R_d values were higher on AFm-OH-CO_3 and on AFm-SO_4 having d-spacings of 8.2 Å and 9.55 Å, respectively, than on AFm-CO_3 and on AFm-Cl_2 having d-spacings of 7.55 Å and 7.88 Å. These observations suggest that SeO_3^{2-} and HSe^- are at least partially retained in the interlayer of the AFm phases explaining why AFm phases with positively charged interlayers are more effective in accommodating anionic Se species than C-S-H phases.

More support for this assumption was obtained from redox transition experiments: Exposing AFm-CO_3 and AFm-OH-CO_3 loaded with SeO_3^{2-} to reducing conditions in an electrochemical cell for 1 month led to a significant reduction of the SeO_3^{2-} sorbed on AFm-CO_3 whereas in the case of SeO_3^{2-} sorbed onto AFm-OH-CO_3, no significant reduction was observed. In a similar way, oxidation of HSe^- sorbed on AFm-CO_3 upon exposure to air, was significantly more distinct than oxidation of HSe^- sorbed onto AFm-OH-CO_3. These observations indicate that Se anions sorbed on AFm-OH-CO_3 are much better protected against redox reactions. The present results highlight the important role of the AFm phases present in cementitious materials to remove SeO_3^{2-} and HSe^- from solution and thus to reduce the mobility of selenium under the reducing conditions prevailing in a L/ILW repository.

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Study of migration processes on cement and concrete materials used in waste management in Czech Republic

Večerník, P., Brázda L., Otcovský T., Havlová V.

ÚJV Řež, a.s., Husinec-Řež, Czech Republic

Corresponding author: petr.vecernik@ujv.cz

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 a deep geology repository (DGR), hereby being considered both for solidification and container construction (concrete container). Being used for such a purpose, it is clear that the material has to contribute to the overall DGR safety function, i.e. to contain radionuclides for at least 100 000 years. In order to evaluate all the processes that the materials can undergo, extensive research has been started, being focused on the migration of radionuclides.

Concerning such presumptions, firstly the materials for the experimental research were chosen, prioritising the available materials used for radioactive waste management. At present, cements and concretes are used in the processing of wastes in the Fuel Cycle Chemistry and Waste Management Division, ÚJV Řež, a. s. Cements are used as a fixation matrix of the wastes in the internal 100L steel drums, concretes are used as a sealing, reinforcement and first barrier surrounding the fixed waste in the 200L steel canisters. Under development is also an option to immobilise spent ion exchange resins in a cement-based matrix. Another type of studied material is the concrete mixture used for fixation and closure of storage niches in the Richard repository, which is operated by SÚRAO.

Studies of the contaminants migration processes are focussed mainly on the diffusion of ^{3}H, as a representative of a non-interacting tracer and ^{14}C as a relevant contaminant of I/LLW and spent resins from nuclear reactor operation and contaminated waters purification. Diffusion processes are studied using the through diffusion method with selected tracers on the cement paste and concrete samples (50 mm in diameter, 10mm in length). Additional sorption and leaching test are performed to evaluate retention coefficients of contaminants on this type of materials.

All these results and obtained data will contribute to improve performance and safety assessments 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.

Interaction of low molecular weight organic compounds with hardened cement paste

Wieland, E.[1)], Jakob, A.[1)], Tits, J.[1)], Lothenbach, B.[2)], Kunz, D.[1)]

[1)] Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland
[2)] Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland

Corresponding author: erich.wieland@psi.ch

Carbon-14 is a radionuclide of particular interest in nuclear power production and a key radionuclide in performance assessment of deep geological repositories for radioactive waste. Carbon-14 is expected to be present as ^{14}C containing low molecular weight (LMW) organic compounds in the near field, such as compounds formed during the anoxic corrosion of activated steel [1]. The current understanding of the retardation of small organic molecules in cementitious systems is very limited. In particular, only limited information on the retention of the aqueous compounds by hardened cement paste (HCP) and cement phases is currently available.

The present study was carried out with the aim of filling this gap in our knowledge and quantifying the uptake of important LMW organic compounds, i.e. methanol, ethanol, formaldehyde (methanal), acetaldehyde (ethanal), formic and acetic acids, by HCP. Diffusion, sorption and hydration experiments were carried out to determine the partitioning of small organic molecules between HCP and pore solution and to elucidate the uptake mechanism [2].

The solid-liquid distribution ratios (R_d) of methanol, ethanol, formaldehyde, acetaldehyde, formic and acetic acids were determined in hydrating cement paste. The sorption values determined for formic and acetic acids were further assessed by studying through- and out-diffusion of these compounds in fully hydrated cement paste. Eventually, sorption studies with the carboxylic acids on cement phases were carried out with the aim of identifying the uptake-controlling cement phase and checking reversibility of the uptake process.

R_d values determined from the hydration experiments were found to be very low (range 10^{-5} m^3 kg^{-1} - 10^{-3} m^3 kg^{-1}). Alcohols and aldehydes showed weakest interaction with HCP indicating non-specific (very weak) bonding onto the surface of the cement phases, e.g. through hydrogen bonding. Hydration, sorption and diffusion studies revealed slightly stronger interaction of the carboxylic acids with HCP compared to alcohols and aldehydes. In the case of acetate uptake by HCP and cement phases was found to be reversible, thus indicating specific adsorption (electrostatic interaction) with partially positively charged surface sites of the cement phases. In contrast, selective binding of a small fraction of formate, as evidenced from both sorption and out-diffusion experiments, suggests the presence of sorption sites capable of strongly bonding this molecule, for example due to SO_4^{2-}/$HCOO^-$ replacement in the ettringite structure.

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Tc(IV) solubility in repository-relevant systems

Yalcintas, E., Baumann, A., Gaona, X., Altmaier, M., Geckeis, H.

Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Karlsruhe, Germany

Corresponding author: marcus.altmaier@kit.edu

Technetium–99 is a β–emitting radionuclide produced in nuclear reactors by the fission of ^{235}U and ^{239}Pu. Due to its significant inventory in spent nuclear fuel, long half-life ($t_{1/2}$ ~211'000 a) and redox-sensitive character, ^{99}Tc is a very relevant radionuclide in Performance Assessment exercises of repositories for radioactive waste disposal. In reducing environments expected for deep geological repositories, Tc(IV) prevails forming sparingly soluble hydrous oxides ($TcO_2 \cdot xH_2O(s)$). An appropriate understanding of the solubility and hydrolysis of Tc(IV) in dilute to concentrated solutions is required for assessing the (geo)chemical behaviour of technetium under the hyperalkaline conditions expected for cementitious environments.

The solubility of Tc(IV) was investigated within a very comprehensive experimental study from undersaturation conditions under Ar atmosphere. Experiments were performed in dilute to concentrated NaCl, KCl, $MgCl_2$ and $CaCl_2$ solutions within $1.5 \leq pH_m \leq 14.6$. Strongly reducing conditions were chemically set for each independent solubility sample with $Na_2S_2O_4$, $SnCl_2$ or Fe powder. Technetium concentration, pH_m and E_h values were monitored at regular time intervals. Thermodynamic equilibrium was assumed after repeated measurements with constant [Tc] and pHm. Solid and aqueous phases were characterized by XRD, XANES/EXAFS and liquid-liquid extraction. Additional solubility experiments were conducted in "simulated systems" with complex mixtures of $NaCl–KCl–MgCl_2–CaCl_2$, based upon reported pore water composition of cement and brine systems for typical scenarios.

Solid phase characterisation and solubility data indicate that $TcO_2 \cdot 0.6H_2O(s)$ is the solid phase controlling the solubility of Tc(IV) in all the evaluated systems. The combination of solvent extraction data and XANES analysis confirms the predominance of Tc(IV) in the aqueous phase, independently of the salt system and concentration. The solubility of $TcO_2 \cdot 0.6H_2O(s)$ decreases with a well-defined slope of –2 in acidic dilute systems. The same slope is retained in concentrated brines, although a very significant increase in the solubility (up to 4 orders of magnitude) is observed with increasing ionic strength. A newly derived chemical model based on these solubility data in combination with spectroscopic evidences, best explains this increase considering the formation of the previously unreported trimeric technetium species $Tc_3O_5^{2+}$. In the near-neutral pH region, the pH-independent behaviour of the solubility is consistent with the formation of neutral $TcO(OH)_2(aq)$ species with a log $*K°s,TcO(OH)_2$ in good agreement with the current NEA–TDB data selection [1]. The formation of the species $TcO(OH)_3^-$ was confirmed in dilute to concentrated NaCl and KCl systems at $pH_m \geq 11$, although a decrease in solubility takes place in concentrated solutions due to ion interaction processes. 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 the corresponding solubility curves and the comparison with previous observations available for An(IV) and Zr(IV) in concentrated $CaCl_2$ solutions. Based on the newly generated experimental data, comprehensive chemical, thermodynamic and activity models using both SIT and Pitzer approaches are derived for the system $Tc^{4+}–Na^+–K^+–Mg^{2+}–Ca^{2+}–H^+–Cl^-–OH^-–H_2O(l)$ at T = 25°C. Tc(IV) solubility investigated in "simulated systems" is in good agreement with quantitative predictions based on pure systems.

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Estimation of Cs ingress from MSWI-fly ash into concrete compared with real contaminated concrete

Yamada, K.[1], Ichikawa, T.[1, 2], Yoshifumi, H.[3], Haga, K.[4], Osako, M.[2]

[1] *National Institute for Environmental Studies, Tsukuba, Japan*

[2] *Hokkaido University, Sapporo, Japan*

[3] *Taiheiyo Cement, Corp., Chiba, Japan*

[4] *Taiheiyo Consultant, Co. Ltd., Tokyo, Japan*

Corresponding author: yamada.kazuo@nies.go.jp

After the Fukushima-Daiichi accident, a wide area of East Japan was contaminated by radio-caesium (r-Cs). Concrete structures were also contaminated by r-Cs. Concrete from real structures was studied by β-ray radiograph with the aim of obtaining information on the contamination depth for decontamination (Figure 1). The penetration depth was found to be very limited.

Information on r-Cs ingress is also important in connection with the safe disposal of contaminated wastes if those wastes contain r-Cs in water soluble form like municipal solid waste incineration fly ash (MSWI-FA) and if those wastes are planned to be disposed of in concrete pits. To this end, concrete made of pure limestone was immersed in a small volume of ^{137}Cs solution. The penetration depth was a few cm even at very low Cs concentrations. This means that there is no effect of binding by C-S-H during Cs ingress. MSWI-FA contains stable Cs on the order of 0.1-1 ppm. A concrete specimen was immersed in a 3 mM CsCl solution for 28 days. The penetration depth of Cl and Cs into the concrete was about 5 mm (Figure 3). Because of Cl binding by AFm phases, the concentrations of the two elements are different while penetration depths are similar. The interesting finding for Cs is the sharp peak at the surface of concrete. This is suggested to be caused by the dissolution of Ca. In view of the latter results, Cs penetration has to be considered differently in decalcified areas and normal C-S-H.

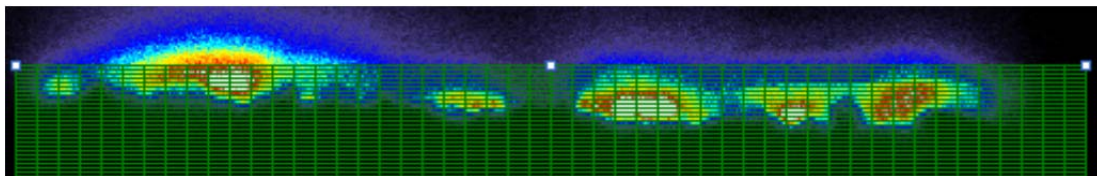*Figure 1: Penetration profile of r-Cs by β-ray radiograph in concrete cored from road structure. Green mesh is 1x0.2 mm. 19 kBq/cm². Brightest position is the surface. Lower part is the inside of core. No penetration into core. From the surface, β-ray was scattered.*

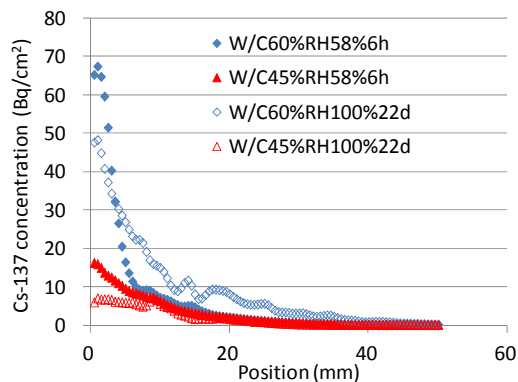

Figure 2: Penetration profile of ^{137}Cs by β-ray radiograph in lab concrete.
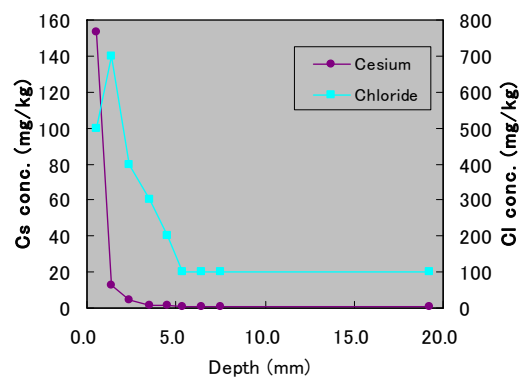
Figure 3: Penetration Cs profile for 3 mM CsCl immersion for 28 day.

Stability of cement solidification of MSWI-fly ash

Yamada, K.[1], Ogawa, S.[2], Haga, K.[2], Ishimori, H.[3], Endo, K.[2], Osako, M.[2]

[1] *National Institute for Environmental Studies, Tsukuba, Japan*
[2] *Taiheiyo Consultant, Co. Ltd., Tokyo, Japan*
[3] *Ritsumeikan University, Shiga, Japan*

Corresponding author: yamada.kazuo@nies.go.jp

After the Fukushima-Daiichi accident, a wide area of East Japan was contaminated by radio-caesium (r-Cs). Municipal solid wastes (MSW) are incinerated in order to reduce the volume of wastes in Japan and r-Cs is concentrated in fly ash (MSWI-FA) by a factor of 20 - 30. For the safe disposal of such wastes, cement solidification has been taken into account in order to reduce the mobility of r-Cs. After immersion tests, however, a hardened body cracked severely as shown in Figure 1. This phenomena has been observed at a high water to cement ratio.

Figure 1: Severe damaged of cement solidified cylinder of MSWI-FA after 256 days dissolution.

Figure 2: Paste expansion and cracking of normal concrete core immersed in concentrated solution from MSWI-FA at 5℃ for 1 year.

Cement solidification is aimed at lowering the leach rate of Cs by reducing the water flow in controlled-type disposal sites compared to uncontrolled disposal of MSWI-FA. In the former case, the required compressive strength is 0.98 MPa. If a solidified body cracks and collapses, it will be difficult to meet the requirement. And further, if cracking causes expansion, the stability or bulge out of the disposal sites will become problematic.

MSWI-FA contains significant amounts (several % order) of alkali chloride, calcium chloride, and gypsum. In the early age, the high Ca concentration in pore solution is caused by the presence of a large amount of $CaCl_2$ leached from MSWI-FA. At lower temperature, cement paste expands and cracks due to the formation of expansive needle-like crystals of $3CaO \cdot CaCl_2 \cdot 15H_2O$. Figure 2 shows an example of concrete made of ordinary Portland cement.

At longer ageing and due to the leaching of soluble salt from MSWI-FA., which occurs during controlled-type disposal, gypsum will convert to ettringite and the solidified body will expand and collapse.

In this study, the expansive pressure changes of MSWI-FA and cement mixtures have been determined using confined but water permeable containers. The cements studied were an ordinary Portland cement as well as fly ash and blast furnace slag cements. The dissolution of major elements was investigated by phase analysis after the tests. The experimental results are compared with thermodynamic phase equilibrium calculations.

Modelling degradation of cementitious materials in sodium sulphate radioactive waste

Yogarajah, E.[1], Nawa, T.[1], Owaki, E.[2]

[1] *Hokkaido University, Sapporo, Japan*
[2] *Taisei Corporation, Yokohama, Japan*

Corresponding author: elakneswaran@eng.hokudai.ac.jp

Sodium sulphate is the main component of the low-level radioactive waste generated from Boiling Water Reactor (BWR) power plants, and the liquid waste contains high concentration of Na_2SO_4, up to 25% of Na_2SO_4. Cementitious materials have been used to immobilise the high concentration of Na_2SO_4 waste at elevated temperature. However, it has long been recognised that sulphate ions causes a serious chemical attack to cement matrix through either ettringite, gypsum, and thaumasite formation or sodium sulphate crystallisation.

In this study the interaction of sodium sulphate in the hydration and the hydration products of cementitious materials is discussed for evaluating Portland cement and the blended cement containing up to 70% of slag on their performance in low- or intermediate-level radioactive waste. A hydration model that coupled PHREEQC with empirical equations for dissolution of clinker minerals and reaction of slag was developed to predict composition of hydrate assemblage and pore solution concentration. A solid solution that consists of various C-S-H and C-A-S-H gel as end members was considered in the hydration model. Further, a reactive transport model was developed in PHREEQC considering phase-equilibrium reaction and multi-species transport. The thermodynamic properties for various phases and minerals found in cementitious materials were collected from CEMDATA07, and the data were converted into a format suitable for PHREEQC. The converted data together with Pitzer model, which is for higher ionic strength calculations, database for PHREEQC were used for simulations.

Hydration of Portland cement in 25% of Na_2SO_4 solution for varying temperature (20→120 ºC for 0→0.5 days, 120→20 ºC for 0.5→3 days) is simulated. The simulation result show the formation of mirabilite ($Na_2SO_4 \cdot 10H_2O$) at the room temperature in addition to the main hydrates in cement hydration (Figure 1), but there is no formation of thenardite (Na_2SO_4) crystals at high temperature. The volume increases due to mirabilite formation causes the crack in the system as observed the experiments. The long-term performance of Portland cement-based materials in sulphate environment is modelled using the reactive transport model which couples the hydration model to predict the performance from the starting materials and mix proportions. The dominant deterioration mechanism in external sodium sulphate transport is the formation of ettringite, gypsum, and thaumasite than sodium sulphate crystallisation (Figure 2).
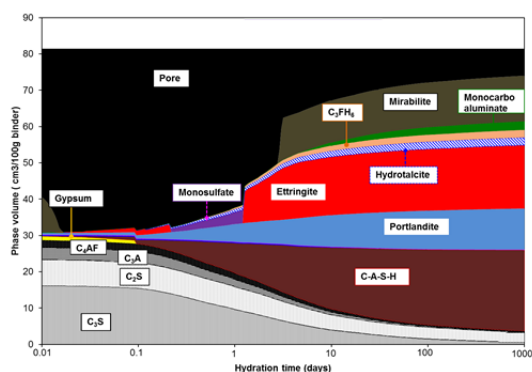

Figure 1: Simulated phase changes as a function of hydration time for Portland cement with 25% of Na_2SO_4.
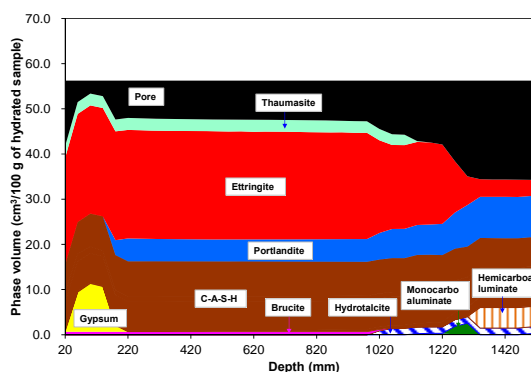
Figure 2: Phase changes of hydrated Portland cement after exposed to 10% of Na_2SO_4 for 300 years.

Topic 4: Nanoscale Characterisation and Molecular Dynamics

Looking inside magnesium silicate hydrate through ^{29}Si solid state NMR and 1h relaxometry: Structure and water status

<u>Borsacchi, S.</u>[1], Ridi, F.[2], Martini, F.[1], Tonelli, M.[2], Calucci, L.[1], Geppi, M.[3], Fratini, E.[2], Baglioni, P.[2]

[1] *Consiglio Nazionale delle Ricerche (CNR), U.O.S. Pisa, Istituto di Chimica dei Composti OrganoMetallici, Pisa, Italy*
[2] *Università di Firenze, Dipartimento di Chimica "Ugo Schiff" and CSGI, Sesto Fiorentino (Florence), Italy*
[3] *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Pisa, Italy*

Corresponding author: silvia.borsacchi@pi.iccom.cnr.it

Magnesium Silicate Hydrate (M-S-H) is the binder phase of magnesium-based cements, which are attracting interest as an eco-sustainable alternative to standard Portland cement. Indeed their production process, taking place from magnesium silicates, brine or seawater, dramatically reduces the CO_2 emissions, and they are well suited to applications for radioactive waste encapsulation [1]. Due to the complete amorphous character, the assessment of the structural properties of M-S-H is still open [1, 2]. In this study multinuclear NMR relaxometry and spectroscopy techniques, which revealed fundamental for the characterization of Portland cement [3], were applied to get insights into the silicate structural properties and water status in M-S-H obtained through room temperature hydration of highly reactive MgO and silica fume. In particular, the analysis of ^{1}H and quantitative ^{29}Si Solid State NMR experiments, together with results obtained from DSC, TGA, XRD and SEM measurements, carried out on M-S-H samples freeze-dried at precise times of hydration, allowed us to propose a detailed structural model of M-S-H. On the other hand, the status of water in pastes and the M-S-H surface to volume ratio were characterized and monitored at different hydration times by analyzing [1]H (and in some cases ^{2}H) T_1 relaxation times, measured by Fast Field Cycling NMR relaxometry, and [1]H T_2 relaxation times. The multi-scale characterization of the structure of M-S-H here obtained can improve the comprehension of MgO-based cements and potentially contributes to tailoring the macroscopic properties from the modification at the nanoscale.

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C-A-S-H-ion interactions from ab initio simulations

Churakov, S.V.[1,2], Labbez, C.[3], Pegado, L.[2,3]

[1] *University of Bern, Institute for Geological Sciences, Bern, Switzerland*
[2] *Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland*
[3] *Université Bourgogne et Franche-Comté, ICB, UMR 630, CNRS, Dijon, France*

Corresponding author: sergey.churakov@psi.ch

Calcium-Silicate-Hydrate (C-S-H), the major product of cement hydration (~60 wt.% of cement hydrates), controls to a large extent the mechanical and ion transport/uptake properties of hardened cement paste. The thermodynamic and physical-chemical properties of C-S-H have been in focus of many studies during last decades. As the result, a reasonable knowledge of the long-term thermodynamic stability, chemical evolution and mechanical properties of C-S-H (obtained from classical Portland cement hydration) has emerged. Urgent need to further reduce the CO_2 footprint of cement industry has led to an overall increase in the use of the so called supplementary cementitious materials (SCM). These new, so-called low CO_2 cementitious materials have inevitably a different chemistry, due to the formation of solids different to the ones of the ordinary Portland cements and therefore perform and behave differently in concrete.

Most often, silica rich SCM are used and are known to lower the calcium content (C/S) of C-S-H which, in turn, facilitates incorporation of other ions in its structure and, in particular, aluminium (C-(A)-S-H). Al in C-S-H modifies its electrostatic properties, and can potentially change the mechanical and sorption/transport properties as well as thermodynamic stability of the final material. In this work, new quantitative insight into the Al incorporation mechanism and its consequences on the surface charging of, and alkali uptake by C-(A)-S-H is presented. It is based on ab-initio molecular dynamics determination of the free energies for the reactions of Al/Si substitution and of aluminol ionization complemented with mesoscale Grand Canonical Monte Carlo (GCMC) simulations of C-(A)-S-H titration and ion uptake.

Atomistic simulations [1] and spectroscopic studies [2] suggest that Al incorporation in C-S-H occurs mainly by substitution of the silicates in the bridging tetrahedral sites. Free energy calculation for the reaction of the Al exchange between aqueous solution and C-S-H surface confirms this result and further shows that it occurs at almost no energy cost. In addition, the calculation of the deprotonation constants of the >Al-OH groups at the C-A-S-H surface combined with mesoscale GCMC simulations suggests that Al tetrahedra remain doubly protonated in the whole range of pH conditions. This leads to a weaker pH dependence of the ion uptake by C-A-S-H compared to Al free C-S-H.

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Micro X-ray diffraction investigation of the reaction products formed by the alkali-silica reaction in concrete structures

Dähn, R.[1], Arakcheeva, A.[2], Schaub, P.[1], Pattison, P.[3,4], Chapuis, G.[4], Grolimund, D.[5], Wieland, E.[1], Leemann, A.[6]

[1] *Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland*
[2] *Phase Solutions Ltd., Lausanne, Switzerland*
[3] *European Synchrotron Radiation Facility, Swiss–Norwegian Beam Lines, Grenoble, France*
[4] *Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Crystallography, Lausanne, Switzerland*
[5] *Paul Scherrer Institut, Swiss Light Source, Villigen PSI, Switzerland*
[6] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*

Corresponding author: rainer.daehn@psi.ch

Alkali-silica reaction (ASR) is one of the most important deterioration mechanism in concrete leading to substantial damages of structures worldwide. Synchrotron-based micro-X-ray diffraction (micro-XRD) was employed to characterize the mineral phases formed in micro-cracks of concrete aggregates as a consequence of ASR. This high spatial resolution technique enables to directly gain structural information on ASR products formed in a 40-year old motorway bridge damaged due to ASR. Micro-X-ray-fluorescence was applied on thin sections to locate the reaction products formed in veins within concrete aggregates. Micro-XRD pattern were collected at selected points of interest along a vein by rotating the sample and revealed that the newly formed phase in the cracks is crystalline. Rietveld refinement determined the structure of the ASR product consisting of a new layered framework similar to mountainite and rhodesite. It is conceivable that understanding the structure of the ASR product may help developing new technical treatments inhibiting ASR.

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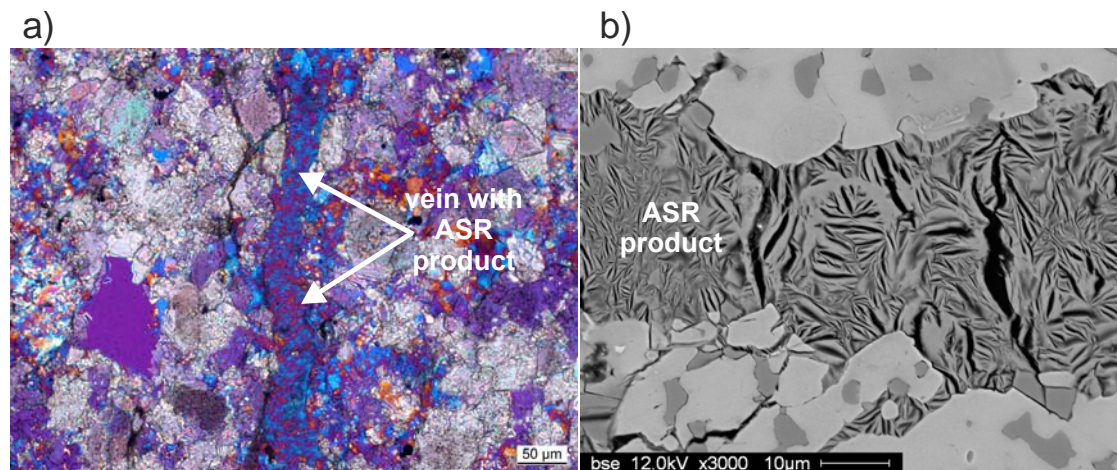
a)   b)

Figure 1: (a) Optical image of the ASR product in the concrete aggregate obtained with a polarization microscope. Crossed polarizers with inserted gypsum plate. (b) SEM image of the vein with ASR product in the concrete aggregate. The light grey mineral of the aggregate is calcite, the dark grey ones are quartz and feldspar.

Synthesis and characterisation of high Ca/Si ratio calcium silicate hydrates – towards better understanding of growth kinetics and atomic structure

Kumar, A.[1)], Scrivener, K.L.[2)], Bowen, P.[1)]

[1)] *Ecole Polytechnique Fédérale de Lausanne (EPFL), Powder Technology Laboratory, Lausanne, Switzerland*
[2)] *Ecole Polytechnique Fédérale de Lausanne (EPFL), Construction Material Laboratory, Lausanne, Switzerland*

Corresponding author: abhishek.kumar@epfl.ch

A better understanding of the kinetics, growth mechanism and atomic structure of calcium silicate hydrate (C-S-H) will provide us with knowledge in assessing new alternative material for substitution of clinker on more scientific basis rather than trial and error. The real cement system is too complex to perform such kind of studies due to the presence of many phases. Hence, we have adopted a synthetic approach to precipitate C-S-H and gain more insight to the kinetics and growth mechanism of C-S-H. According to the state of the art in synthetic systems, it has been very difficult to achieve higher Ca/Si ratio (1.7~ 1.9) with the highest reported ratio of Ca/Si ratio around 1.6 whereas in real systems it is often > 1.6. The aim of this project is to synthesize C-S-H via a precipitation route at Ca/Si ratio varying from 0.7 to 2 with high uniformity (~ nm range).

The precipitate is separated after 3 hours of reaction, washed and filtered over a 200 nm filter. The collected solid and the aqueous phase has been characterized by XRD, TGA, ICP, FTIR, Raman, SEM-TEM, BET and ^{29}Si NMR. The results confirmed the formation of high Ca/Si: 2, with $Ca(OH)_2$ less than 1 wt%. This has been achieved for the first time in any synthetic system. Also, on comparison with thermodynamic modeling software i.e. Gibbs energy minimization software (GEMS) a good match was found when the formation of $Ca(OH)_2$ is prohibited in the simulations. The produced precipitate remains stable (in its pore solution) for a period of 12 months with no noticeable changes, either in its stoichiometry or its morphology (foil-like particle). Also, conditions for the precipitation of a Ca/Si ratio from 1 to 2 could be predicted using GEMS, and results were reproducible. The structural characterization and kinetics data (pH, Ca^{2+} ion concentration, reactant, conductivity) of uniformly precipitated C-S-H will be further used to develop a new structural model and growth equation.

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Atomistic structure of C-S-H from defective tobermorite structures: Variations of defects and features

Kunhi Mohamed, A.[1], Galmarini, S.C.[2], Bowen, P.[3], Scrivener, K.L.[1]

[1] *Ecole Polytechnique Fédérale de Lausanne (EPFL), Construction Material Laboratory, Lausanne, Switzerland*
[2] *Empa, Dübendorf, Switzerland*
[3] *Ecole Polytechnique Fédérale de Lausanne (EPFL), Powder Technology Laboratory, Lausanne, Switzerland*

Corresponding author: aslam.kunhimohamed@epfl.ch

Understanding the underlying mechanisms of cement hydration has been quite difficult due to the complexity of the system and its continued reaction over time making it hard to observe experimentally. Although atomistic simulations might be useful to study how the presence of different species affect the nucleation and growth of hydrates, the atomic structure of calcium silicate hydrate (C-S-H), the main hydrate phase, is not clearly known or agreed upon and remains an open question. Proposed structures of C-S-H have been mainly based on tobermorite and a model structure is created by introducing defects in the original non-defective tobermorite structure. A defective structure matching the Ca/Si ratio needed is simply created by depolymerizing Si chains and/or by addition of Ca in the interlayer space. In a recent work, Galmarini et. al [1] explored the stability of possible defects from the structural and energetic point of view using classical molecular dynamics and DFT. This work aims at exploiting these identified stable defective structures to create a realistic C-S-H structure. Given the fact that the structure of a non-defective 14 Å tobermorite itself is quite complicated, we propose a new methodology to easily represent and visualize the structure by breaking the unit cell into smaller units (bricks). This methodology will be then used to combine different defects in a bulk structure and study its stability using genetic algorithm and molecular dynamics simulations.

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A microscopic model for equilibria of phases and at interfaces in the SiO$_2$-CaO-H$_2$O system: Application of the reactive ensemble

Labbez, C.[1], Churakov, S.V.[2,3], Pegado, L.[1], Nonat, A.[1]

[1] *Université Bourgogne et Franche-Comté, ICB, UMR 630, CNRS, Dijon, France*
[2] *Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland*
[3] *University of Bern, Bern, Switzerland*

Corresponding author: christophe.labbez@u-bourgogne.fr

Ion uptake by cement hydrates and in particular by C-S-H, is one of the key parameters governing the ion transport, liquid and solid phase speciation, paste stability and finally the cohesion of cementitious materials. Equilibria of phases and at hydrate/solution interfaces, that is phase compositions and ion adsorption, are typically dealt with using phenomenological models combined with classical surface complexation models and/or solid solution models. Here, we introduce the basis of a microscopic model in the reactive ensemble that goes beyond this classical approach, where all individual ions, active surface sites, interfaces and chemical reactions are treated explicitly. Such a model is developed for the SiO$_2$-CaO-H$_2$O system and solved by Monte Carlo simulations. The obtained results (solubilities, phase compositions and equilibria, ion adsorption, interfacial electrokinetic properties, etc.) are compared with experimental data. Finally, we discuss the limits, potentialities and advantages of the proposed microscopic model in regard to, as well as its complementarity with, molecular and pheno-menological models.
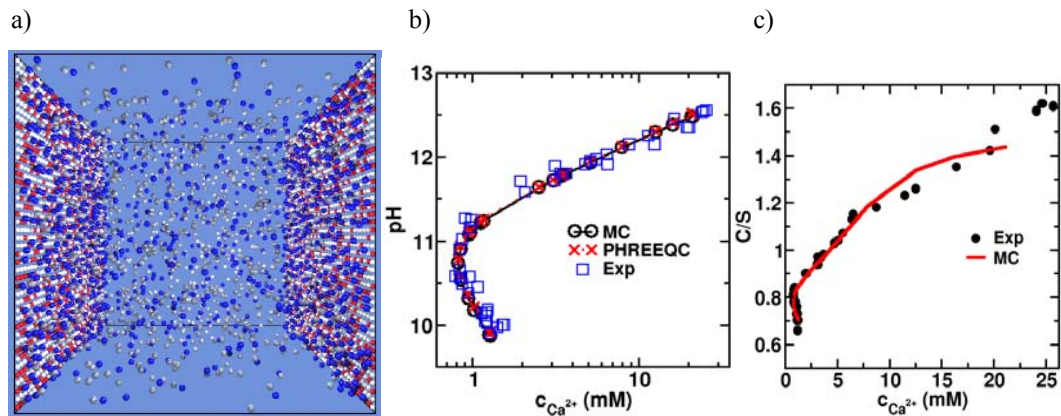
Figure 1: a) Snapshot of a Monte Carlo simulation in the reactive ensemble; b) Predicted C/S ratio of C-S-H (MC) in comparison with experimental data. c) Predicted solution pH (MC) in comparison with pH values at equilibrium in the SiO$_2$-CaO-H$_2$O system varying the calcium content obtained from experiments and from PHREEQC calculations.

Development of atomistic force field and interfacial study of cementitious minerals

Mishra, R.K.[1,2], Jamil, T.[1,4], Flatt, R.J.[2,3], Heinz, H.[4]

[1] *University of Akron, Department of Polymer Engineering, Akron, USA*
[2] *ETH Zurich, Institute for Building Materials, Zurich, Switzerland*
[3] *Sika Technology AG, Zurich, Switzerland*
[4] *University of Colorado-Boulder, Department of Chemical and Biological Engineering, Boulder, USA*

Corresponding author: rkmishra@ethz.ch

We present and validate atomistic force field models of cementitious minerals, such as tricalcium silicate, tricalcium aluminate, dicalcium silicate, calcium sulphate (anhydrite, bassanite and gypsum), lime, portlandite and tobermorite. The atomistic model based on interface force field [1-3] parameters provides a wide range of properties such as densities, surface energies, solid-water interface tensions, anisotropies of interfacial energies of different crystal facets, structural (IR and Raman spectra) properties, thermal and mechanical properties. More importantly, simulated values show excellent agreement with experimentally determined ones. Applications of validated models include: adsorption energies of organic molecules on various mineral surfaces, mechanisms of molecular interactions, modelling of pH-dependent mineral surfaces, and incorporation of impurities in crystal lattice [4] etc.

Our validated models using molecular dynamics simulations in all-atomic resolution aid in understanding molecular-level processes related to grinding of cement clinkers, adsorption of organic additives, effects of aluminate ions in blended cement and the action of superplasticizers on hydrated phase of cement.

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Spectroscopic investigations of the Mg speciation at the cement-clay interface

Vespa, M.[1], Lothenbach, B.[2], Jenni, A.[3], Dähn, R.[4], Huthwelker, T.[5], Wieland, E.[4]

[1] *Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, Karlsruhe, Germany*
[2] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*
[3] *University of Bern, RWI, Institute of Geological Sciences, Bern, Switzerland1)*
[4] *Paul Scherrer Institut, Laboratory for Waste Management, Villigen PSI, Switzerland*
[5] *Paul Scherrer Institut, Swiss Light Source, Villigen PSI, Switzerland*

Corresponding author: marika.vespa@kit.edu

Cement is an important constituent of the engineered barrier systems in underground repositories for high (HLW) and low and intermediate level (L/ILW) radioactive waste. It is used for the construction and backfilling of the cavern within the L/ILW and as liner for the HLW tunnelling system. Cement is a highly heterogeneous and alkaline material with pH >12. Within a geological deep repository it is in direct contact with the host rock. In Switzerland as well as in other countries in Europe clay formations are considered to be a potential host rock. In Switzerland the argillaceous rock formation foreseen for deep geological disposal is the so called Opalinus clay (OPA). The chemical gradients at interface between OPA (near neutral pH of the pore water) and the alkaline cement gives rise to mineral reactions, impacting the retention of the radionuclides and the gas release out of the repository. Thus, it is important to study this interface in order to better understand the processes occurring.

Investigations at the cement-clay interface using different cements, a low alkali cement (LAC) and a silica fume rich cement (ESDRED), are currently being carried out at the Mont Terri underground rock laboratory in the framework of the Cement - OPA Interaction (CI) experiment. The investigations have shown that the reaction zone at the cement - OPA interface is relatively narrow, i.e. in the range of a few mm [1]. Furthermore, it has been observed that Mg is enriched at the interface. X-ray diffraction data did not reveal any Mg-rich minerals, indicating that Mg is accommodated by an amorphous phase. X-ray absorption spectroscopy (XAS) is a versatile tool to study such amorphous phases at the micro-meter scale. Spectroscopic investigation at the Mg K-edge show that a Mg silicate sheet-like structure has formed. Moreover, the fingerprinting analysis of the XAS spectra reveal that a possible mixture of Mg-Si-hydrate (M-S-H) and Mg-Ca-Si-hydrate (M-C-S-H) phases has formed in the LAC-OPA system, whereas in the ESDRED-OPA system a further mineral, presumably talc, could be involved. The results suggest that the mineral composition at the interface between cement and OPA is independent of the type of cement used, and that Mg plays a major role.

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Topic 5: Deteroriation and Leaching

Reactive transport and double porosity in concrete: Experiments and modelling

Chaparro, M.C.[1,2,3], Soler, J.M.[2,3], Saaltink, M.W.[1,3], Mäder, U.K.[4]

[1] *Universitat Politècnica de Catalunya (UPC), Department of Civil and Environmental Engineering, Barcelona, Spain*
[2] *CSIC, Institute of Environmental Assessment and Water Research (IDAEA), Barcelona, Spain*
[3] *Associated Unit: Hydrogeology Group (UPC-CSIC)*
[4] *University of Bern, Rock-Water Interaction, Institute of Geological Sciences, Bern Switzerland*

Corresponding author: m.carme.chaparro@upc.edu

A laboratory-scale test was carried out to characterize the transport properties of concrete from the Radioactive Waste Disposal Facility at El Cabril (Spain). A hyperalkaline solution (K-Ca-OH, pH=13.2) was injected into the concrete under a high entry pressure in order to perform the experiment in a reasonable time span. The concentrations of major elements (Ca^{2+}, SO_4^{2-}, K^+ and Na^+) and pH were measured at the outlet of the concrete sample. A reactive transport model was built based on a previous conservative transport model, which considers diffusion between a mobile zone, where water can flow, and an immobile zone without any advective transport [1]. The numerical model takes into account the mineralogy that was identified by X-ray diffraction. The cement paste consists of C-S-H gel, portlandite, ettringite, calcite and gypsum, together with residual alite and belite. Overall the results show mineral dissolution in the mobile zone and mineral precipitation in the immobile zone. The numerical model shows dissolution of alite, belite and gypsum. As a consequence, C-S-H gel, porlandite, ettringite and calcite precipitate. These mineralogical changes produce small changes in porosity, with increased values at the inlet of the mobile zone and decreasing values in the immobile zone.

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Modelling of boric acid attack of ordinary Portland cement paste

Chomat, L.[1], Benakli, A.[1], Le Bescop, P.[1], Wall, J.[2]

[1] *CEA, DEN/DPC/SECR, Laboratory of Study of Concrete and Clay Behavior, Gif-sur-Yvette, France.*
[2] *EPRI, Electric Power Research Institute, Charlotte, USA*

Corresponding author: laure.chomat@cea.fr

In the framework of Spent Fuel Pools lifetime studies, an investigation of the concrete degradation in aqueous boric acid has been requested by the Electric Power Research Institute. The main goal of this study is to identify the physico-chemical degradation mechanisms involved in a boric acid medium. A well-tested methodology for testing cementitious materials degradation in other solutions (water, sulfate solution…) was applied. This methodology was based on an experimental study and computational modelling. The degradation experiments were carried out for three to eight months in 2400 ppm boric acid solution. Aggressive solution conditions were maintained by pH regulation and periodical renewal. Characterization concerned the composition of the degradation solution during the experiments, as well as the mineralogical evolution of the degraded cementitious materials at the end of the experiments. Solution analysis was performed by ion chromatography and solid characterization was carried out by the means of XRD and SEM observations. The study of the Portland cement paste degradation shows that the leaching mechanism is driven by diffusion. The degradation kinetics in boric acid is higher than the one in pure water. Reactive transport numerical simulations were carried out with the HYTEC platform to be compared with experimental results. The modelling results reproduce the four zones composing the degraded Portland cement paste profile pattern that were identified experimentally. It is also demonstrated that the definition of the modelled system and of the external part of the degraded zone are the key points.

A study on the diffusion coefficient of the hardened cement leached by ammonium nitrate solution

Haga, K.[1], Shibata, M.[1], Kurumisawa, K.[2], Hayashi, D.[3], Owada, H.[3]

[1] *Taiheiyo Consultant Co., Tokyo, Japan*
[2] *Hokkaido University, Faculty of Engineering, Sapporo, Japan*
[3] *Radioactive Waste Management Funding and Research Center, Tokyo, Japan*

Corresponding author: Kazuko_Haga@taiheiyo-c.co.jp

In radioactive waste disposal, it is necessary to predict a change in the performance of cementitious materials. For this purpose, the elucidation of the leaching alteration phenomena of the cementitious material should be considered an important technical issue. To assess the change of diffusion coefficients due to leaching, it is necessary to produce homogeneous leached samples. However, it is extremely difficult to produce the leached samples homogeneously in a short time. As a method for dissolving the hardened cement pastes homogeneously, a method based on immersing in ammonium nitrate solution has been proposed [1]. In this study, changes in the mineral phase and the pore structure and a diffusion coefficient of hardened cement pastes due to leaching were determined by preparing a leached cement paste immersed in ammonium nitrate solution. It was possible to vary the leaching ratio by changing the weight ratio of ammonium nitrate to sample. In the sample obtained after the leaching test, the volume of the pores larger than 20 nm in diameter was enhanced. Fig.1 shows the relationship between porosity and diffusion coefficient. This porosity corresponds to the volume percentage of the pores having a diameter larger than 20 nm. There is a good correlation between the pore volume and the diffusion coefficient. Thus, the increase in pore volume due to leaching was found to affect the diffusion coefficient.
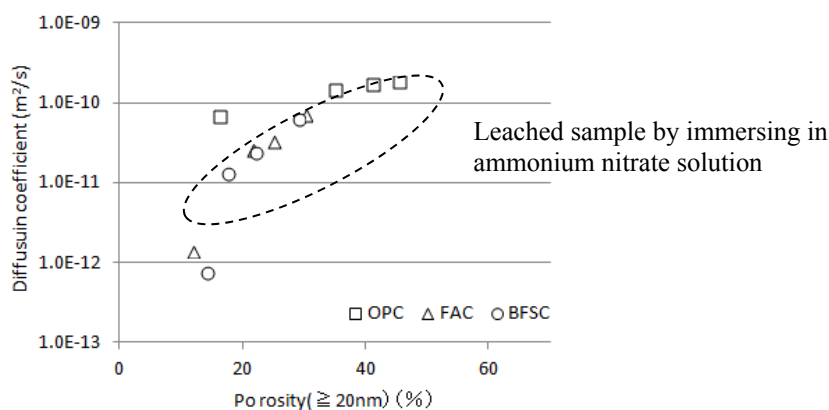

Figure 1: Relationship between porosity (pores $\geqq$ 20 nm) and diffusion coefficient.

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Carbonation resistance of calcium sulfoaluminate cement mortars

Hargis, C.W.[1)], Winnefeld, F.[1)], Müller, C.J.[2)], Lothenbach, B.[1)]

[1)] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*
[2)] *Saint-Gobain Weber AG, Winterthur, Switzerland*

Corresponding author: Craig.Hargis@empa.ch

Calcium sulfoaluminate (CSA) cements are promoted as more environmentally friendly alternatives to ordinary Portland cements due to their lower CO_2 emissions during manufacturing and their ability to be made from a variety of waste feedstock promoting industrial ecology [1-2]. Additionally, the utilization of CSA cements to immobilize hazardous wastes has been proposed [3-4]. During the hydration of CSA cement, AFm phases ($[Ca_2(Al,Fe)(OH)_6]\cdot X\cdot yH_2O$, where X denotes 1 singly or ½ of a doubly charged anion, and y denotes a variable water content) and AFt phases ($[Ca_3(Al,Fe)(OH)_6\cdot 12H_2O]_2\cdot X_3\cdot yH_2O$, where X denotes 1 doubly or with reservations 2 singly charged anions and y denotes a variable water content) are produced in abundance [5]. AFm phases have a double layer structure and a strong ability to bind substituting ions, with trivalent cations, such as Cr^{3+}, substituting for Al^{3+} and anions substituting readily in the water rich interlayer.
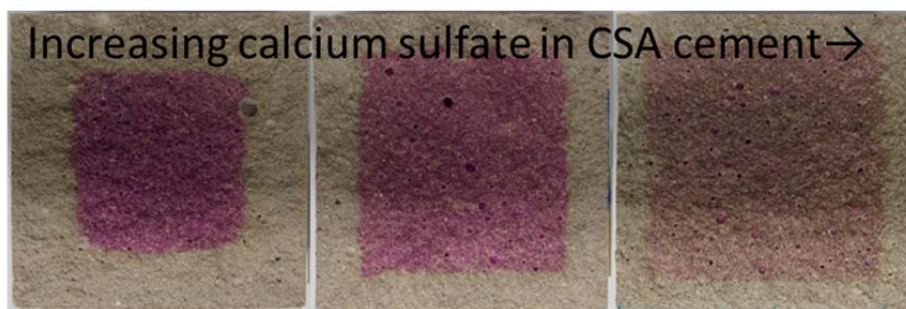

Figure 1: Carbonation front in three CSA mortars with increasing calcium sulfate contents from left to right indicated by phenolphthalein on fractured surface.

Carbonation of the hydration products poses a threat to the long-term durability of CSA cement. Additionally, the chemical reaction between CO_2 and AFm/AFt phases presents a pathway for the release of previously bound chemical species. Utilizing a combination of experiments and thermodynamic modelling, this study sought to elucidate chemical and physical parameters that contribute to the carbonation resistance of CSA cement. It was found that the carbonation resistance of CSA cement depended on (1) the amount of CSA clinker per unit volume of mortar and (2) reaction kinetics of the CSA cement, which was accelerated by higher calcium sulfate contents in the cements.

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Diffusivity of altered hardened cement paste by 3D spatial image model

Kurumisawa, K.[1], Haga, K.[2], Hayashi, D.[3], Owada, H.[3]

[1] *Hokkaido University, Faculty of Engineering, Sapporo, Japan*
[2] *Taiheiyo Consultant Co., Tokyo, Japan*
[3] *Radioactive Waste Management Funding and Research Center, Tokyo, Japan*

Corresponding author: kurumi@eng.hokudai.ac.jp

It is very important to predict the alteration of concrete that is used for a disposal container for radioactive waste. To this end, it is necessary to understand the alteration of cementitious materials caused by calcium leaching in contact with the ground water in the long term. To evaluate the transport characteristic of cementitious materials in the long term, the microstructure of cementitious materials will be altered by external impact, which requires the microstructure of cementitious materials to be considered in these studies. However, many predictive models of transport characteristic focus on the pore structure, while there are only few predictive models of transport characteristic that consider the spatial distribution of C-S-H, portlandite, and pore space. This study focused on the spatial distribution of these cement phases. The auto–correlation function of each phase of cementitious materials was calculated from 2–D backscattered electron imaging, and the 3–D spatial image of cementitious materials was estimated by using the auto–correlation functions [1]. An attempt was made to estimate the diffusion coefficient of chloride from the 3–D spatial image. The estimated diffusion coefficient of the deteriorated sample from the 3–D spatial image was comparable to the measured value as shown in Figure 1. This shows that it is possible to predict the diffusion coefficient of altered cement paste by the proposed model.
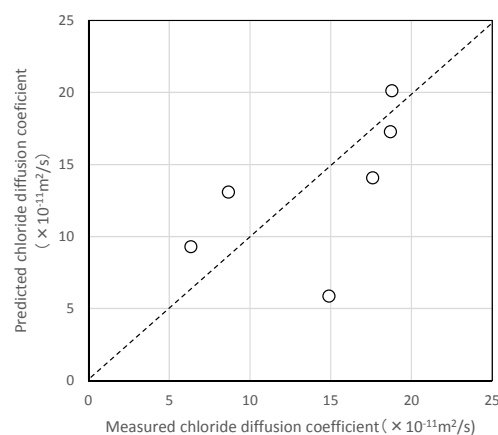

Figure 1: Plot of measured and predicted chloride diffusion coefficient of deteriorated cement pastes.

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Transport properties of cement model system (C_3S and C-S-H): Experiments dedicated to implement a new approach of the microstructure / diffusion properties relation in the reactive transport code

L'Hôpital, E.[1], Seigneur, N.[2], Voutilainen, M.[3], Dauzères, A.[1]

[1] *IRSN, PRP-DGE/SRTG/LETIS, Fontenay-aux-Roses, France*
[2] *Université Libre de Bruxelles,, Brussels, Belgium*
[3] *University of Helsinki, Helsinki, Finland*

Corresponding author: emilie.lhopital@irsn.fr

The current option for the future radioactive waste geological disposal chosen by France involves a structure based on a large amount of cementitious materials in contact with a clayey environment. Such environmental condition, on a long time scale, will undergo chemical modification such as leaching or/and carbonation of the cementitious material. Reactive transport modelling is an important tool to predict the evolution of the cementitious structure. However, it has been observed that actual models do not reproduce correctly the evolution and perturbation of an experimental degraded area due to the fact that Archie's law is not sufficient to describe the behaviour of multi-porous material (abstract Nicolas Seigneur). A valuable experimental data set is needed for the implementation of a new approach in the reactive transport codes. The purpose of this work was to investigate the microstructure and the diffusive properties of cement model system (C_3S and C-S-H).

C_3S hydrated paste were synthetized with C_3S (mineral research processing) and milli-Q water with solid to water ratio (s/w) of 0.47. C-S-H with different stoichiometry (calcium to silica ratio (Ca/Si) = 0.8 and 1.7) were synthetized with calcium oxide (VWR chemical), silica fume (Aerosil 200, Evonik) and milli-Q water with a solid to water ratio (s/w) of 60. After drying, C-S-H was compacted to form a C-S-H disk used for the diffusion test. The microstructure will be analysed with a multi-scale approach. Autoradiography allows the determination of the meso and macro-porosity. Micro-tomography allows the quantification of the different phases (macro-porosity, C-S-H, portlandite and C_3S) and determines the fraction of connected phases. TGA allows the detection and the quantification of portlandite. The diffusion coefficient was determined with a set of through diffusion tests. The diffusion cells are composed of two reservoirs (upstream and downstream reservoir) and one sample holder. Each reservoir was filled with a solution in chemical equilibrium with the sample. In the upstream reservoir, approximately 1 mmol/L of lithium chloride (and 1mmol/L of caesium chloride for the C_3S paste and the high Ca/Si C-S-H) was added to follow diffusion through the sample. Over time, pH was measured and the solution composition was analysed with ion chromatography (for chloride), ICP-OES (for lithium) and ICP-MS analyses (for caesium).

The results show that the C_3S paste porosity is composed of 4±1 vol.% of not connected macro-porosity($\geq$ 0.9 μm), 49±5 %vol of meso-porosity ($\geq$ 2 nm). The preliminary results from the diffusion tests show that, at low Ca/Si ratio, lithium and chloride ions diffuse relatively fast and reach a study state after 15 to 45 days. No preference between anion and cation regarding the diffusion though the C-S-H was observed. A first estimate of the effective diffusion coefficient is $\approx 4.10^{-12}$ m^2 s^{-1}. At high Ca/Si ratio and in the C_3S paste, lithium does not diffuse through the structure, while some chloride diffusion was observed. A new data set is actually running to confirm the first results. The degradation process such as leaching and carbonation will also be studied in the second part of the project in order to follow the evolution of the microstructure and the impact on the diffusion process.

Modelling of chemical degradation of blended cement-based materials by leaching cycles with Callovo-Oxfordian porewater

Olmeda, J.[1], Henocq, P.[2], Giffaut, E.[2], Grivé, M.[1]

[1] *Amphos 21 Consulting S.L., Barcelona, Spain.*
[2] *Andra, Châtenay-Malabry, France.*

Corresponding author: mireia.grive@amphos21.com

The French radwaste geological disposal project Cigeo has been designed in the Callovo-Oxfordian formation, including massive concrete packages and structures in the context of the Intermediate Level Long Lived Wastes (IL-LLW). The long term chemical evolution of these cement-based materials is especially relevant to account for the radionuclides behaviour.

The leaching process of soluble components from cement-based material is driven by the difference of composition and chemical activity between the clay porewater and the cementitious pore solution leading to evolution in porewater composition and mineral structure. Leaching experiments in cementitious systems typically show different dissolution fronts from the boundary aqueous solution towards unaltered core [1, 2]. This work describes modelling simulations of the chemical evolution of cementitious material by its interaction with external Callovo-Oxfordian porewater inflow and how the evolution of its contact porewater is able to reproduce laboratory degradation experiments. Two approaches are considered: (i) renewing porewater by a leaching cycle procedure and (ii) a reactive transfer model applied to a hardened system in contact with the host-rock porewater.
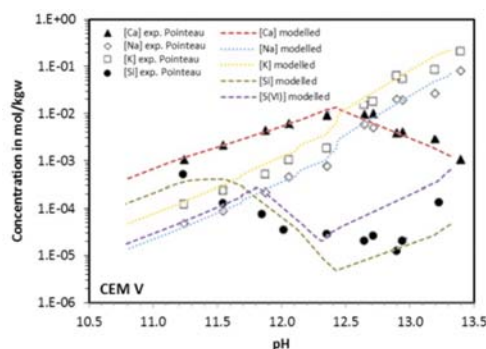

Figure 1: Evolution of [Ca], [Na], [K] and [Si] as a function of pH in solution. Lines represent data modelled in this work and symbols experimental data [3].

A consistent thermodynamic model with a mass-balance approach is used to calculate the geochemical changes during chemical interactions of cementitious materials with external inlet water. Calculations have been performed at 25 ºC using an up-to-date thermodynamic database (ThermoChimie v.9.0 [4]). The model replicates experimental data with a high level of accuracy (Figure 1). Further, the employed database is also capable to reproduce reasonably the fate (precipitation/dissolution) of cementitious minerals in a complex cementitious phase system. The approach followed in this study allows an in-depth analysis of the chemical evolution in both solution and solid phase to obtain a fast assessment of the geochemical effects associated to an external water intrusion of variable composition on concrete structures.

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Multi-scale modelling of calcium leaching in cement-based materials

Patel, R.A.[1,2], Perko, J.[2], Jacques, D.[2], Seetharam, S.C.[2], De Schutter, G.[1], Ye, G.[2,3], Van Breugel, K.[3]

[1] *Ghent University, Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent, Belgium*
[2] *Belgian Nuclear Research Centre (SCK•CEN), Mol, Belgium*
[3] *Delft University of Technology, Microlab, Delft, The Netherlands*

Corresponding author: rpatel@sckcen.be

Calcium leaching is an important deterioration mechanism to be accounted for in the service life analysis of structures in contact with water such as a subsurface nuclear waste disposal system. Calcium leaching leads to the dissolution of crystalline minerals such as portlandite and decalcification of amorphous C-S-H phase. This leads to the increase in porosity and, in turn, in further increase in diffusivity and permeability of cement based materials and decrease in the mechanical strength. The progression of leaching fronts is slow in nature with up-to few mm in hundred years. Hence leaching is often studied under accelerated experimental conditions using aggressive solutions such as deionized water or ammonium nitrate solutions. Alternatively, predictive multi-scale models, which can account for geochemical and microstructural changes occurring in the concrete (from nano- to macro-scale) during leaching, can be developed. Such models serve as powerful tools to investigate the influence of calcium leaching under various environmental conditions on the performance of cement-based materials.

An integrated numerical approach to simulate leaching at the micro- and meso-scale has been developed. The geochemical reaction network is implemented with an abstracted reaction model. At the micro-scale, the evolution in transport properties of C-S-H (alteration in C-S-H structure at the nano-scale) is accounted for by using a two-scale analytical homogenization scheme. Two different homogenization schemes are analysed: a closed-form continuum micromechanics solution and an asymptotic homogenization approach. The appropriate homogenization approach is selected by comparing simulations from the equivalent homogenised model with those of a detailed micro-scale model. The micro-scale homogenized model is subsequently used at the meso-scale for both hardened cement paste and the interfacial transition zone (ITZ). Again, two different homogenization techniques are tested at the meso-scale. A suitable approach is then identified by comparing the simulations from the equivalent homogenised model with those of a detailed meso-scale model. The resulting homogenized macro-scale model describes the changes at different scale in concrete during calcium leaching.

Changes in diffusion properties of cement paste induced by leaching and carbonation accounting for the effects of limestone fillers and water/powder ratio

Phung, Q. T.[1], Maes, N.[1], Jacops, E.[1], Jacques, D.[1], De Schutter, G.[2]

[1] *Belgian Nuclear Research Centre (SCK•CEN), Institute for Environment, Health, and Safety, Mol, Belgium*
[2] *Ghent University, Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent, Belgium*

Corresponding author: quoc.tri.phung@sckcen.be

To assess the long-term performance of concrete used as engineered barrier for disposal of radioactive waste, the knowledge of the diffusive transport characteristics is important because diffusion plays a key role in most of the chemical degradation processes (governs the transport of reactive species responsible for degradation). Alteration of the microstructure, due to degradation, induces changes in diffusivity. This work quantitatively studies to what extent the diffusivity of cement pastes changes as a result of carbonation and Ca-leaching. The experiments were performed on cement paste samples with different water/powder (w/p) and limestone filler (LS) replacement ratios. Ca leaching was performed using an ammonium nitrate solution of 6 mol/l to accelerate the process. Carbonation was performed by controlled "purging" of the samples with pressurized pure CO_2. To investigate the changes in diffusive behavior, a through-diffusion method was applied in which non-reacting dissolved gases were used as diffusing species. To characterise the microstructural changes, different post-analysis techniques including SEM, MIP, and N_2-adsorption were used.

Higher w/p ratios and LS replacements increased the degree of carbonation and leaching, hence the degree of degradation. Changes in w/p ratios had a more significant effect. The accelerated leaching significantly altered the microstructure, while the alteration extent for carbonation was lower. But both, led to a significant, but opposite, modification in diffusivity depending on the degradation state. After 28 day carbonation, the diffusivity of carbonated zone decreased by a factor of 5. On the other hand, the modification for the leached zone was more pronounced, as the diffusivity increased by more than one order of magnitude.

A new microstructure-based analytical and numerical approach to describe the diffusive transport properties evolution in model cement pastes during degradation

<u>Seigneur, N.</u>[1], L'Hôpital, E.[2], Dauzères, A.[2], Dubus, A.[2], Labeau, P-E.[1]

[1] *Université Libre de Bruxelles, Brussels, Belgium*
[2] *IRSN, PRP-DEE/SRTG/LETIS, Fontenay-aux-Roses, France*

Corresponding author: nseigneu@ulb.ac.be

When trying to assess the long-term safety of radioactive waste management solutions, the durability of the engineered barriers, often consisting of cementitious materials, is an important matter. Whether it is from infiltrated water or from chemical interactions at clay interfaces, these materials will undergo porosity-modifying reactions. So far, research has not been able to fully understand the effects of chemical degradations at the micro- and nano-scale. The extent of the physicochemical perturbation, which could compromise mechanical and diffusion properties, is controlled by the effective transport properties of the materials. For cementitious materials, there exists no suitable law able to predict those properties, neither for the sound materials, nor for the degraded ones. Archie's law and other more sophisticated homogenization schemes fail to capture the sensitive evolution of the pore network and its impact on diffusivity.

This research aims to a better understanding of these effects, by focusing on model cementitious materials. Three complementary approaches are used: an experimental, a numerical and a mathematical one. The experimental part, described in details in the article of L'Hôpital, E, consists of a delicate characterization of the microstructure and the diffusive transport properties of both sound and degraded materials. The numerical part aims to replicate these experiences by generating elementary representative volumes of the materials (Figure 1, left). A detailed study of the sound microstructure is given, leading to a good agreement between measured and simulated diffusion coefficient. The evolution of these numerical microstructures is then considered for leaching and carbonation and preliminary results are presented and confronted to experimental results. The mathematical part consists of a new homogenization scheme based on a statistical description of the diffusive transport. A quite simple and innovative model is described. The latter brings out some key features to establish the link between microstructure and the effective transport properties, such as generalized-chord-length distributions. Its results are in very good agreement with numerical simulations (Figure 1, right), which gives confidence about this new approach and its further development.
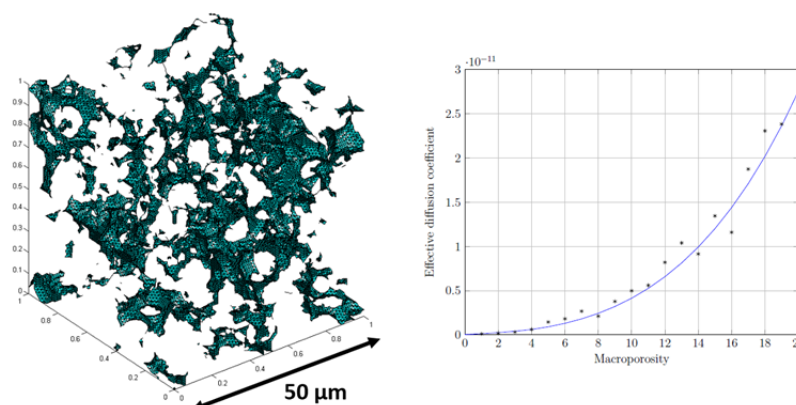

Figure 1: Left: Macroporosity inside the numerical representative elementary volume. Right: Simulated diffusion coefficients of REVs (dots) compared to modelling results.

Impact of cations on chloride binding in hydrated portland cement – metakaolin – limestone blends

Shi, Z.[1], Geiker, M.R.[2], De Weerdt, K.[2], Østnor, T.A.[3], Lothenbach, B.[4], Winnefeld, F.[4], Skibsted, J.[1]

[1] *Aarhus University, Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus, Denmark*
[2] *Norwegian University of Science and Technology (NTNU), Department of Structural Engineering, Trondheim, Norway*
[3] *SINTEF Building and Infrastructure, Trondheim, Norway*
[4] *Empa, Laboratory for Concrete and Construction Chemistry, Dübendorf, Switzerland*

Corresponding author: zshi@chem.au.dk

The chloride binding has been investigated for three well-hydrated paste samples made from pure Portland cement (P), 65 wt.% Portland cement – 35 wt.% metakaolin (M), and 65 wt.% Portland cement – 26.25 wt.% metakaolin – 8.75 wt.% limestone (ML). The samples have been exposed to NaCl and $CaCl_2$ solutions with chloride concentrations of 0, 0.125, 0.25, 0.5, 1.0 and 2.0 mol/L. Chloride binding isotherms are obtained by potentiometric titration. The pH of the exposure solution is determined and the amounts of Friedel's salt are quantified using thermo-gravimetric analysis (TGA). The changes in phase assemblages, pH and Ca concentration in the exposure solution are predicted by thermodynamic modelling.

The results show that the use of metakaolin as an supplementary cementitious material (SCM) increases the chloride-binding capacity compared to P sample and to a similar extent for both the ML and M samples, regardless of the addition of limestone. This is mainly attributed to the formation of a larger quantity of Friedel's salt in the ML and M samples rather than to the formation of more C-S-H with a lower Ca/Si ratio, as compared to the C-S-H in the P sample, since a lower Ca/Si ratio of the C-S-H phase is known to lower the chloride binding capacity [1]. The results also show that the chloride binding increases significantly for the samples exposed to a $CaCl_2$ solution rather than to a NaCl solution. For the P sample, this is ascribed to the higher Ca/Si of the C-S-H for samples exposed to the $CaCl_2$ solution, since the amount of Friedel's salt is independent on the types of cations according to the TGA data and thermodynamic calculations. However, the thermodynamic modeling clearly shows that the increased chloride binding for the ML and M samples exposed to $CaCl_2$ is ascribed to formation of a larger amount of Friedel's salt. Moreover, the higher Ca/Si ratio of the C-S-H for the ML and M samples exposed to the $CaCl_2$ solution may also contribute to an increased chloride binding. The pH is found to decrease with increasing $CaCl_2$ concentration, whereas no major changes are observed with increasing NaCl concentration, in accordance with other studies [1,2]. An earlier study of chloride binding in hydrated Portland cement samples [2] has suggested that the measured change in chloride binding for different cations is mainly governed by the pH of the exposure solution and thereby the binding capacity of the C-S-H. However, the increase in chloride binding for the ML and M samples with increasing $CaCl_2$ concentration is mainly ascribed to formation of different amounts of Friedel's salt according to the TGA data and thermodynamic modelling.

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Study on leaching of hydrated cement system by non-destructive integrated CT-XRD method

Sugiyama, T.[1], Takahashi, H.[1], Hitomi, T.[2], Kajiwara, K.[3]

[1] *Hokkaido University, Sapporo, Japan*
[2] *Obayashi Corp. Ltd., Tokyo, Japan*
[3] *Japan Synchrotron Radiation Research Institute, Hyogo, Japan*

Corresponding author: takaf@eng.hokudai.ac.jp

A non-destructive integrated CT-XRD method (hereinafter, CT-XRD) has been developed to study the alteration of hydrated cement system due to leaching. This newly developed CT-XRD allows the determination of both changes in the microstructure and crystals in the hydrated cement system. X-ray computed tomography (CT) clarifies three dimensional microstructure in the hydrated cement system. Then any regions of interest in the space are directed so as to measure X-ray diffraction (XRD). Accordingly, detailed characterization of physical and chemical feature in micro meter's order can be made for the hydrated cement system.
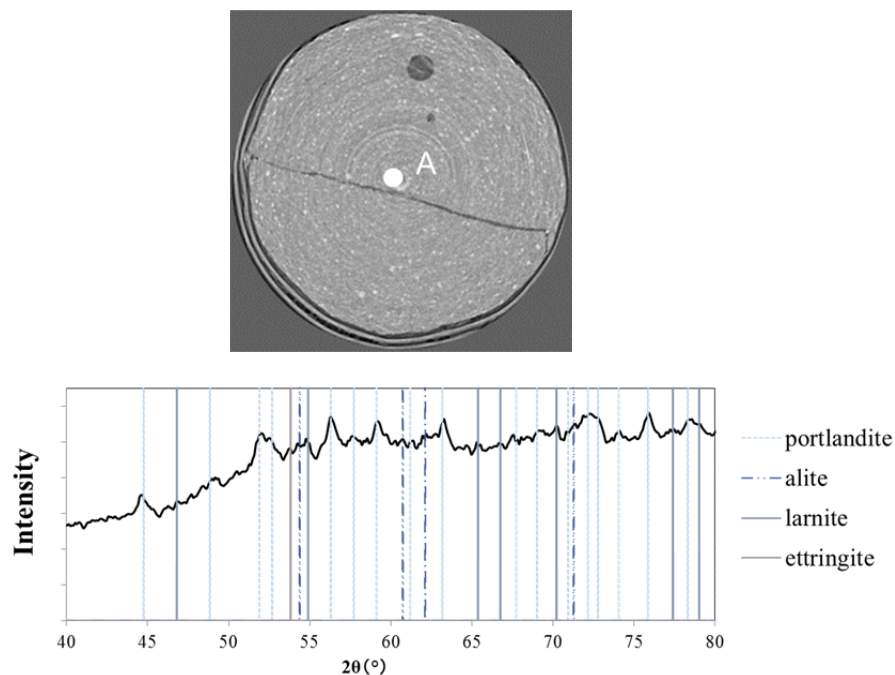

Figure 1: Cross sectional image of cracked cement paste by CT and XRD result at Point A.

In this research the effect of cracks on the leaching behaviour in cement paste subjected to the action of water flow was investigated. Figure 1 shows the cross section of the cracked cement paste before the water attack. Point A in Figure 1 was selected as a region of interest for the XRD. In Figure 1 the result of XRD is also given for Point A where portlandite, larnite, alite and ettringite are identified. The CT-XRD was repeatedly applied to the identical sample but in this time after leaching. In this way we could quantify not only changes in the crack space but also the leaching of portlandite and the formation of calcite in the vicinity of the crack boundary over time and space.

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