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3rd International Workshop

Mechanisms and modelling of waste/cement interactions

Ghent, 06-08 May 2013

NRG

ECN
Energy research Centre of the Netherlands

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3rd International Workshop

Mechanisms and modelling of waste/cement interactions

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Status: Unclassified

Introduction

This workshop is the third in a series of International Workshop on Mechanisms and Modelling of Waste/Cement Interactions. The first workshop was hold in Meiringen, Switzerland in 2005. The second was hold in Le Croisic, France in 2008.

The focus of the workshop is on the chemical understanding and the thermodynamic/kinetic modelling of the processes responsible for the stabilization of hazardous and nuclear wastes in cementitious systems. These processes are both from endogenous origin in the cementitious and waste material or external through geochemical interactions with the surroundings. Critical elements are, amongst others, the geochemical properties of the cementitious materials, the interactions and chemical consequences of the waste cement interactions for both the contaminants and other waste constituents as organics, and alterations of cement-based engineered barriers and of the cement/waste interactions in waste disposal facilities. Understanding and modelling of these processes are crucial aspects in a scientific-based approach for disposal of waste stabilized within cementitous materials or waste containment using cementitous-based engineered barriers.

The workshop is centered on three central themes:

(1) Mechanisms and modeling of cement systems: chemistry and microstructure
with a focus on the kinetics and thermodynamics of cement systems, and nano-scale and molecular modelling.

(2) Mechanisms and modeling of waste-cement or interface interactions
with a focus on sorption of contaminants on cementitious materials, effects of organics, effects of interfaces with waste forms and other engineered or natural materials or water compositions.

(3) Advancement in modelling coupled transport and geochemical alterations in cement systems
covering a wide range of spatial and temporal scales relevant for waste/cement interactions

Beside the scientific objectives of the workshop, the workshop also aims at bridging different research communities such as cement chemistry, nuclear waste and non-radioactive hazardous waste from different fields of interest (regulatory, waste agencies, scientific community and engineering consultancies). It wants to be a forum for both internationally recognized experts in these domains and young or new researchers.

In this way, it is hoped that the workshop stimulates new research domains, methodologies or strategies, and promotes international collaboration.

Programme

MONDAY 6 MAY

8:00 AM	8:30 AM	Registration

8:30 AM	8:40 AM	Welcome and Workshop Introduction

Topic I		Mechanisms and modelling of cement systems: Chemistry and microstructure

Chair		M. Altmaier

8:40 AM	9:10 AM	Local- and partial equilibria in thermodynamic- and transport modeling of cement systems *D.A. Kulik, G. Kosakowski, B. Lothenbach, E. Wieland, U. Berner*
9:10 AM	9:30 AM	HydraHydration of fly ash blended Portland cement at different temperatures *F. Deschner, F. Winnefeld, B. Lothenbach, J. Neubauer*
9:30 AM	9:50 AM	Influence of temperature on the hydration of blended cements *B. Lothenbach, G. Le Saout*
9:50 AM	10:10 AM	Predominant surface reactions towards a kinetic model for the C3S dissolution *L. Nicoleau, BASF C.C. Trostberg*
10:10 AM	10:30 AM	Change of microstructure of hardened cement paste with a low alkali binder due to leaching *T. Sugiyama, I.S. Darma, T. Hitomi, M.A.B. Promentilla*

10:30 AM	10:55 AM	Coffee break

Chair		R. J.-M. Pellenq

10:55 AM	11:15 AM	C-A-S-H thermodynamics modelling in CaO-Al2O3-SiO2-H2O system *J. Haas, I. Pochard, A. Nonat*
11:15 AM	11:35 AM	Crystal structure of nano-sized synthetic CSH *S. Grangeon, F. Claret, C. Lerouge, F. Warmont, T. Sato, Y. Linard, B. Lanson*
11:35 AM	11:55 AM	Determination of the Fe speciation in cementitious materials using synchrotron-based micro-spectroscopic techniques *E. Wieland, R. Dähn, B.Z. Dilnesa, B. Lothenbach*

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11:55 AM	12:15 PM	**Reaction of aluminium with composite cements based on calcium aluminate phosphate system** *P. Swift, H. Kinoshita, C. Utton, N. Collier*
12:15 PM	1:30 PM	Lunch

Chair		U. Berner
1:30 PM	1:55 PM	**Understanding ion adsorption by C-S-H: From ab initio simulations to thermodynamic equilibrium** *S.V. Churakov, C. Labbez, L. Pegado, M. Sulpizi*
1:55 PM	2:20 PM	**Docking 90Sr Radionuclide in Cement: an Atomistic Modeling Study** *R. J.-M. Pellenq*

Topic II		Mechanisms and modelling of waste-cement or interface interactions

Chair		M. Grivé
2:20 PM	2:50 PM	**Actinide solubility and speciation in alkaline CaCl2 brine solutions** *M. Altmaier, D. Fellhauer, X. Gaona*
2:50 PM	3:10 PM	**Competition behavour of metal uptake in cementitious systems** *M. Vespa, R. Dähn, D. Kunz, E. Wieland*
3:10 PM	3:30 PM	**Sorption of actinides onto TiO2, calcium silicate hydrates and hardened cement paste** *J. Tits, A. Laube, E. Wieland*
3:30 PM	3:50 PM	**Nickel, Caesium and Selenium retention by degraded cement** *C. Borkel, M. Grivé, J. Bruno*
3:50 PM	4:15 PM	Coffee break

Short Oral Presentations

Topic I		Mechanisms and modelling of cement systems: Chemistry and microstructure

Chair		G. De Schutter
4:15 PM	4:20 PM	**NEA TDBIV Project: Preparation of a state-of-the art report on thermodynamic data for cements** *P. Blanc, B. Lothenbach, J. Perrone, B. Schwyn*

4:20 PM	4:25 PM	Aluminium and alkali uptake n calcium silicate hydrate *E. L'Hôpital, B. Lothenbach, D.A. Kulik, K. Scrivener*
4:25 PM	4:30 PM	Development of Low-pH Cement Mixtures for Further Use in Radioactive Waste Disposal *P. Večerník, M. Kiselová, V. Havlová*
4:30 PM	4:35 PM	Solubility, hydrolysis and redox behaviour of Np(VI) in alkaline NaCl solutions *X. Gaona, D. Fellhauer, M. Altmaier*
4:35 PM	4:40 PM	Radionuclide sorption at high pH in calcite systems *K. Smith, N. Bryan, , K. Morris*
4:40 PM	4:45 PM	The Effect of Isotope Exchange on the Mobility of Calcium in Cementitious Backfill *J. Hinchliff*
4:45 PM	4:50 PM	Studies of the effect of organic materials and their degradation on radionuclide behavior *R. Beard, T. Beattie, S. Norris, S. Williams*
4:50 PM	4:55 PM	Complexation of Nd(III)/Cm(III) with gluconate in dilute NaCl and $CaCl_2$ alkaline solutions: solubility and TRLFS studies *H. Rojo, X. Gaona, Th. Rabung, M. Garcia, T. Missana, M. Altmaier*
4:55 PM	5:00 PM	Migration of acetate, formate and propionate species in cementitious materials *L. Clément, N. Macé, I. Pointeau, E. Giffaut, N. Marmier*

Poster Session and Drink

5:05 PM	5:30 PM	Poster Session
5:30 PM	7:00 PM	Poster Session + Reception

TUESDAY 7 MAY

Topic II		Mechanisms and modelling of waste-cement or interface interactions
Chair		C. Landesman

8:30 AM	9:00 AM	Geochemical modelling of leaching tests data on cementitious barrier materials as basis for long term release prediction *H. van der Sloot, D. Kosson, J. Arnold, P. Seignette, H. Meeussen*
9:00 AM	9:20 AM	In-diffusion experiments of 36Cl in composite concrete *N. Macé, L. Chomat, J. Page, V. Blin*
9:20 AM	9:40 AM	Radial diffusion of radionuclides through a cementitious

		backfill material *M. Felipe-Sotelo, J. Hinchliff, N.D.M. Evans, D. Read*
9:40 AM	10:00 AM	Combining thermodynamic simulations, element and surface analytics to study U(VI) retention in a corroded cement monolith upon >20 years of leaching *C. Bube, K. Dardenne, M.A. Denecke, V. Metz, J. Rothe, D. Schild, E. Soballa, T. Vitova, B. Kienzler*
10:00 AM	10:20 AM	Predicting long term cement-radionuclide interactions: sensitivity analysis for selected thermodynamic databases *J. C.L. Meeussen, H. A. van der Sloot, D. S. Kosson*
10:20 AM	10:45 AM	Coffee break

Chair		C.A. Rochelle
10:45 AM	11:05 AM	Influence of borate ions on the hydration of calcium sulfoaluminate cement at early age *J.B. Champenois, C. Cau dit Coumes, P. Le Bescop, C. Mercier, B. Revel, L. Petit, D. Damidot*
11:05 AM	11:25 AM	The interaction between nuclear waste glass and cement *K. Ferrand, K. Lemmens*
11:25 AM	11:45 AM	Interactions of americium with cement alteration products in brines *V. Metz, E. Bohnert, C. Bube, K. Garbev, M. Schlieker, B. Kienzler*
11:45 AM	12:05 PM	Radionuclide Retention onto Heat Treated Concrete under Sea Water Conditions *B. Kienzler, N. Finck, S. Hilpp, V. Metz, M. Plaschke, T. Cron, A. Miassoedov*
12:05 PM	1:30 PM	Lunch

Chair		E. Giffault
1:30 PM	1:50 PM	Concrete-Opalinus Clay interaction *A. Jenni, U. Mäder, C. Lerouge, S. Gaboreau, B. Schwyn*
1:50 PM	2:10 PM	Sulfur reactivity at concrete/claystone interfaces *C. Lerouge, F. Claret, S. Gaboreau, Y. Linard, B. Boyer*
2:10 PM	2:30 PM	Mg-perturbation in the low-pH cementitious materials in contact with a clayey rock: the M-S-H question *A. Dauzères, B. Lothenbach, E. L'Hopital, I. Estève, B. Schwyn, U. Mäder, A. Jenni*
2:30 PM	2:50 PM	The Effect of Cellulose Degradation Products on the Diffusion and Advection of 90Sr in Cementitious Backfill *J. Hinchliff*

2:50 PM	3:10 PM	Influence of organic ligands on the sorption and solubility of radionuclides in cement environments M. Grivé, E. Colàs, D. García, M.R. González-Siso, L. Duro, J. Bruno
3:10 PM	3:30 PM	Effect of Ca in the Np(IV)-gluconate system under hyperalkaline conditions *X. Gaona, H. Rojo, C. Adam, M. Böttle, M. Garcia, T. Missana, P. Kaden, M. Altmaier*

3:30 PM	3:55 PM	Coffee break

Topic II		Mechanisms and modelling of cement systems: Chemistry and microstructure

Chair		R. Gens

3:55 PM	4:00 PM	In-situ X-Ray Micro-Diffraction Analysis of Heterogeneous Cementitious Materials *P. Schaub, R. Dähn, D. Popov, A. Leemann, U. Mäder, A. Jenni, P. Pattison, E. Wieland*
4:00 PM	4:05 PM	Experimental characterization of cement-bentonite interaction using core infiltration techniques and 4D computed tomography *F. Dolder, U. Mäder A. Jenni*
4:05 PM	4:10 PM	Processing of chemical data from phase mixtures: cement at interfaces *A. Jenni, U. Mäder*
4:10 PM	4:15 PM	Cement/clay interfaces, evolution of structural and transport properties *A. Shafizadeh, T. Gimmi, L. Van Loon, S. Churakov, E. Lehmann, U. Mäder*
4:15 PM	4:20 PM	Stabilisation of polluted sediment in cementitious system *G. Aouad, M. Benzerzour, C. Alary, R. Zentar, N.E. Abriak*
4:20 PM	4:30 PM	Speciation of C-14 during the anoxic corrosion of activated steel: Set-up of a long-term corrosion experiment *J. Schenzel, E. Wieland, G. Schlotterbeck, I. Günther-Leopold, S. Szidat*
4:30 PM	4:35 PM	Interactions of cationic exchange resins (saturated with Na+, K+, or Ca2+) with Portland cement during hydration *E. Lafond, C. Cau Dit Coumes, S. Gauffinet, D. Chartier, P. Le Bescop, L. Stefan, A. Nonat*

Topic III		Advancement in modelling coupled transport and geochemical alterations in cement systems

Chair		J.C.L. Meeussen	

4:40 PM	4:45 PM	A Local Sensitivity Analysis of the Influence of Mesoscale Components of Concrete on Effective Diffusivity *A. Soto Masip, G. Ye, S. Seetharam, D. Jacques, K. Van Breugel, G. De Schutter*	
4:45 PM	4:50 PM	Reactive Transport Modeling of Organic Complexing Agents in Low and Intermediate Level Waste *H. von Schenck, K. Källström*	
4:50 PM	4:55 PM	High temperature impact on geochemistry and diffusion at concrete/argillite interfaces in a radioactive waste disposal *P. Lalan, A. Dauzères, L. De Windt*	
4:55 PM	5:00 PM	A discussion on simplification of the long-term modelling of chemical alteration of cement materials in radioactive waste repository environment *D. Sugiyama*	

Poster Session			

5:00 PM	6:30 PM	Poster Session	

7:30 PM		Workshop Dinner	

WEDNESDAY 8 MAY

Topic III		Advancement in modelling coupled transport and geochemical alterations in cement systems
Chair		F. Claret

8:30 AM	9:00 AM		Reactive transport with OpenGeoSys-GEM: developments and applications related to the evolution of cement materials in radioactive waste repositories *G. Kosakowski, U. Berner , D. A. Kulik*
9:00 AM	9:20 AM		C-S-H gel dissolution kinetics. Flow-through experiments *A. Trapote-Barreira, J. Cama, J. M. Soler*
9:20 AM	9:40 AM		Modelling approach to evaluate changes in hardened cement paste microstructure under the influence of aggressive pore water *R. Patel, J. Perko, D. Jacques, G. De Schutter, K. Van Breugel, G. Ye*
9:40 AM	10:00 AM		Carbonation of repository cement: Impact of CO2 on cement mineralogy and porewater chemistry *G. Purser, A.E. Milodowski and C.A. Rochelle*
10:00 AM	10:20 AM		A Model to Predict Carbonation of Cementitious Materials under a High CO2 Pressure Condition *Q.T. Phung, N. Maes, D. Jacques, G. De Schutter, G. Ye*
10:20 AM	10:40 AM		Coffee break

Chair		U. Mäder

10:40 AM	11:00 AM		Modeling of cementitious matrices deterioration by organic acids from agricultural wastewaters *L. De Windt, S. Larreur-Cayol, A. Bertron, G. Escadeillas*
11:00 AM	11:20 AM		Modelling degradation fronts in cracked concrete due to chemical leaching *J. Perko, S. Seetharam, D. Jacques, J. Govaerts*
11:20 AM	11:40 AM		Modeling the interaction between concrete and Boom Clay *S. Liu, D. Jacques, J. Govaerts*
11:40 AM	12:00 PM		Monitoring and modelling the behavior of synthetic cementitious like pore waters injected in an equipped borehole of the Meuse Haute Marne Underground Research Laboratory *F. Claret, Y. Linard, S. Gaboreau, X. Bourbon, C. Lerouge, C. Tournassat*
12:00 PM	12:20 PM		Uncertainty Assessment in High Level Tank Waste Closure performance evaluation *K. Brown, S. Sarkar, J. Arnold, H.A. van der Sloot, J.C.L. Meeussen, S. Mahadevan, D. Kosson*

12:20 PM	1:00 PM	Closure : Workshop Round-Up
	Chair	*B. Lothenbach*
		E. Wieland
		Impressions from various experts.

1:00 PM	2:00 PM	
		Lunch

Oral presentations

Actinide solubility and speciation in alkaline CaCl$_2$ brine solutions

M. Altmaier, D. Fellhauer, X. Gaona
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Abstract

Cementitious waste forms are used in the context of the final disposal of low- and intermediate level nuclear waste. Repositories for nuclear waste disposal in rock salt, as discussed in Germany and being realized in the USA (WIPP), are constructed in an exceptionally dry and geologically stable surrounding. In the unlikely case of water intrusion, concentrated salt brine solutions (NaCl, MgCl$_2$) can be generated. Corrosion of cementitious waste in concentrated MgCl$_2$ brines may lead to the generation of highly concentrated and strongly alkaline CaCl$_2$ brine systems. The solubility and speciation of actinides in alkaline CaCl$_2$ solutions was therefore investigated at KIT-INE within a comprehensive experimental research program including trivalent Cm(III), Nd(III), tetravalent Th(IV), Np(IV), Pu(IV), pentavalent Np(V) and hexavalent U(VI), Pu(VI).

Based upon conventional batch solubility studies, robust solubility limits were derived for dilute to concentrated CaCl$_2$ solutions at 9 < pHm < 12. A significant increase of solubility was observed at high pHm relative to the expected radionuclide concentrations derived for concentrated NaCl solutions. Actinide chemistry in alkaline CaCl$_2$ brines exhibits unique chemical features and cannot be estimated by simple analogy. Using a combination of conventional solubility experiments and advanced spectroscopic speciation techniques (TRLFS, XANES, EXAFS) the observed solubility increase was correlated with the formation of hitherto unknown ternary calcium-actinide-hydroxo complexes like Ca$_3$[An^{III}(OH)$_6$]$^{3+}$, Ca$_4$[Th^{IV}(OH)$_8$]$^{4+}$ or Ca$_3$[Np^{V}O$_2$(OH)$_5$]$^{2+}$ dominant in solution. As the solubility limiting solid phases were binary An(III)- and An(IV)-oxohydroxides, pentavalent Np(V) solubility is controlled by ternary Ca-neptunate phases, most importantly Ca$_{0.5}$NpO$_2$(OH)$_2 \cdot$1.3H$_2$O(s), similar to the Ca-uranate solids reported. Based on the SIT and Pitzer approaches for modeling ion interaction processes (activity coefficients), comprehensive thermodynamic model descriptions were derived for tri-, tetra- and pentavalent actinides in dilute to concentrated alkaline CaCl$_2$ solutions.

Nickel, Caesium and Selenium retention by degraded cement

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Abstract

The stage of degradation of a cement barrier surrounding an underground radioactive waste disposal as part of an engineered barrier system is important for the chemical retention of radionuclides. A series of small-scale laboratory experiments on the retention of radionuclides by progressively degrading cement is performed. In a previous study, a thin layer flow-through setup (Bruno et al., 1989) was adapted for its application with ground cement. Different degradation agents (deionised water, synthetic granite groundwater) and conditions (carbonate concentration) are compared with respect to their influence on the mechanisms of radionuclide retention. The experimental setup proofed to be fast and to provide repeatable kinetic data on cement pore water evolution in degradation experiments (Borkel et al., 2011) which are comparable to long-term experiments (e.g., Trapote-Barreira et al., 2011). In the present study, retention of three chemically distinct elements, Cs(I), Ni(II) and Se(VI), is observed under conditions ranging from sane cement to depleted cement, which lost the capacity to buffer input solutions.

Cs(I) is completely dissolved and mainly present as Cs+ ion in the conditions of interest (pH 8 to 12), although ion-exchange reactions cannot be disregarded in cement phases. Concentrations of Ni(II) are governed by its solubility that depends on pH and therefore the degradation stage of the cement. Its main aqueous species at early stages of cement degradation is a hydroxide ion, while at lower pH Ni^{2+} becomes the dominant species, accompanied by an increase of its solubility. Se(VI) is the dominant redox state under oxidising conditions in Portland cement systems and present as selenate which over all degradation stages is the main species. For their different chemical characteristics the three elements interact with different cement phases and show different sorption behaviour to cement material.

At first, the geochemical evolution of the cement powder is addressed to clarify the conditions under which sorption processes occur. Dissolved ions are quantified by Inductively Coupled Plasma – Mass Spectroscopy and Ion Chromatography and the cement is characterised by Scanning Electron Microscopy, X-Ray Diffraction and Thermogravimetric Analysis. The association of the different radionuclides with distinct phases and combination with mass balances of the outflow solutions will be established by a geochemical model following the sorption processes of the different elements. The results obtained from this study, considering evolution of liquid as well as solid phase, will contribute to a better understanding of the mechanisms controlling radionuclide retention by cement.

References

Bruno, J, Casas I & Puigdomènech I (1991) The kinetics of dissolution of UO_2 under reducing conditions and the influence of an oxidized surface layer (UO^{2+x}): Application of a continuous flow-through reactor, Geochim Cosmochim Acta, 55, 647-658

Borkel C, Grivé M & Bruno J (2011) Development of a continuous flow reactor - first study of cement paste degradation, 1st International Symposium on Cement-based Materials for Nuclear Wastes, Avignon, France, 11pp

Trapote-Barreira A, Soler JM, Cama J, Galí S & Lothenbach B (2011) C-S-H gel dissolution kinetics: first results. 13th International Congress on the Chemistry of Cement (XIII ICCC), Madrid, Spain, 6 pp

Uncertainty Assessment in High Level Tank Waste Closure Performance Evaluation

K. Brown[1], S. Sarkar[1], J. Arnold[1], H.A. van der Sloot[2], J.C.L. Meeussen[3], S. Mahadevan[1] and D. Kosson[1]
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Abstract

Large, underground cylindrical tanks have been used for the storage of high level nuclear waste from former defense processing at several sites in the United States. There are more than 200 HLW tanks, typically with a capacity of ca. 4 million liters each, that require waste removal and closure. Typical tank construction is a carbon steel tank liner within a reinforced concrete shell. Closure of the tanks will involve removing waste to the extent practical or based on regulatory requirements, followed by filling the emptied tanks with a cementitious grout, intended to provide physical stability and retention of radionuclides present in residual waste on the tank bottom and coating interior surfaces. The challenge is estimating the timeframe and rate of release of radionuclides from the tanks after closures, which are largely controlled by the degradation of the tank's steel liner and concrete and grout barriers.

The following are primary degradation mechanisms that together can lead to radionuclide release from the closed tanks: (i) ingress of carbon dioxide and major constituent leaching affecting the integrity of the reinforced concrete tank, (ii) corrosion of the carbon steel tank liner, (iii) cracking of the reinforced concrete top, leading to water infiltration, (iv) cracking and gaps in the closure grout allowing water percolation and leaching, and (v) ingress of carbon dioxide and oxygen resulting in pH and redox change and respeciation of grout and waste constituents. A set of geochemical speciation and reactive transport models have been developed by the Cementitious Barriers Partnership (CBP) supported by the U.S. Department of Energy to address this challenge. A coupled liquid and gas phase diffusion model is used to evaluate carbon dioxide ingress and major constituent leaching from the tank shell, leading to reinforcement and tank liner steel corrosion. A model incorporating unsaturated percolation through cracks with orthogonal diffusion to/from crack interfaces has been developed to evaluate impacts of infiltration, cracking, oxidation and carbonation on radionuclide leaching. Each of these models has underlying uncertainties with respect to parameterization, boundary conditions and model assumptions. This paper will systematically evaluate the various sources of uncertainty and the relative magnitude of each, including chemical speciation and thermodynamic parameters within the models.

Combining thermodynamic simulations, element and surface analytics to study U(VI) retention in a corroded cement monolith upon >20 years of leaching

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Abstract

Retention or release of radionuclides in a deep geological repository for radioactive wastes strongly depends on the geochemical environment and on the interaction with near-field components, e.g. waste packages and backfill materials. In Germany, deep geological disposal in rock salt is one of the concepts considered not only for high-level wastes but also for lowand intermediate-level wastes. Long-term experiments were performed to observe the evolution of full-scale cemented waste simulates (doped with $(NH_4)_2U_2O_7$) upon reaction with relevant salt brines, e.g. $MgCl_2$-rich (Q-) and saturated NaCl solutions, and to examine the binding mechanisms of uranium. Throughout the experiments, concentrations of major solution components, uranium and pH values were monitored regularly and compared to thermodynamic equilibrium calculations, which indicate that close to equilibrium conditions have been achieved already after 13-14 years duration of the leaching experiments. Two of the cement monoliths considered in this study were recovered from the solutions after 17-18 years and studied by different analytical methods to characterize the solids, especially with respect to uranium incorporation. In an earlier work, (Kienzler et al., 2010) studied bulk samples by means of TRLFS, XRD and bulk XAFS. Analyses of U-enriched aggregates by space-resolved techniques, e.g. Raman μ-spectroscopy and μ-XAFS, complement the earlier work. Finally, the results of the solid phase analyses are compared to calculations of the solids that potentially control U(VI)-solubilities.

Reference

Kienzler, B., Metz, V., Brendebach, B., Finck, N., Plaschke, M., Rabung, T., Rothe, J., Schild, D., 2010. Chemical status of U(VI) in cemented waste forms under saline conditions. Radiochim. Acta 98, 675-684.

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

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Abstract

A boric acid solution with fixed pH is injected in the primary circuit of pressurized water reactors. Boron acts as a neutron moderator and helps controlling the fission reactions. The treatment of this solution produces two types of low-level or intermediate-level and short lived radioactive wastes depending on the process used: either evaporator concentrates with a high boron concentration (up to 1 to 3 mol/L), or ion exchange resins saturated with borate ions. Stabilization/solidification of such wastes with calcium silicate cement is complicated by the strong retarding effect of borate ions on cement hydration. Belite calcium sulfoaluminate cements with high ye'elimite content may be more appropriate: their rate of 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].

In this work, hydration of calcium sulfoaluminate cement by a borated solution ([B]$_{tot}$ = 1 mol/L, pH = 11) was investigated at early age as a function of the gypsum content in the binder. A specific cell was designed 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 ^{11}B MAS-NMR. The pore solution was also extracted using pressure and analysed by ICP-AES.

Gypsum appeared to play a key role in controlling the cement reactivity. Two types of reaction schemes were identified.

- The gypsum addition set, by an indirect mechanism, the interstitial solution pH at a value close to 11, which promoted the precipitation of a poorly crystallized borated compound, identified as ulexite. Dissolution of the anhydrous phases was strongly slowed down until the exhaustion of gypsum, and important setting delays were observed.

- In the absence of gypsum, the interstitial solution pH rapidly increased above 12. The precipitation of ulexite no longer occurred. Borate ions were inserted into an AFt phase where they formed a solid solution with sulphate ions. A slight delay was still observed as compared with a reference prepared with pure water. It may have resulted from the sorption of borate ions onto aluminium hydroxide, which would slow down the crystal growth.

The phase evolution at early age with and without gypsum was well reproduced by thermodynamic modelling using the CEMDATA07 database [3] enriched with borate minerals and (poly)borate anions.

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Understanding ion adsorption by C-S-H: From ab initio simulations to thermodynamic equilibrium

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Abstract

Calcium-Silicate-Hydrates (C-S-H) are one of the major phases responsible for uptake of alkali and alkali earth ions, transition metals, lanthanides and actinides in hardened cement paste. Aggregates of C-S-H emerge between clinker grains within a few minutes after mixing with water and progressively gain strength as the hydration proceeds. Understanding the interplay between the mechanism of ion uptake by C-S-H at an atomistic scale, and bulk thermodynamic properties of cement systems is essential for the long term safety and performance of waste disposal sites. Because of the amorphous character and nano- to micro-meter particle size of C-S-H, computer simulations are virtually the only tool able to reveal the link between experimentally measured macroscopic properties of concrete and the structure of C-S-H at an atomistic scale.

Titrating Monte Carlo simulations in the Grand Canonical ensemble (GCMC) at the level of the Primitive Model have been particularly successful in predicting cations and anions uptake by C-S-H [1] despite its simplicity. In particular, neglecting structural and thermodynamic details, C-S-H was described in its simplest form as a surface decorated with titrating sites regularly distributed on a square lattice and having the same dissociation constant (pKa) set to the first deprotonation constant of silicic acid. In the present work, we extend the existing model by including a more realistic distribution of the titrating sites and calculating their pKa values based on quantum mechanical calculations.

In crystalline C-S-H phases protolysis reactions take place on the OH groups associated with the bridging sites of the silica tetrahedra chains [2] and OH groups associated with the "pair" tetrahedra situated next to Si-defects in the bridging tetrahedral sites [3]. We calculate pKa values of all these sites using the thermodynamics integration technique based on molecular dynamics simulations on the density functional level of theory [4]. To complete the model, we also calculate protolysis constants of H_2O molecules adsorbed on C-S-H surface. Incorporating ab initio pKa values and a more realistic site distribution in the GCMC simulations we estimate their effects on ion uptake. The new data and extended model allow us to better account for the variation of the acid-base properties of C-S-H with the polymerization degree of the silicate chains.

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Monitoring and modelling the behavior of synthetic cementitious like pore waters injected in an equipped borehole of the Meuse Haute Marne Underground Research Laboratory

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Abstract

Since July 2010, Andra is conducting an in situ experiment within the Meuse Haute Marne Underground Research Laboratory. Two synthetic cementitious like pore waters (pH 13.5 and 12.5) are circulating in two separated chambers (75 cm height, diameter 76 mm) in an equipped borehole drilled in the GED gallery. In the following these two solutions are called Alc (synthetic pore water with alkali ions) and EqPort (synthetic solution in equilibrium with portlandite). Samplings are performed as a function of times and the gathered solution is then analyzed. Major cations and anions are monitored with time as well as pH and alkalinity. After 265 days the pH has dropped to pH 7.2 for the EqPort solution and 8.6 for the Alc solution. The two solutions have been renewed after 265 days and a second time after approximately 1 year. D2O has been also injected as a tracer. Iodine and bromide have been spike in the cementitious synthetic solutions to quantify the anions accessible porosity. In order to reproduce the pH decrease, the major ions changes within the solution a coupled geochemistry transport model has been built using PHREEQC. The model proposed by Appelo et al.(2008) to obtain the porewater composition of a clay rock by modeling the in- and out-diffusion of anions and cations from an in-situ experiment has been adapted to model to our experiment. The transports parameters (diffusion coefficient, porosity, size of the zone around the borehole disturbed mechanically by drilling and equipement) have been calibrated on the D2O data. Regarding the setting up of the geochemical reaction two models have been tested. The first one integrates multicomponent diffusion (MCD) and diffuse double layer effects in clays in conjunction with ion exchange and calcite dissolution, whereas in the second one a full mineral assemblage has been taken into account. .In this second model MCD was still considered but not diffuse double layer effects in clays. The full mineral assemblages was chosen according to the clay pore water robust model described by Gaucher et al.(2009). The first simplified model duly calculates transport of the K and Na in clay rocks for both EqPort and Alc solutions, indicating that their behavior is driven by the exchange on the clay. Taking into account the full mineral assemblage and allowing precipitation and dissolution of the minerals allow to properly reproduce the Ca profile over time.

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Mg-perturbation in the low-pH cementitious materials in contact with a clayey rock: the M-S-H question

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Abstract

Within the framework of geological repositories for radioactive waste, structural concretes have to be adapted to minimise damage to the clay or rock. Portland cements (PC) are characterised by high pH values that may produce an alkaline plume in the repository near-field, possibly damaging the rock. In order to minimise the pH increase, lowpH cements (binary or ternary mixes with silica fume and fly ash or slag) have been designed [1-3]. Recent studies were carried to study the durability of low-pH materials in clayey environment [4-7]. A Mg-perturbation is systematically observed for low-pH cementitious materials placed in contact with a clayey rock. The formation of Mg-Si amorphous gel is regularly suggested in experiments but never taken into account in modelling studies due to lack of thermodynamic data. Thermodynamic modelling based on the available databases predict generally either the precipitation of brucite, hydrotalcite or Mg-clay phases, which are generally not observed in this environment. Therefore an effort is necessary to acquire knowledge on these phases and consequently improve the thermodynamic calculation.

Currently, in the framework of the CI-project (Cement Clay Interaction Experiment), two different low-pH cements were emplaced at Mont Terri rock laboratory to study their interactions with the surrounding Opalinus Clay (OPA): ESDRED (shotcrete mixture: 60% of CEM I 42.5 N + 40% of silica fume + aluminiumsulfate salt as accelerator) and LAC composed of CEM III/B 42.5 L (60% of blast furnace slag + 10 % nanosilica).

After 2 and 5 years of interactions, SEM-EDS analyses show a systematic Mg-perturbation associated with a high decalcification near the surface of both cementitious materials. After 5 years, the Mg-perturbation zone has a thickness of 1.5 mm in the ESDRED concrete and of 0.4 mm in the LAC concrete. An investigation by FIB-EDS and TEM shows the presence of three different textures in the LAC Mg-perturbation zone: Two pure Mg-Si phases and a mixed Ca-Si-Mg phase. The MgO/SiO_2 and CaO/SiO_2 atomic ratios are approximately 0.5 indicating the possible formation of M-S-H (near the interface) and M-C-S-H gels (between the M-S-H and the C-S-H zones) due to a progressive substitution of calcium by magnesium coming from the OPA.

In addition, synthetic M-S-H ($0.4 < MgO/SiO_2 < 1.7$) and M-C-S-H ($0.4 < MgO,CaO/SiO_2 < 0.8$) phases were prepared in order to compare their texture and chemistry with Mg-phases formed in the cement-based materials. Thermodynamic properties deduced from

these experiments will be used to improve the database for the future reactive transport modelling.

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Modeling of cementitious matrices deterioration by organic acids from agricultural wastewaters

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Abstract

The wide range of carboxylic acids present in agricultural effluents - such as liquid manure, silage juices or sugar or beet cane molasses - is responsible for severe attack of concrete facilities (storage silos, cowsheds, housing structures). Carboxylic acids react with the cement matrix and lead to the dissolution of most hydrated and anhydrous cementitious phases and the formation of calcium salts (when their solubility is appropriate). The physico-chemical properties of the acids and their salts play an important role in the aggressiveness of the acids toward the cement paste [1,2], these effects being not well understood yet. To appreciate the degradation mechanisms of cement pastes by such organic acids, the links between the chemical properties of the acids and their aggressiveness for cementitious materials need to be highlighted. In the laboratory, CEM I cement pastes have been immersed in aggressive solutions for one year. Different mixtures based on real effluent compositions were realized with acetic, citric, oxalic and succinic acids. Kinetics and mechanisms of alteration were analyzed using mass losses, degraded depths, XRD and EPMA measurements.

The reactive transport code HYTEC has already been used for modeling the degradation of Portland cement pastes by biogenic organic acids [3]. The related physical and thermodynamic database has been further extended from a literature review for the present study. The first part of this paper deals with a set of representative geochemical modeling to better discriminate between (i) acid strength, (ii) aluminum and calcium complexation, (iii) salt solubility under wastewater conditions among the parameters likely to influence the phenomenology of the attack. The second part is devoted to the modeling of the leaching experiments with HYTEC by taking into account the organic acid compositions, the chemical evolution of pore water, the progression of mineralogical alteration fronts, and the concomitant changes in porosity and diffusion coefficients. Experiments and modeling led to similar results in terms of degradation rate and depth, except for citric acid that was found to be more aggressive in the laboratory. Modeling indicates that the organic acids strongly accelerate hydrate dissolution by acidic hydrolysis whilst their complexation of aluminum has an effect on the secondary gel stability only. The coupling of chemical alteration, changes in porosity and diffusion properties is a key step yielding either strongly enhancing deterioration by porosity aperture or, to the contrary, inhibiting alteration by clogging, depending on the nature of the organic acid. The acid mixtures were mostly protective, showing the predominant role of oxalic acid.

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Hydration of fly ash blended Portland cement at different temperatures

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Abstract

Cementitious materials are exposed to various temperature ranges during hardening due to different climatic conditions and the heat arising from the hydration of cement. The temperature has a strong impact on the hydration kinetics, hydrate phase assemblage, microstructure and strength development. Since fly ash blended Portland cements are increasingly used, the aim of this study was to investigate the effect of a variety of temperatures, ranging from 7 to 80 °C, on the hydration of Portland cement pastes blended with 50 wt% of siliceous fly ash (Type V, EN 197-1) between 1 and 180 days. Additionally, reference samples of the same Portland cement blended with 50 wt% of quartz powder were prepared. The hydration kinetics during the first 5 days were analysed by means of isothermal heat flow calorimetry. The hydrate phase assemblage was characterized by X-ray diffraction and thermogravimetric analyses, and the pore solutions were extracted and analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES). Additionally, mechanical testing was performed on mortar prisms.

Increasing temperatures generally caused a faster hydration of both Portland cement and fly ash. This was indicated by the faster formation of portlandite due to the increased OPC hydration rate and the earlier onset of the portlandite consumption due to the enhanced pozzolanic reaction of fly ash.

The development of compressive strength showed the so-called "temperature inversion effect". At early hydration times, higher temperatures caused an increase of the compressive strength. Afterwards the rate of strength development was lower at elevated temperatures compared to low temperatures. After 7 days of hydration the strength of the sample was higher at 50 °C than at 80 °C and after 90 days the sample at 40 °C showed the highest compressive strength. The "temperature inversion effect" is related to the microstructure. At elevated temperatures the hydration products were distributed more heterogeneously than at low temperatures, and the porosity was increased.

At 80 °C ettringite and AFm phases were destabilized and hence the sulphate concentrations in the pore solution significantly increased.

Radial diffusion of radionuclides through a cementitious backfill material

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Abstract

The present concept for the disposal of intermediate- and some low-level radioactive waste (ILW and LLW) in the UK is based on a multi-barrier geological disposal facility (GDF) concept. Most ILW would be conditioned by encapsulation with a grout and packaged in stainless steel containers that would be placed in an engineered vault deep underground. Prior to closure of a GDF, the vaults would be backfilled with a cementitious admixture; the NRVB (Nirex Reference Vault Backfill) is one possible material. The backfill plays an important role within the multi-barrier concept; a key function is to contribute to the chemical containment of many radionuclides by buffering the pH to alkaline values and providing a surface for the sorption of radionuclides. This limits their aqueous concentration and hence their release from the engineered barrier system into the host rock. Consequently, it is important to understand how radionuclides interact with the backfill to build confidence in their behaviour over the very long timescales considered in post-closure safety assessments of a GDF.

A series of 4-year duration diffusion experiments is being carried out at Loughborough University to assess the diffusion of Cs, Ni, Eu, Th, U and I (as I⁻) through NRVB. The method uses cylinders of NRVB (40 mm diameter and 45 mm height) which can be doped via a central well with a slurry or solution of the elements of interest so that the diffusion occurs radially outwards into a surrounding solution. In order to study the interaction or competition between radionuclides, single element and multi-element experiments have been set up in which equimolecular amounts of the elements of interest were spiked simultaneously into the cores of NRVB cylinders.

ILW and LLW can contain significant amounts of organic constituents including cellulosic materials which under alkaline conditions degrade to a complex mixture of highly-complexing short chain organics. Complexation by these cellulose degradation products (CDP) can affect the mobility of radionuclides by increasing their solubility or decreasing their sorption. In this study, diffusion experiments have been performed both in NRVB-equilibrated water and in a CDP leachate produced by the degradation of cellulose in the presence of NRVB.

This paper shows some of the interim results obtained two years after the commencement of the experiments. In NRVB-equilibrated water, no breakthrough was observed for Ni, Eu, Th or U with concentrations in the surrounding solutions below detection limits. In contrast, breakthrough of Cs and I occurred within the first week of the experiments and steady concentrations are now observed in the surrounding solutions. These have not reached the maximum concentration that would be expected from the original inventory based on a simple dilution calculation. The corresponding CDP experiments showed an increased rate of diffusion for both Cs, I and also Ni. The migration profile of the radionuclides through the NRVB has also been visualised using autoradiography. Scanning electron microscopy (SEM), X-ray tomography and powder X-ray diffraction

(XRD) have been used to assess any alteration of mineral phases and physical changes to NRVB during the experiments.

The interaction between nuclear waste glass and cement

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Abstract

Since 2004, the Belgian agency for radioactive waste (ONDRAF/NIRAS) has selected the *Supercontainer design* with an Ordinary Portland Cement (OPC) buffer with limestone aggregates as the reference design for geological disposal of vitrified nuclear waste and Spent Fuel in the Boom Clay formation.
In this *Supercontainer design*, the canisters with the waste glass will be enclosed by a 30 mm thick carbon steel overpack and a concrete buffer about 700 mm thick. The overpack has to prevent contact of the vitrified nuclear waste with the cementitious pore water at least during the thermal phase. After local perforation of the overpack, the high pH of the infiltrating water may have an impact on the lifetime of the vitrified waste. To evaluate the durability of the glass matrix and to identify the key mechanisms responsible for glass alteration in such a cementitious environment, a set of experiments was performed using the Belgian reference nuclear waste glasses SON68, SM539 and SM513.

Static glass leach tests were conducted at 30°C under Ar atmosphere in suspensions of OPC and synthetic young cement water (YCWCa) with pH 13.5. This water simulates the composition and pH in a pore water in equilibrium with OPC concrete in the first stage of degradation. Different ratios of cement to glass powders were tested. Glass dissolution rates were determined from the mass losses of the glass monoliths. Concentrations of the major solution components were measured and solid analyses such as X-ray diffraction, ToF-SIMS and High Resolution Transmission Electron Microscopy were performed to determine the main key mechanisms of glass/cement interaction.

In these tests, the concentration of the major solution components is initially imposed by the cement phases, but as more glass dissolves, these phases are converted by reaction with glass components, and the equilibria shift. An inverse correlation between the Ca and the Si concentrations was observed suggesting the formation of a Ca-Si phase in the first stage. Finally, the concentrations are imposed by the glass implying a very significant increase of the Si and Al concentrations, and a decrease of the Ca concentration.

The cement appears to trigger the glass dissolution by consumption of glass matrix components leading to a fast glass dissolution. Glass dissolves at a high rate with the formation of a porous gel layer (10 nm for SON68 altered for 1 year). This rate is similar to that determined in dynamic leach tests with YCWCa without OPC (0.37-0.41 $g.m^{-2}.d^{-1}$ for SON68).
The glass alteration proceeds at this high rate as long as the solution composition is imposed by the original cement phases. After the conversion of these phases by reaction with glass components, the glass dissolution rate decreases significantly. In tests with a low cement content, we observe that dissolution rates are around 6-8 times lower.

The key mechanism driving the long term glass dissolution is secondary phase formation with Si and Al from the glass matrix. Two key reactions have been identified at ambient temperature (30°C): the reaction of Si released by the glass with portlandite, leading to the

formation of C-S-H phases (pozzolanic reaction) and the further conversion of C-S-H phases with Al from the glass to form Calcium Aluminum Silicate Hydroxide phases. XRD analysis conducted on samples altered for 1 and 2 years has revealed the disappearance of the portlandite and the formation of tobermorite and a CASH phase identified as katoite for SM539 glass, this glass dissolving faster than SON68 glass.

The reaction of portlandite with silica from the glass will accelerate the evolution of the concrete towards the 'old concrete stage', with C-S-H replacing the portlandite. However, pH will remain high (close to 13.5) as long as the K^+ and Na^+ concentrations remain high. Their concentration can decrease by diffusion towards the far field and by precipitation of secondary glass alteration phases .

Effect of Ca in the Np(IV)-gluconate system under hyperalkaline conditions

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Abstract

Radionuclide sorption and solubility in cementitious and saline systems can be affected by the presence of organic ligands. Gluconic acid (GLU, $C_6H_{12}O_7$) is a poly–hydroxocarboxylic acid expected in repositories for low and intermediate–level radioactive waste (LILW) as component of cementitious materials. The formation of very stable An(IV)–GLU complexes has been reported in the literature; the stability of these complexes can be further increased in the presence of Ca^{2+} due to the formation of ternary Ca–An(IV)–GLU complexes. To the date, all studies available in the literature have focussed on low ionic strengths and low Ca^{2+} concentrations. In CaCl2–rich brines, the formation of highly stable Ca–GLU complexes may outcompete Ca–An(IV)–GLU complexes. Np(IV) was obtained by chemical reduction of a Np(V) stock solution with $Na_2S_2O_4$ 0.05 M at pH = 8, and quantitatively precipitated at pH_m = 12 as NpO_2(am,hyd). The resulting solid phase was divided in different series with 0.1 M ≤ $[CaCl_2]$ ≤ 3.5 M as background electrolyte. GLU concentration ranged between 10^{-6} M and 10^{-2} M.
The solubility of $Ca(GLU)_2$(s) was investigated in dilute to concentrated NaCl and $CaCl_2$ solutions, and complemented with ^{13}C NMR measurements on a Bruker Avance III 400 spectrometer equipped with a broadband observe probe head (BBFO).

The presence of GLU induced a significant increase on NpO_2(am,hyd) solubility in $CaCl_2$ solutions. This increase was stronger at higher concentrations of Ca^{2+}, very likely because of the formation of ternary complexes analogous to those described in the literature for Th(IV) $(CaAn(IV)(OH)_4GLU_2(aq))$. The system reached a saturation level at [Np] $\sim 10^{-5.5}$ M, independently of $[CaCl_2]$. This observation was explained with the formation of a Np(IV)–GLU solid phase, although this hypothesis remains to be confirmed by appropriate solid phase characterization (XRD, SEM–EDS). $Ca(GLU)_2$(s) set very high and pH–independent solubilities in both NaCl and $CaCl_2$ solutions. At high $CaCl_2$ concentrations (≥ 3.5 M), all the initial $Ca(GLU)_2$(s) dissolved resulting in GLU concentrations above 0.5 M. C1 to C6 peak shifts observed in ^{13}C NMR were consistent with the formation of a single Ca–GLU aqueous species, likely $CaGLU^+$. At $[CaCl_2]$ ≥ 2.5 M, however, the strong shift in C4 hinted to either the re–ordination of the $CaGLU^+$ structure or to the formation of an additional (not previously described) Ca–GLU complex.

Crystal structure of nano-sized synthetic CSH

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Abstract

The main component of Portland cement is a nano-sized and poorly-ordered phase commonly referred as "Calcium Silicate Hydrate" (CSH). Although the nature of this phase was first discussed almost 100 years ago, its detailed crystal structure is still uncertain, mainly because its X-ray diffraction (XRD) pattern exhibits only a few and broad diffraction maxima. As a consequence, CSH is often assumed to be "X-ray amorphous" and classical XRD pattern refinements cannot be performed. This difficulty has been circumvented by numerous authors by using a wide variety of physical methods taking advantage of magnetic radiations, X-rays, or neutrons (FTIR, NMR, EXAFS, SANS, PDF…) to probe the short-range order around Ca, Si and O. These data contributed to the development of, or supported, the currently held view that CSH are structurally related to the rare minerals tobermorite and/or jennite. Discrimination between these two models using local probes is highly difficult because tobermorite and jennite are both layered minerals and they have similar local order, i.e. layers built up of ribbons of silicon tetrahedra, with wollastonite-like structure, running at the surface of calcium layer (Figure 1).
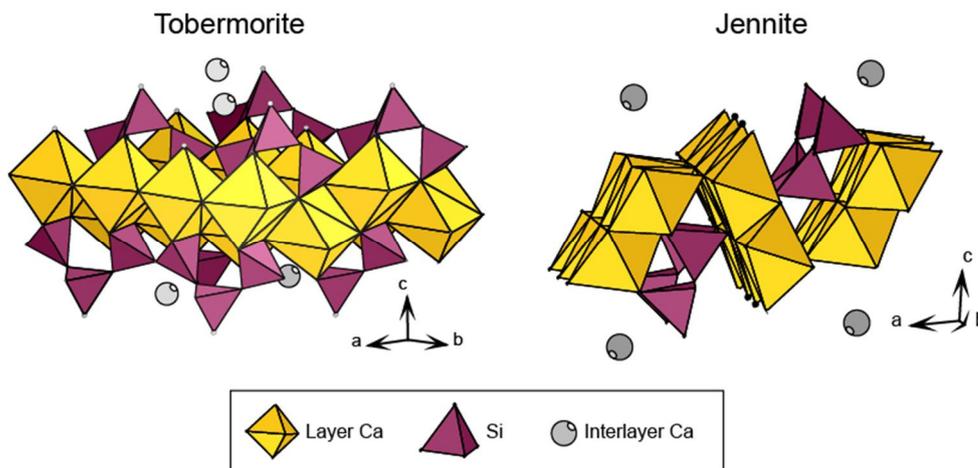
Figure 1: Tobermorite (left) and Jennite (right) model layer structures. Yellow pseudo-octahedra, purple tetrahedra and grey spheres are, respectively, layer Ca and its coordination sphere, Si and its coordination sphere and interlayer Ca. Interlayer water molecules omitted for clarity.

To date, no structural model was unambiguously determined, because no modeling of methods probing the long-range order was performed. We combined electron probe micro-analyses (EMPA), transmission electron microscopy (TEM) and powder XRD to determine the structure of four different nano-crystalline CSH synthetized at laboratory temperatures ranging from room temperature to 110 °C. It is demonstrated that the modeling of XRD patterns using a specifically developed method is able to capture most of the structural details from CSH crystals, such as crystallite size, lattice parameters and interlayer occupancy. The genetic link between CSH and its hypothesized natural equivalents is discussed.

Influence of organic ligands on the sorption and solubility of radionuclides in cement environments

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Abstract

Low- and intermediate- level radioactive wastes usually have a very diverse origin and composition. A wide variety of organic materials (such as packaging plastics, clothes, paper, gloves, cement additives, cleaning agents or ion-exchange resins) are generally present among them [1]. In particular,

- Polyaminocarboxilic acids such as EDTA or NTA, which may be used in decontamination procedures.
- Polyhydroxycarboxylic acids such as gluconate (a simple model to account for complex cement additives) and isosaccharinate (the most important degradation product of cellulose in alkaline pore waters) are likely to be present due to the important amount of cement used in the building of the repository and the conditioning of waste.
- Dicarboxilic acids such as oxalate may be formed due to bitumen or ion-exchange resin degradation, and tricarboxylic acids as citrate are also used in decontamination procedures.

Those organic materials are of special interest as they may influence the mobility of radionuclides [2], and may exhibit different behaviour depending on their chemical characteristics. In this work, we have reviewed the affinity of these ligands with different radionuclides at different oxidation states (Cs(I), Ni(II), Eu(III), Th(IV)) in the alkaline pH range characteristic of cement environments. Using this information, a simple calculation tool has been developed in order to easily handle the influence of organic compounds on the mobility of radionuclides by considering both, the stability of the aqueous species formed and its impact on the radionuclide sorption behaviour.

Calculations have shown that tetravalent (and trivalent) elements are expected to be the ones most influenced by the presence of organic ligands in the pH range $11 < pH < 13.5$, while caesium is not significantly affected by their presence. Gluconate and isosaccharinate are expected to have a high impact on radionuclide mobility; on the contrary, EDTA, NTA, citrate and oxalate speciation is significantly affected by calcium presence in the system, thus reducing the effect of those ligands on radionuclide speciation.

Knowledge gaps relevant for the safety assessment in the radionuclide –organic ligand – calcium system have been identified. The results of automatized Monte-Carlo (MC) simulations in order to perform sensitivity analysis on the identified key parameters will also be presented.

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C-A-S-H thermodynamics modelling in CaO-Al$_2$O$_3$-SiO$_2$-H$_2$O system

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Abstract

Ordinary Portland cement (OPC) is being increasingly replaced by blended cements, where art of the clinker is replaced by secondary cementitious materials (SCM) such as blast furnace or fly ash. The use of SCM enables to achieve various aims as the cost reduction by recovery of by-products, the CO$_2$ emission reduction, the obtaining of specific properties such as low pH. So, blended cements are more and more current in different fields as civil engineering and nuclear waste repository.

The use of silica and/or aluminium rich SCMs directly impacts the amount and the kind of hydrates formed, hence the volume and the porosity and finally the durability of these materials.

Aluminates containing hydrates formation is not well understood. Al content can lie from Aluptake in C-S-H due to Al-substitution of Si-tetrahedra to well-crystallised hydrates like strätlingite or katoïte phases.

This study proposes a surface dependant thermodynamic model to predict and to correlate the Al-uptake (substitution) of C-A-S-H with solutions representative of that of cement pores chemistry. The model is based on surface reactions accounting for the silicate chain polymerisation by silicate and aluminate tetrahedra as well, the silanol deprotonation and calcium adsorption. The different equilibrium constants were determined from simple experimental models in the CaO-SiO$_2$-H$_2$O and CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O systems by reproding the C-S-H and C-A-S-H properties such as stoichiometry, solubility and surface charge.

These results allowed evaluating the Al-availability in the cementitious system and especially for aluminates containing hydrates precipitation.

The effect of cellulose degradation products on the diffusion and advection of ^{90}Sr in cementitious backfill

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Abstract

Many concepts for the geological disposal of intermediate level (ILW) and low level radioactive waste (LLW) include backfill materials based on admixtures of Ordinary Portland Cement (OPC). It is expected that these backfill materials will generate high pH conditions and further, the eventual corrosion of the metal canisters used for disposal will promote a low Eh environment. It has been generally assumed that the safety functions of the cement within the near field of a Geological Disposal Facility (GDF) will include reduction of the solubility of many radionuclides and retardation of migration by sorption and incorporation.

Whilst diffusion is likely to be the dominant migration mechanism for radioisotopes throughout the post closure period, advection may also be important during groundwater re-saturation and equilibration. The radioisotope ^{90}Sr will be a significant component of the disposed waste and its half-life of 28.8 years means that escape and migration from the GDF could be of importance if it occurs within the operational phase or first few hundred years post closure. Cellulosic materials will also be inherent components of the wastes and previous studies have shown that cellulose degradation products (CDP) produced anearobically at high pH can enhance the migration of metal ions.

The radial diffusion and advection experimental techniques used involve small pre-cast cylinders of the cementitious matrix under investigation, in this case, NRVB (Nirex Reference Vault Backfill). For diffusion an appropriate concentration of ^{90}Sr is introduced into a cavity in the centre of the cylinder, which is then sealed and placed in a solution previously equilibrated with the solid matrix. The increase in concentration of the isotope in the external solution is then determined at defined time intervals. For the advection experiments a rig has been designed and manufactured to enable radial flow from the central core to be collected as it exits the outer surface of the cement cylinder. The isotope is added via a modified gas liquid chromatography injector port.

The experiments have been undertaken using 90Sr in the presence and absence of CDP. The results show mobility significantly decreased and sorption increased by 30-50% in the presence of CDP at "tracer" concentrations of the radionuclide. The advection experiments are currently underway and the results agree well with physico-chemical models previously constructed for scoping experiments undertaken earlier in the research.

Concrete-Opalinus Clay interaction

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Abstract

Interactions between cementitious materials and claystone are mostly driven by chemical gradients in pore water and might lead to mineralogical modifications in both materials. This again might influence safety-relevant clay properties like swelling pressure, permeability, or specific retention. Existing studies revealed significant modification in both cement and claystone, e.g. [1]. Phase dissolution, precipitation, and carbonation, were found to change porosities [2]. Most of the work was done on cement pastes rather than concretes to avoid analytical complications caused by aggregates, and the scale of investigation was chosen in the range of centimetres rather than micrometers.

In this study, interfaces of Opalinus Clay (OPA) and three concrete formulations from the Cement-Clay Interaction (CI) experiment at the Mont Terri Underground Laboratory (St. Ursanne, Switzerland) were analysed after two years of interaction. The three formulations contain 1) Portland cement (OPC), 2) ESDRED cement especially designed for repository applications (40% of cement substituted with silica fume), and 3) low alkali cement (LAC, containing slag and nanosilica).

Energy dispersive spectrum (EDX) element maps by scanning electron microscopy (SEM) of the OPC-OPA interface show a significant sulphur (S) enrichment in the cement at ca. 600 μm from the interface. The main feature of the ESDRED alteration is a distinct zone depleted in Ca but enriched in Mg at around 600 μm distance, whereas the LAC shows a strong Mg enrichment adjacent to the interface. Transmitted light microscopy and Raman spectroscopy give evidence for a carbonated zone, whose thickness seems to depend on water to binder ratio of the cement. Consistently, this zone shows lower porosity. Element ratio diagrams from SEM EDX point measurements give indications of ettringite in the S enriched zone in the OPC, but closer to the interface, monosulphate as S-containing phase explains the compositional trends. Hydrotalcite and/ or MSH phases are expected in Mg enriched zones of all three cements. In OPA, the first 100 μm next to the interface show increased Ca (OPC) and Mg (LAC) content. The cation occupancy of clay exchanger phases within 1 mm next to the OPC interface is depleted in Mg, but enriched in Na, whereas porosity shows no gradient at all.

The current data suggests migration of CO_2/HCO_3^-, SO_4^{2-}, and Mg species, from OPA into cement. pH decrease in the cement next to the interface leads to instability of ettringite, and the S liberated diffuses towards higher pH regions (away from the interface), where ettringite can form and incorporate S.

Examination of nearly 5 years old samples taken recently is underway and expected to reveal the evolution with time of the alteration zones and any changes in reaction mechanisms. An ongoing micro X-ray diffraction project carried out at PSI [3] will result in phase identification at high spatial resolution in cement and in OPA. A detailed reactive transport modelling interpretation will be initiated in this current phase of the project.

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Radionuclide Retention onto Heat Treated Concrete under Sea Water Conditions

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Abstract

In the research center Karlsruhe, Germany, a series of experiments have been performed to investigate postulated severe accidents in a Light Water Reactor where a core melt penetrates the pressure vessel and accumulates on the basement of the containment [1-3]. For these investigations, concrete cavities were used in which a steel melt covered by an oxide melt was formed interacting thermally, mechanically, and chemically with the concrete. The decay heat was simulated by inductive heating of the metal melt. The investigations covered the temperature profiles in the concrete structures, and the concrete erosion by the melt under various conditions. The Fukushima accident in 2011 directed our attention to these heat treated concrete materials as potential barrier for radionuclide retention.

Material from a cavity was drilled, obtaining concrete which was exposed to temperatures up to 800°C. This material was milled and a grain size of ~100 µm was selected for further investigations. The investigations covered a characterization of the solids by several methods, such as XRF for quantification of elemental composition, XRD for determination of the mineral phases, BET for determination of the surface area, DTA for determination of volatile compounds, and SEM-EDX for identification of specific morphologies und related element.

The sorption samples are prepared by preconditioning the solids with a simulated sea water of pH 8.22. The sea water was simulated according Kester et al. [4] resulting in an ionic strength of 0.7 molal. When the equilibration yields steady state in solution composition and pH, the solid is separated and the solution is used to prepare radionuclide solutions using I(-I), Cs(I), Co(II), and Eu(III). Then part of the radionuclide solution is added to the preconditioned solid so that the target solid/liquid ratio (m/V) is achieved. The sorption tests are performed under oxic conditions and ambient temperature. The samples are agitated slowly and after several time intervals, pH was measured and the radionuclide concentration in the solution was measured.

Results of the characterization of solids and of the sorption tests will be reported in the final paper.

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Reactive transport with OpenGeoSys-GEM: developments and applications related to the evolution of cement materials in radioactive waste repositories

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Abstract

This contribution will give an overview of the PSI work related to reactive transport simulations in cementitious systems. Since 2000, development of the Gibbs Energy Minimization GEM-Selektor software for geochemical modeling took place at PSI's Laboratory for Waste Management. With the GEM-Selektor v.3 software and its numerical kernel GEMS3K (http://gems.web.psi.ch), we are able to simulate very complex geochemical models. For reactive transport modeling, we use the OpenGeoSys code (www.opengeosys.org) coupled to GEMS3K code.

At present, most of common reactive transport codes still make use of Law of Mass Action LMA-based chemical solvers. We developed the OpenGeoSys-GEM coupling to take advantage of the GEM method for modeling complex geochemical systems involving multiple non-ideal phases-solutions.

The current version of OpenGeoSys-GEM can simulate advective – dispersive – diffusive multispecies transport in fully- or partially saturated media in combination with partial chemical equilibrium with kinetically controlled mineral precipitation/dissolution reactions. Due to the modular structure of OpenGeoSys, other processes like heat transport can easily be added. An limitation of the first OpenGeoSys-GEM coupling was the rather long calculation time compared to other codes. To overcome this disadvantage, we developed a hybrid (threaded MPI) parallel version that can be used on high-end supercomputers.

The applications are driven by the specific advantages of GEM-Selektor in calculating geochemically realistic partial equilibria including several (non-)ideal solid solution models. Using a Cemdata'07 thermodynamic database extension from EMPA (www.empa.ch/cemdata), we developed a thermodynamic system setup for reference concretes, which is consistent with a setup for clay containing materials like bentonites and argillaceous host rocks proposed in the framework of the Swiss site selection procedure for radioactive waste repositories. A specific feature of this setup is the incorporation of several solid-solutions for cement minerals and the use of a solid-solution-sorption model for describing cation exchange and surface complexation simultaneously on the montmorillonite phase. This setup was calibrated to the mineralogy and porewater composition of several host rocks, to MX80 bentonite, to a low pH concrete, and an ordinary concrete.

The new chemical thermodynamic setup was applied in reactive transport models that help to investigate the mineralogy and porosity evolution of interfaces between cementitious and clay-containing materials specific for the Swiss disposal system. As typical for low-permeability host rocks, the transport across such interfaces is dominated by diffusion. The strong geochemical gradients between clayish and cementitious media

drive reaction fronts in both media. In the clay medium, clay minerals are partly replaced by secondary phases like zeolites. In the concrete, portlandite and other cement phases are dissolved, and C-S-H phases are formed. In good agreement with former reactive transport studies on such systems, porosity clogging at the interface is observed.

Further applications include simulations of the evolution of a low pH concrete liner in a high level waste emplacement tunnel, and the long-term evolution of engineered barrier elements in a low level waste repository. Next to applications directly related to waste repositories, the thermodynamic setup was also tested for the Maqarin natural analogue describing the alteration of a marl rock in contact with the hyperalkaline groundwater. This successful application supports confidence in our approach for predicting the long-term evolution of cementitious waste repositories.

Local- and partial equilibria in thermodynamic- and transport modeling of cement systems

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Abstract

Hydration, setting and degradation of cements are time-dependent processes that include kinetically controlled dissolution of clinker and blend minerals with precipitation of C-S-H and other hydrated phases. External influences on cementitious systems result in formation of calcite, amorphous silica and other end products upon leaching and degradation. In the special case of waste disposal, interactions between cement, waste, clay materials and host rocks need to be considered.

Waste-cement interaction may be related to several processes/mechanisms. The uptake of minor elements into hydrated cement minerals and degradation products may occur via ion exchange and inner-sphere adsorption through surface entrapment or in-diffusion up to structural incorporation upon (re)precipitation. Interplay of these mechanisms, affected by main hydration or degradation processes, may lead to metastable distributions of minor elements deviating from 'true' aqueous - sorption - solid solution equilibria. To model and understand such phenomena, one has to go beyond the 'complete equilibrium' concept, and invoke a model setup based on the principles of local and partial equilibrium.

In the partial equilibrium concept, the typical assumptions are: at least one phase is not in chemical equilibrium with the rest of the system; dissolution of minerals is the rate-limiting step; solid solutions dissolve stoichiometrically; precipitation of secondary minerals is faster than the primary mineral dissolution; some species or solid phases remain inert. In reaction-path thermodynamic models, these assumptions of different validity turn into the time-step-dependent metastability constraints on amounts of species or phases, their surface areas and sorption capacities. Changes in amounts of metastable phases are linked to amounts of other phases and to their 'reactive surface areas'. The reactive surface area is a non-thermodynamic property that accounts for different structural properties of the medium and even for the influence of micro-scale transport processes. Various feedbacks between mineral dissolution and precipitation rates that influence sorption or entrapment rates may form metastability 'chains' or 'loops' that need to be adequately represented in reaction-path models.

The local equilibrium concept is used in most reactive transport simulation setups. The typical approach is to divide a system into many small enough homogeneous 'Representative Elementary Volumes' (REVs) in order to properly approximate the compositional heterogeneity, as well as temperature, concentration and pressure gradients. Effective transport parameters normally depend on the porosity, which can be changed by precipitation/dissolution reactions, which, in turn, are highly dependent on the transport. In case if the 'complete equilibrium' is assumed, a minimum REV may not exist. Even if metastable amounts of all mineral phases are under kinetic rate controls, the fastest reaction rate may induce unrealistically small REVs and/or time step duration.

Predictive thermodynamic and reactive transport modeling of cement systems, as well as of cement-clay interfaces of relevance for waste management, will gain trust only if the underlying assumptions behind local- and partial-equilibrium concepts are carefully checked on the basis of available microstructural and spectroscopic information, using the knowledge of characteristic heterogeneity of the system.

This contribution is aimed at initiating a discussion on how the time-dependent metastability of cement phases and minor/trace element uptake in them can be accounted for in chemical thermodynamic and reactive transport models, and how this can be reconciled with the data on cement microstructure, hydration, and degradation with contaminant sorption or leaching.

Sulfur reactivity at concrete/claystone interfaces

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Abstract

Since 2004, the National Radioactive Waste Management Agency of France (ANDRA) has been developing an Underground Research Laboratory (URL) at Bure, located in the Eastern part of the Paris Basin, in order to study the feasibility of a deep (400m) nuclear waste disposal in a thick clay-rich formation of Callovian-Oxfordian age (noted COx Clay) (ANDRA 2005). With the French concepts, concrete will be one of the materials use to build access structures, galleries and nuclear waste packages, and consequently will be in contact with Cox Clay. In order to constrain the long term behavior of these concrete/claystone interfaces, predictive modeling have been performed and validated by both in-situ Laboratory experiments of alkaline perturbation (Claret et al., 2012) and mineralogical, chemical and physical characterization of different cement material/clay interfaces sampled in the URL (Gaboreau et al., 2012).

Alkaline perturbation due to the highly contrasted pH and Eh conditions between cement materials and claystone is marked by a reactivity of the Fe-S-C system at concrete /claystone interface. Sulfate profiles obtained by leaching of clay samples and concrete at different distances from concrete/claystone interface show increasing contents at interface. On the concrete side major mineralogical changes are the <1mm-scale carbonatation associated with the portlandite disappearance and slight sulfur zoning depending of the cement type. On the claystone side, pyrite shows altered aspect on a cm-scale limited zone and gypsum rarely occurs as micron-sized coronas surrounding pyrite, as µm-sized fibers growing perpendicularly to fissures and to the concrete/claystone interface. The origin of gypsum at the interface remained unknown. In natural reduced conditions of claystone, gypsum is not present. Several assumptions can explain the gypsum formation at interfaces: (1) claystone desaturation, (2) pyrite oxidation, and (3) reactivity of claystone and concrete with a sulphate support due to ettringite dissolution. Sulphur isotopes were measured in gypsum in order to discriminate its origin, using SIMS technique. Analyses of sulphur isotopes in gypsum using SIMS analyses were corrected from the isotope fractionation of the machine by analysing an internal gypsum reference. Several analyses were performed by gypsum grain and averaged. Due to high fragility of sulphate under the beam, the standard deviation is estimated at 9 ‰; however it allows discriminating the origin of sulphur. Sulphur from the pyrite oxidation has a sulphur isotopic composition of the pyrite. Pyrite $\delta^{34}S$ at the level of the gallery ranges between -38 and -20 ‰$_{CDT}$. Sulphur in concrete was obtained by leaching of concrete with pure deionized water and precipitation as $BaSO_4$. Its $\delta^{34}S$ is about +8 ‰$_{CDT}$. Sulphate from desaturation should have a $\delta^{34}S$ close to those of porewater which is essentially controlled by celestite equilibrium (Gaucher et al., 2009), i.e. around +21 to 26 ‰$_{CDT}$ (Lerouge et al., 2011).

Two concrete/COx clay interfaces sampled at the level of the main gallery and previously studied for chemical and physical characterization were chosen for the gypsum presence at interface (Figure 1). Gypsum $\delta^{34}S$ are highly heterogeneous, ranging from -39 to -19 ‰. This range of values, despite the significant standard deviation, is almost close to the range of values of pyrite, suggesting that pyrite oxidation is the main origin of gypsum at concrete/ clay interface.
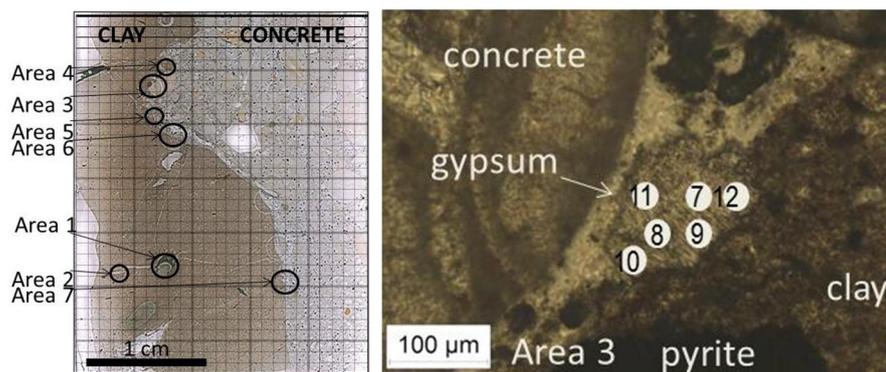
Figure 1 - (left) : General observation of a concrete / clay interface ; (right) : detail of pyrite and gypsum at interface (natural light).

Modeling the interaction between concrete and Boom Clay

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Abstract

In Belgium, Boom Clay is the reference hosting formation for the disposal of high-level radio-active waste. The current reference design of the engineered barrier system (EBS) is the so-called super container which plans to use cementitious material as construction, buffer and backfill material. The interaction between cementitious and clayish materials affects the durability and the functionality of the EBS.

To model the interaction between cementitious and clayish materials, a coupled diffusion-reaction code in axisymmetric coordinates is developed. The coupling is done using a sequential non-iterative approach. The diffusive transport is calculated using an explicit finite difference scheme and the reaction is calculated using PHREEQC. The code is parallelized using MPI (message passing interface) which greatly decreases the calculation time. PHREEQC version of CEMDATA07 database is used for concrete.

The simulation results show that concrete becomes almost clogged very fast at the concrete-clay interface caused by mineral precipitation. As a consequence, the effective diffusion coefficient at the interface becomes very small almost closing the concrete EBS. A sensitivity analysis is carried out to investigate the influence of cell sizes, time step and equilibrium/kinetic reaction. Since cell size directly determines the amount of minerals containing within a cell, it is very sensitive in the calculation of the clogging time. Time step has almost no influence on the modeling results. Due to the existence of "quasi-stationary" states, a large time step can be used. Results from kinetic and equilibrium reactions do not show much difference. This is probably because the time scale used for the reaction is still shorter than the time scale for diffusive transport.

Keywords: Concrete, Boom Clay, Parallel Computing, PHREEQC, Clogging, Radioactive Waste, Reactive Transport Modeling

Influence of temperature on the hydration of blended cements

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Abstract

The use of supplementary cementitious materials (SCMs) such as blast furnace slag or fly ash represents a viable alternative to Portland cements and utilizes by-products of industrial manufacturing processes. In Si-rich systems, portlandite can be absent and a calcium silicate hydrate phase (C-S-H) with a low Ca/Si ratio develops. A lower Ca/Si ratio leads also to an increase in alkali uptake by C-S-H and to a reduction of pH values in the pore solution. Little is known about the fundamental connection between the cement composition and hydrates formed and its impact on the long-term development of such systems. In this paper, the hydration of a 50 wt% of a Portland cement and 50 wt% of silica fume (SF) was investigated experimentally at 7, 20 and 50 °C. Thermodynamic modelling was used to predict the changes during hydration and the changes associated with the presence of different amounts of SiO_2.

An increase in temperature was found to accelerate the reaction of the silica fume more significantly than the OPC reaction. After 1 year and longer, however, a similar degree of silica fume reaction of approximately 70 to 80 wt% was reached at 7, 20 and 50 °C.

During the first day, the hydration of the blended cement at 20 °C proceeded similarly to OPC hydration. Ettringite formed during the first minutes. The presence of portlandite was observed between 1-7 days and the presence of hemi- and/or monocarbonate up to 28 days. The relatively low amount of portlandite formed and its consumption with time is related to the reaction of the silica fume. At 7 °C, the reaction of the silica fume was much slower, thus the presence of portlandite was observed up to 28 days, while at 50°C, the reaction of both the cement clinkers and of the silica fume occurred much faster and the presence of portlandite was observed after 6 hours only. The main hydration products that could be identified by XRD and TGA were ettringite and tobermorite-like C-S-H at 7 and 20 °C. At 50 °C, some ettringite had formed initially, which was destabilised after 28 days while poorly crystalline gypsum was observed. The temperature had also a significant influence on the composition of the pore solution. The fast reaction of the silica fume at 50 °C was mirrored by the fast decrease of K concentrations. The strong decrease of the alkali concentration with time was also mirrored in the decreasing hydroxide concentrations. The hydroxide concentrations at 7 and 20 °C decreased parallel to the decrease of the K and the increase of sulphate concentrations. The sulphate concentrations increased by a factor of 2 between 7 and 20 °C and factor of 5 between 20 and 50 °C, as the solubility of ettringite increases with increasing temperature.

Thermodynamic modelling indicated that the replacement of PC by SiO_2 leads to significant changes in the composition of the hydrate assemblage. Not only portlandite was depleted to form more C-S-H but also the amount and kind of AFm and AFt phases were affected. Monocarbonate and monosulfate were calculated to be unstable with regard to strätlingite and calcite as more and more SiO_2 becomes available. If even higher quantities of SiO_2 are available, eventually also ettringite is calculated to be unstable as the pH decreases.

In-diffusion experiments of [36]Cl in composite concrete

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Abstract

Irradiated graphite waste from the first generation gas-cooled French reactors (UNGG) is classified as long-livedand low-level radioactive waste (LLW-LL). Concrete and cement-based materials will play an important role, as container and backfill materials, in the disposal concept under study for this kind of radioactive waste. At the present time, it is planned to emplace graphite waste in metal baskets which are then put into concrete containers. Cement would then be injected in the container, to be completely closed with a concrete lid. Available data on irradiated graphite waste show that the long-lived activation product [36]Cl ($T_{1/2} = 3.01 \ 10^5$ years) was produced from [35]Cl impurities during reactor operation [1]. Although its content in irradiated graphite is very low, [36]Cl is a highly soluble element in water and mobile in environment so that it may contribute to a significant dose peak at the outlet after water ingress into the repository site. In order to improve the disposal concept and performance, an accurate knowledge of [36]Cl migration is required by the French National Radioactive Waste Management Agency (ANDRA). In such a context, understanding the behaviour of [36]Cl towards cement-based materials is of interest for long-term performance assessment.

[36]Cl diffusion experiments through non-degraded cement pastes have already been reported in literature [2]. Modelling work on [36]Cl experiments, using a simple diffusion/sorption model, couldn't correctly describe the experimental results. As these experiments were performed using specific experimental conditions (cement composition, water to cement ratio and porosity), it was necessary to complete the available results by new sets of data using chemical conditions relevant for the disposal. In that purpose, wet chemistry measurements have been performed at CEA to investigate the Cl retention onto a F44-like cement paste (EDF reference concrete) [3]. Using [36]Cl as radiotracer, Blin *et al.* [3] observed a slight retention of [36]Cl onto the altered cement paste and a sorption-site saturation effect created by stable chloride ions, which should be present in the natural water in the vicinity of the disposal facility. However, interaction processes between the cement paste and [36]Cl were not precisely identified.

The present study aims at investigating [36]Cl migration in a F44-concrete sample by in-diffusion experiments using similar chemical conditions as Blin *et al.* [3]. The main objective of these tests, performed on compacted samples, is to confirm previous results by determining effective diffusion coefficients (D_e) and especially, rock capacity factors (porosity $\omega \times$ retardation factor R) using the [36]Cl diffusion profile in the solid.

Two concrete samples with different alteration state, a fresh concrete sample and an alkali-free concrete, have been saturated with various stable chloride ion concentrations, prior to in-diffusion of [36]Cl. The in-diffusion experiments have been performed during more than a year and [36]Cl activities in the solid have been obtained after grinding (profile-grinder, Germann Instruments) and leaching in acidic conditions. The total chloride ion concentration has an effect onto [36]Cl diffusion in concrete. The migration of [36]Cl is delayed

and correlated with chloride ion concentration, which is confirming the sorption-site saturation effect as previously observed onto similar composite cement paste samples [5].

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Predicting long term cement-radionuclide interactions: sensitivity analysis for selected thermodynamic databases.

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Abstract

Concrete is an important material that is used in radioactive waste repositories as a physical and chemical barrier between waste and the environment. It has a complex physical and chemical properties, with a low porosity that reduces diffusion rates of radionuclides, and a high chemical reactivity that strongly binds a number of important radionuclides. However, because of its reactive chemical nature it will gradually change over time as a result of internal ageing and of interactions with the environment.

These long term changes are likely to affect radionuclide migration rates through concrete. In order to estimate the order of magnitude of these changes in migration rates, numerical models are required that describe both the physical chemical changes of the concrete in combination with the radionuclide interactions.

Such reactive-transport models, that are commonly used in risk assessments, rely on a description of the chemical processes that are relevant for concrete aging as well as relevant reactions for concrete-radionuclide interactions. This type of information is available in thermodynamic databases such as the Cem07 database (cement reactions), NEA database (radionuclide reactions) and Thermoddem (cement + radionuclide reactions), that can be used in combination with general reactive transport codes such as PHREEQC, TOUGHREACT, CRUNCH and ORCHESTRA.

In this work we will evaluate the sensitivity of predicted radionuclide migration rates in a concreteclay scenario, for a number of radionuclides (U, Pu, Tc, I, Np) to the selection of thermodynamic data used. Specifically, the impact of integrating the Cem07 database with the NEA database for radionuclides will be examined by comparing results for ORCHESTRA with integrated NEA/Cem07 database, with NEA database only, and with the Thermoddem database.

Finally the sensitivity of the results for different numerical approaches will be evaluated by comparing ORCHESTRA or PHREEQC simulations that use the same Thermoddem thermodynamic database.

Interactions of americium with cement alteration products in brines

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Abstract

Retention of radionuclides in the near field is critical for the safety of long-term disposal of radioactive waste in deep geological formations. Ordinary Portland cement is used as matrix material for solidification of low / intermediate active waste (L/ILW). Alteration of radionuclide bearing cement products in diluted aqueous solutions has been studied quite extensively. However, in chloride-rich solutions, which are relevant for final LLW/ILW disposal in rock salt, there is still a lack of thermodynamic data and understanding with respect to both cement corrosion and radionuclide behaviour. In the present study, interactions of americium with hardened cement paste (HPC) corroding in $MgCl_2$–rich brines were investigated using laboratory scale batch experiments and geochemical modelling.

Initially Am-free experiments with HPC powder and concentrated $MgCl_2$ brine, Q- and Rbrine were performed in inert-gas glove boxes ($CO_2(g) < 5$ ppm) at different cement product / brine ratios (m/V). After equilibration of the systems, the non-agitated experiments were doped with small quantities of acidic $^{241}Am(III)$ and $^{243}Am(III)$ solutions (10^{-9}, 10^{-8} and 10^{-7} mol Am (kg H_2O)$^{-1}$). Compositions of altered solution and altered solid were analyzed regularly to monitor the equilibration of the cement / brine systems and the Am sorption kinetics. The Geochemist`s Workbench® (GWB) software package (Bethke and Yeakel, 2009) was used for thermodynamic equilibrium calculations, simulating compositions of the equilibrated cement / brine systems. Details on the applied thermodynamic database are given by Bube et al. (submitted).

Due to dissolution of hydration phases (mainly portlandite ($Ca(OH)_2$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}:26H_2O$)) and other mineral phases (e.g. mayenite ($Ca_{12}Al_{14}O_{33}$)), the initially $MgCl_2$-rich solutions altered to alkaline $CaCl_2$-rich solutions. Besides reprecipitation of gypsum ($CaSO_4 \cdot 2H_2O$), formation of hydrotalcite (($Mg_{1-x}Al_x)(OH)_2(CO_3)_{0.5x}:0.5(H_2O)$) hydrocalumite ($Ca_8Al_4(OH)_{24}(CO_3)Cl_2(H_2O)_{1.6}(H_2O)_8$), Mg-Ca-Al hydroxide ($(Ca,Mg)_4(Al,Si) (Cl,SO_4)_2:n(OH,H_2O)$) and brucite ($Mg(OH)_2$) was observed. Compositions of the altered solution and solid phases depended strongly on the cement / brine ratio. At lower m/V ratios, solutions were still dominated by $MgCl_2$ at weakly alkaline pH_m ($-\log(m_{H+}) = pH_m$) values, while at m/V ≥ 0.65 g mL^{-1}, final solutions were $CaCl_2$-rich with strongly alkaline pH_m values. Measured solution compositions agreed well with results of thermodynamic calculations for the studied cement / brine systems.

Sorption equilibria in the Am/brine/cement systems at pH_m ~8.5, ~10 and ~12 were approached within less than one year. Data of the equilibrated systems were characterized by linear sorption isotherms, which allowed determining apparent sorption coefficients, R_s. In mixed $MgCl_2$-$CaCl_2$ and weakly alkaline $CaCl_2$ systems (7.3 < pH_m <9.0), R_s was measured in the range of 2000 to 5900 ml g^{-1}, whereas in highly alkaline $CaCl_2$ systems (pH_m ~ 11.5) R_s = 12800 ±7700 ml g^{-1} was observed.

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Predominant surface reactions towards a kinetic model for the C$_3$S dissolution

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Abstract

A specially designed reactor connected to an ICP spectrometer enabled the careful determination of the dissolution rate of the main anhydrous phase of cement, C$_3$S, under conditions devoid of C-S-H. The kinetic laws, bridging the dissolution rate and the undersaturation, were obtained after extrapolation of rate zero allowing the estimation of the true experimental solubility product of C$_3$S (K_{sp} =9,6.10^{-23}). The latter are then compared to the solubilities calculated from the enthalpies of formation. We propose that the observed deviations result from the protonation of the unsaturated oxygen atoms present at the surface of these minerals. This hypothesis is comforted by the same analysis done on C$_2$S and CaO, showing coherent results. It is also presented that aluminates ions, even present at low concentration in typical cement pore solutions, have a large influence on the solubilization of silicate and calcium species out of the C$_3$S surface. A tentative explanation by interfacial reactions involving silanols and protonated oxygens at C$_3$S surface sites and aluminate ions is proposed. This work is a first step towards a complete modeling of the C$_3$S dissolution according to the composition of the cement pore solution.

Modelling approach to evaluate changes in hardened cement paste microstructure under the influence of aggressive pore water

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Abstract

Cement based materials are one of the important construction materials for radioactive waste disposal systems providing favourable physical and chemical conditions for the long-term encapsulation of radioactive waste. Cementitious engineered barriers (CEB) delivers important safety functions such as limiting water flow through the disposal facility and providing high and long-lasting sorption of radionuclides.

Interaction between cement and aggressive surface water in a near surface disposal are typically subject to detrimental processes such as carbonation and decalcification which may induce changes in physical and chemical properties of CEB. These processes induce chemical interaction between pore-water and solid phase (at the scale of capillary pores) which in turn affects physical and mechanical properties of cement based materials at macro-scale. Simulations of these geochemical changes at pore scale can be done by the discrete representation of pore structure.

As opposed to the existing studies focusing mostly on microstructural changes occurring during hydration of concrete, here a generic approach based on Lattice Boltzmann method is proposed to model the evolution of microstructure of cement based materials under geochemical interaction with aggressive pore water. This microstructural solver consists of flow and reactive mass transport modules. The flow module solves the Navier-Stokes equation for fluid flow through a porous media and is coupled with a reactive transport module in case of pressurized flow. Reactive mass transport module consists of a Lattice Boltzmann mass transport solver coupled with a geochemical equilibrium and kinetic solver. The reactive transport solver handles multicomponent advective-diffusion mass transport, equilibrium and kinetic reactions occurring within the fluid phase and equilibrium and kinetic reactions occurring at the mineral surface. The reactive transport module has the capability of altering the solid phases to take into account mineral precipitation and dissolution reactions. The developed model can be used to evaluate changes in HCP microstructure under the influence of aggressive pore water resulting in carbonation or calcium leaching.

Docking ^{90}Sr Radionuclide in Cement: an Atomistic Modeling Study

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Abstract

Cement-based materials in general and concrete in particular are used in the construction of various nuclear facilities because of three major reasons. First, these materials are known for their structural strength and durability over very long periods of times. Second, they are able to shield effectively against radiation and against the migration of radionuclides. Third, a great experience in producing these materials at very low cost compared to other structural materials was accumulated over time.

At every stage of the nuclear fuel cycle, cement-based materials play a major role in providing support, shielding and containment. For example, concrete structures are used as storage pool for the fresh nuclear fuel. Later on when the nuclear fuel is in operation in the nuclear power plant, the concrete containment is the outermost barrier that shields against any leakage of radioactivity to the biosphere and is also known to be the only irreplaceable component of the nuclear power plant. Furthermore, concrete structures serve as an interim for the spent nuclear for decades after the operation in the nuclear power plants. Finally, cementitious materials can be used as the waste form and/or a container for the whole waste package for the ultimate disposal of radioactive materials in geological repositories.

Understanding on a fundamental level the long-term performance of cement-based materials and developing capabilities to project their lifetimes is of utmost importance. To that end we believe that computational science techniques exemplified by atomistic simulation is able to provide such a fundamental understanding and can be utilized as a predictive tool as well. Historically atomistic simulation techniques were not used in concrete/cement science because of the complexity involved in modeling these materials. However, with the recent advances in our understanding of the structure of cementitious materials at the nanoscale it is possible now to incorporate atomistic simulation techniques in studying cementitious materials on equal footing with experimental techniques.

In this work we address the problem of exploring the stability of cementitious materials upon cationic exchange between the host cations and radionculides. The mechanical integrity of the cement/radionuclide waste form system is also investigated to assess its ability to prevent the release of radionuclides into the environment. In the assessment of the performance of cementitious materials in the nuclear fuel cycle, we investigated by means of atomistic simulations the encapsulation of strontium-90, an important radionuclide, in C-S-H and its crystalline analogue tobermorite 9 Å. Strontium was shown to favor energetically substituting calcium in the interlayer sites in C-S-H and tobermorite 9

Å with the trend more pronounced in the latter. The silicate chains in both cementitious waste forms were not affected by strontium substitution within our molecular dynamics simulation. Finally, we observed degradation in the mechanical properties in the strontium-containing cementitious waste form. The degradation increases with the increase of strontium concentration, but overall this degradation is not limiting for the use of C-S-H or tobermorite 9 Å as candidates in immobilizing radioactive strontium. We then consider the Strontium to Yttrium reaction and study the docking of Y^{3+} in CSH in order to assess the stability and mechanical properties of this phase.

Modelling degradation fronts in cracked concrete due to chemical leaching

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Abstract

Durability of concrete structures used in civil engineering is typically assessed for periods shorter than 100 years. On the other hand, concrete structures used as an engineered barrier in radioactive waste disposal systems have to perform their safety functions for much longer periods. One of the most important long term safety functions is sorption of radionuclides to cementitious materials, especially in a near surface disposal system. Concrete will be exposed to infiltrating water over a long time period. This water is not in equilibrium with cement pore water and, as a consequence, cement minerals are dissolved and leached out of the engineered system. Leaching/degradation of concrete results in less favorable physical and chemical properties as larger porosity, larger diffusivity, larger permeability, lower bulk density, lower sorption of radionuclides and poorer mechanical properties.

Concrete as a porous material is characterized by both a complex structure (multi-scale media) and chemical composition. Large concrete structures typically involve discrete discontinuities as micro- or macro-cracks which has to be taken into account when addressing the transport and degradation of concrete on large scale.

Numerical solution of complex and fully coupled chemical-physical transport system requires an efficient solution algorithms and a complete and accurate thermodynamic database for geochemical evolution simulation together with constitutive relations for microstructural evolution of the cement paste. Due to above-mentioned complexity the uncertainties of involved numerical model could be large. In the absence of experiments due to long periods required for complete chemical evolution, the only viable way to evaluate accuracy is extensive benchmarking.

In this presentation a larger scale benchmarking campaign of different codes, solution algorithms and databases is presented. The comparison gives an idea of possible uncertainties related to numerical solutions of such complex system. The benchmarked results will serve for the development of a hybrid approach (based on model abstraction) for large-scale and long-term assessments which serve as a basis for performance assessment analysis for near surface radioactive waste disposal facilities.

A Model to Predict Carbonation of Cementitious Materials under a High CO$_2$ Pressure Condition

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Abstract

The carbonation process in cement-based materials is a chemical degradation through reactions between carbon dioxide and alkaline ions when CO$_2$ penetrates the materials. Carbonation is mainly known as a deterioration phenomenon for reinforced concrete structures because of the dissolution of the passive layer protecting steel bars when the pH decreases after carbonation. For the case of cementitious-based solidified waste, it has also a beneficial effect on the leaching/transport processes by decreasing the porosity and thus tortuosity and permeability and by increasing the strength of the cementitious materials.

Civil concrete structures are rarely submitted to a high pressure gradient of gases or liquids. Therefore, most carbonation models only account for diffusion as the main transport mechanism rather than advection. However, in some applications like the use of underground concrete structures in radioactive waste disposal which are subjected to higher partial CO$_2$ pressure than in the atmosphere (in case of unsaturation) or/and higher liquid pressure gradient (in case of saturation), the advection term should be taken into account. It is also the case of carbon dioxide sequestration in cement-based materials. This study aims at developing a model to predict the carbonation of cement-based materials under accelerated conditions in which a high pressure gradient of pure CO$_2$ is applied to the specimens of different relative humidity. The proposed model is one-dimensional and couples both diffusion and convection as the main transport mechanisms. This model is based on macroscopic mass balance for carbon dioxide in gaseous and aqueous phases and is developed for isothermal conditions. The model only considers the carbonation of calcium hydroxide and C-S-H. The hydration during carbonation is not taken into account in the model due to the accelerated conditions. Beside the prediction of the carbonation depth the model also enables to calculate the mass gain due to carbonation. Data from acceleration tests are used to validate the model.

Carbonation of repository cement: Impact of CO_2 on cement mineralogy and porewater chemistry

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Abstract

In the current UK reference concept, large quantities of cementitious materials will be used for both repository construction and as a buffer/backfill for low/intermediate radioactive wastes. Degradation of organic material within the waste will produce carbon dioxide (CO_2), leading to the conversion of cement minerals to secondary phases, such as carbonates. This will reduce the capacity to maintain highly alkaline conditions, and possibility the ability to limit radionuclide migration. While some carbonation reactions might improve material properties, it is currently unclear whether the overall changes due to carbonation will be beneficial or deleterious to longterm radionuclide immobilisation.

As part of a pan-European Euratom 7th Framework initiative examining the fate of repository gases (FORGE project - Grant Agreement 230357), BGS has undertaken a laboratory study to examine the impact of carbonation on samples of 'Nirex reference vault backfill' (NRVB) cement. Aims for the work included quantification of changes in cement mineralogy, structure and porosity/permeability, together with monitoring changes in the composition of coexisting aqueous fluids. Laboratory investigations involved a series of static and flowing experiments under a range of potential in-situ conditions; 20°C or 40°C, 4 MPa or 8 MPa, 'young' (Na/K/Carich) or 'evolved' (Ca-rich) cement porewaters, with or without CO_2. Experimental durations lasted from 10 days to 1 year.

The range of experimental variables was investigated using over 30 static 'batch' experiments, each containing small cores of NRVB. All the cement samples showed rapid reaction with CO_2, increasing in weight by up to 9%, though not changing in overall size. Free phase CO_2 gave slightly more reaction than dissolved CO_2, possibly because of its higher concentration and greater ability to penetrate the samples. Major reactions were the breakdown of portlandite and calcium silicate hydrate (CSH) phases and the formation of carbonate phases and silica. These resulted in several reaction zones which moved through the cement over time: Zone 1 = minor carbonation with minimal apparent volume change, Zone 2 = significant carbonation and localised shrinkage, Zone 3 = complete conversion of portlandite and CSH, Zone 4 = dissolution of initially-formed carbonate minerals in the outermost parts of the sample by the surrounding, slightly-acidic water. Zone 3 contained higher-density carbonate-filled fractures and concentric 'relic' reaction fronts, which separated areas having lower-density and high porosity. Appreciable amounts of a Cl-rich phase were formed at the boundary of Zones 2 and 3.

Controlled flow-rate carbonation experiments on cores of NRVB reveal decreases in overall sample permeability. These reflect porosity reduction due to conversion of portlandite and CSH to secondary carbonate minerals. Small discharges of water were also released as a by-product of CSH phase carbonation. Detailed petrogaphic observations of partly-reacted cement samples show a series of reaction zones as per the static experiments. These observations, coupled with micropermeameter data, show the greatest reductions in porosity and permeability in a very narrow zone at the leading edge of the visible alteration front.

Carbonation features and secondary phases observed in these experiments using a relatively porous/permeable cement, bear many similarities to those found in far lower porosity/permeability borehole cements used in CO_2-storage operations. There are also similarities to samples of naturally-occurring CHS phases which have been naturally-carbonated over prolonged timescales. A number of common carbonation processes may be operating in all these systems.

Change of microstructure of hardened cement paste with a low alkali binder due to leaching

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Abstract

The dissolution phenomena of cement hydrates is one of important considerations in designing radioactive waste repositories. Leaching test was carried out using an electrochemical migration technique. This method enables to accelerate the dissolution of cement hydrate from cement paste in contact with water. Two types of low alkali cement blend were prepared and a water to binder ratio (*w/b*) of 0.5. Combination of low heat Portland cement (LPC) and fly ash at cement replacement level of 30% was used as binary cement blend. Ternary cement blend included combination of silica fume 20% and fly ash 40% at OPC cement replacement levels. OPC cement paste was used as a control mix. After leaching test, the samples were observed by using X-Ray computed microtomography at SPring-8, Japan. The result of image analysis of deteriorated specimens shows that the pore volume and pore connectivity increased as the effect of cement hydrate dissolution. Deterioration scattered evenly in OPC specimens, spotted in binary specimens and slight in ternary specimens. This is particularly notable that the incorporation of pozzolanic admixture in cement blend shows a good performance against leaching.

Keywords: dissolution, low alkali cement, leaching, Synchrotron X-Ray CT, pore structure, random walk simulation

Reaction of aluminium with composite cements based on calcium aluminate phosphate system

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Abstract

Cementation is the preferred method for the encapsulation and immobilisation of low- and intermediate-level radioactive waste in the UK. There are concerns about the compatibility of the conventional cement systems based on ordinary Portland cement with certain reactive metallic wastes such as aluminium, magnesium and uranium arising from Magnox waste stream. The availability of free water and high alkalinity (pH > 12.5) of ordinary Portland cement based systems causes corrosion of these reactive metals, which results in expansive reaction products and the generation of significant amounts of hydrogen gas, both which are detrimental to the solid wasteform.

The authors have been developing a new cement system for the encapsulation and immobilisation of problematic reactive metals derived from the Magnox waste stream in the UK [1]. In the present investigation, calcium aluminate phosphate (CAP) systems, prepared by acid-base reaction between calcium aluminate cement (CAC) and phosphate solution have been blended with pulverised fuel ash (PFA), and basic properties of pastes, hydration phases, and reaction with aluminium studied. The obtained results showed that the tested pastes were able to fulfil the basic properties required for industrial application. It was also found that the hydrogen generation in the initial 7 days due to the corrosion of aluminium was suppressed in the CAP based systems, showing a good potential of the systems for aluminium encapsulation.

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Sorption of actinides onto TiO$_2$, calcium silicate hydrates and hardened cement paste

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Abstract

Cementitious materials are an important component in the multi-barrier concepts developed in many countries for the safe storage of low and intermediate level (L/ILW) radioactive waste in deep geological repositories. Reliable thermodynamic models able to predict the interaction between radionuclides and cementitious materials in the long term are important for performance assessment. The development of such models requires a sufficiently detailed macroscopic and molecular-level understanding of the uptake processes involved. Studies on the retention of radionuclides by cementitious materials have focused predominantly on adsorption as the relevant uptake process. However, other potentially important immobilization processes, such as incorporation in the solid matrix, may take place and, thus, exert a beneficial effect on radionuclide retardation. Calcium silicate hydrates (C-S-H), the major cement constituent, are characterized by high recrystallisation rates making them an ideal system for the incorporation of radionuclides present in cement-based repositories.

In the present study, batch sorption experiments have been performed under high pH conditions with the aim of determining the speciation and sorption of actinides (uranium, neptunium, thorium) in cementitious systems under both oxidizing and reducing conditions. Batch sorption experiments were carried out with C-S-H phases, hardened cement paste (HCP) and titanium dioxide, a solid phase stable under high pH conditions and often used as a model sorbent in surface complexation studies. Comparison of the sorption of the actinides on TiO$_2$ and cement phases allows the influence of incorporation processes on the immobilisation of actinides by C–S–H phases and HCP to be assessed.

Actinide uptake was found to be fast and sorption distribution ratios (R_d values) were high, indicating strong retention by all solids. The similar sorption behaviour in C-S-H systems and in HCP observed from the batch sorption experiments indicated that the actinides were predominantly bound to the C-S-H fraction in HCP. The experimental data further indicate that the sorption of tetravalent actinides on all solids is independent of pH and solution composition. In contrast, the sorption of pentavalent and hexavalent actinides was found to be highly dependent on pH and Ca concentration in solution.

The sorption behaviour of pentavalent and hexavalent actinides on TiO$_2$ can be described by an adsorption process on the assumption that: 1) Anionic hydrolysed species are not adsorbed on the negatively charged TiO$_2$ surface, 2) The formation of anionic hydrolysed species in solution competes with adsorption of the species onto the TiO$_2$ surface, 3) Specific adsorption of Ca$_{2+}$ cations on the TiO$_2$ surface results in a positive surface charge and promotes adsorption of anionic hydrolysed actinide species.

The R_d values for pentavalent and hexavalent actinides measured on C-S-H phases with varying composition were found to decrease with increasing C:S ratio. The combined effect of pH and Ca concentration in solution on the uptake by C-S-H phases suggests

that the sorption behaviour of pentavalent and hexavalent actinides on C-S-H can be explained by processes similar to those on TiO_2, i.e. competition between adsorption of actinide species onto the C-S-H surface and the formation of anionic hydrolysed species in solution, and further formation of positively charged surface sites on TiO_2 due to specific Ca^{2+} sorption, which results in an increased adsorption of anionic hydrolysed species of pentavalent and hexavalent actinides. These findings are compared with earlier results from spectroscopic studies suggesting incorporation of pentavalent and hexavalent actinides in the C-S-H interlayers.

Overall it appears that the sorption data of pentavalent and hexavalent actinides on C-S-H phases and HCP can be interpreted in a manner consistent with adsorption of actinide species on the surface of cementitious materials, thus implying that sorption measurements cannot give clear evidence for incorporation processes.

C-S-H gel dissolution kinetics. Flow-through experiments

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Abstract

Although the solubility of C-S-H gel, which is the main responsible for the durability and barrier properties of cement, has been studied by many authors, its dissolution kinetics is not known. In this work we present kinetic data based on results from flow-through experiments.

The C-S-H gel used in the experiments was obtained by hydration of synthesized C_3S ($3CaO \cdot SiO_2$), which results in the formation of C-S-H gel and portlandite. C_3S was hydrated during either 28 days or 4 months at room temperature with a w/s ratio of 0.5. For the sample hydrated during 28 days remanent C_3S was observed in Rietveld analysis. Only trace amounts of C_3S could be detected in samples hydrated during 4 months. The hydrated cement was ground and the fraction <25 μm selected. All operations were performed inside a glove box filled with N_2 gas to prevent carbonation. The Ca/Si ratio of the solid was measured by electron microprobe and a Ca/Si ratio of 1.65 was obtained.

The stirred and non-stirred flow-through experiments were performed at room temperature ($22 \pm 2\,°C$) and under CO_2-free N_2 atmosphere. In order to know the evolution of Ca/Si ratio of the solid, several flow-through experiments were performed in parallel and stopped at different times. Ca and Si concentrations and pH were monitored during the experiments. The flow rate was kept constant at either 0.05 or 0.13 mL min^{-1}.

The evolution of pH, Ca and Si concentrations showed 3 distinct stages during the experiments. In the first stages, the dissolution of the C-S-H gel is incongruent (preferential release of Ca). In stage 1, Ca concentration was much larger than Si, indicating preferential dissolution of portlandite ($Ca(OH)_2$) and slow close-to-equilibrium dissolution of C-S-H. The initial Ca/Si ratio in solution was much larger than in the solid and the pH was around 12. In the second stage, as the portlandite content diminished, a gradual decrease in Ca and increase in Si was observed, indicating an increase in C-S-H gel dissolution. The aqueous Ca/Si ratio decreased to values below 10 and the ratio also decreased in the solid. pH decreased to values about 11.5 - 11. In the last stage, concentrations of Ca and Si and pH (≈11) reached steady state. At this stage the Ca/Si ratio in the solid and in the aqueous phase tended to a constant value of about 0.9 suggesting that (i) the C-S-H gel was the main dissolving phase and (ii) the dissolution reaction evolved to the congruent dissolution of a phase with tobermorite stoichiometry (Ca/Si = 0.83), which is consistent with current C-S-H solubility models (e.g. Kulik and Kersten, 2001). Steady-state dissolution rates of the C-S-H gel normalized to the final BET specific surface area ranged from 10^{-12} to 10^{-11} mol/m^2/s.

The experimental results are being modeled with the CrunchFlow reactive transport code (Steefel, 2009) assuming a dissolution rate law of the form $R = A \cdot k \cdot (1-\Omega)$, where R is rate (mol/m^3/s), A is surface area (m^2/m^3), k is the rate constant (mol/m^2/s) and Ω is the saturation degree (ionic activity product divided by equilibrium constant). First results (Fig.1) are consistent with a rate constant ranging from 10^{-8} mol/m^2/s (Ca/Si = 1.67) to 10$^-$

[11]mol/m^2/s (Ca/Si = 0.83) for the C-S-H solid solution, when normalizing to BET specific surface area. These values highlight the necessity of considering C-S-H dissolution kinetics in cases where water flows by advection through mortar or concrete (fast transport; dissolution rate limiting C-S-H dissolution).
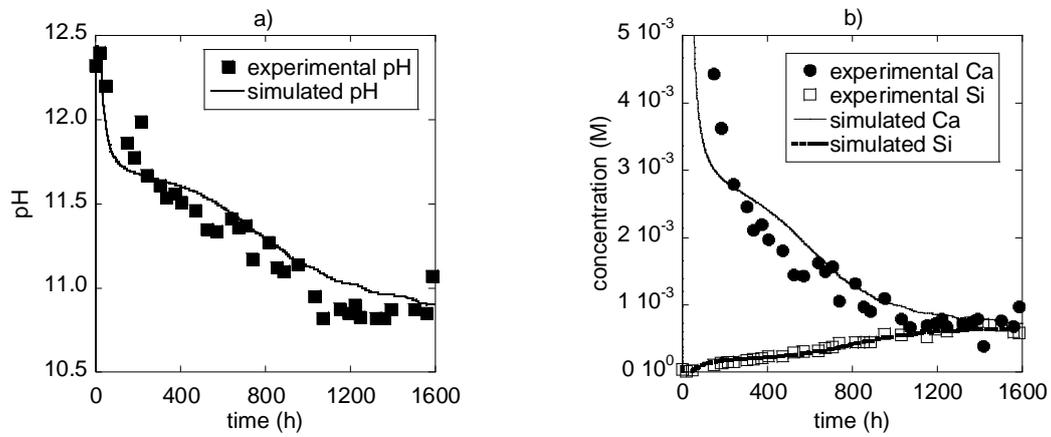

Fig. 1. Solution composition at the outlet of the flow-through reactor for a single C-S-H dissolution experiment. (a) pH, (b) [Ca] and [Si]. Points are experimental data; lines are model results.

Geochemical modelling of leaching tests data on cementitious barrier materials as basis for long term release prediction

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Abstract

Recently validated leaching test methods for assessing release from stabilised waste and cementitious products have been applied to reference materials prepared in the context of the Cementitious Barriers Partnership (CBP supported by US DOE). These comprise amongst other vault concrete, backfill grout mortar and stabilised waste. The test results have been used as basis for geochemical speciation modelling to obtain chemical speciation fingerprints (CSF) to be used in subsequent reactive transport modelling. The dynamic tests in the laboratory tool set (monolith leach test and percolation test) are used to verify the suitability of the reactive transport models based on CSFs as basis for predictive release modelling. The modelling considers mineral precipitation/dissolution, incorporation into solid solutions, ion exchange on clay surfaces, sorption onto hydrated iron oxide surfaces, particulate and dissolved organic matter. The first step in the process is to obtain a good match between the multi-element release description covering all of these competing phases and the test results from the pH dependence test. In the multi-element model run a prediction at low liquid to solid ratio is included as starting point for the assessment of porewater conditions in both percolation conditions and monolith leaching. Gaps in the available thermodynamic data set can be readily identified to focus research needs. The release prediction for the dynamic tests – monolith leaching and percolation – make use of the CSF as basis for the chemistry of the system in addition to representative model descriptions to capture relevant mass transport processes like dual porosity and radial diffusion in percolation. The modelling results for concrete and stabilised waste leaching will be presented in context with experiences on a wider range of nuclear and hazardous waste applications.

Competition behaviour of metal uptake in cementitious systems

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Abstract

Cement is an important constituent of the engineered barrier systems in underground repositories for low and intermediate level radioactive waste. Cement is used to solidify and stabilize the waste materials and, furthermore, it is used in huge amounts for the construction and backfilling of the cavern. The release of radionuclides from the cementitious near field into the underground is retarded due to their strong interaction with cement mineral phases. In hydrated cement, calcium silicate hydrates (C-S-H), $(CaO)_{x(}SiO_2)y(H_2O)_z)$ are quantitatively the most abundant and most important phases. They are chemically the most stable minerals in a cementitious environment and exhibit a wide diversity of structural sites exposed for cation binding. Three different modes of heavy metal interaction with C-S-H phases can be envisaged: 1) surface complexation, 2) uptake in the interlayer, and 3) incorporation in the octahedral Ca sheets.

In this study, 11 Å tobermorite, a crystalline C-S-H phase, was doped with both Nd and Zn in order to investigate whether or not the competition between the two metals has an influence on the binding mechanism and the coordination environment of these metals in the C-S-H structure. On the basis of previous EXAFS studies a structural model for the site occupation of Zn in C-S-H phases was proposed [1,2]. Zn(O,OH)4 tetrahedra substitute for silicate bridging tetrahedral and/or they are bound at terminal silicate chain sites, thus suggesting Zn binding in layer positions of C-S-H phases rather than the interlayer. In contrast, spectroscopic studies on lanthanide binding to crystalline C-S-H phases indicate that Eu (and Nd) forms inner sphere surface complexes with the C-S-H surface in the early phase of the sorption process. However, with time, Eu and Nd binding into the structure of crystalline C-S-H phases occurs, occupying positions in the interlayer and the Ca layer of the C-S-H structure [3,4]. Therefore, Nd and Zn are expected to be taken up into the structure of C-S-H phases whereby they occupy neighbouring crystallographic positions. In this study Zn K-edge and Nd L-edge EXAFS spectroscopy was used to discern the possibility of backscattering contributions from neighbouring Zn and Nd atoms on the absorption spectra.

The Zn and Nd doped 11 Å tobermorite samples had metal concentrations ranging from 5000 to 50000 ppm, while the reaction times varied from one to six months. X-ray absorption spectroscopic data suggest that Nd has an influence on the incorporation of Zn in the tobermorite structure. The Zn K-edge EXAFS data exhibit distinct differences in the presence and absence of Nd as neighbouring element. Zn has a tetrahedral coordination environment with Zn-O distances of 1.96 Å, whereas Nd is octahedral coordinated with Nd-O distances of 2.45 Å. These findings indicate that competitive uptake of metal cations

with similar sorption behaviour by C-S-H phases can take place, which deserves further attention in future assessments of the safe disposal of radioactive wastes in cement-based repositories.

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Determination of the Fe speciation in cementitious materials using synchrotron-based micro-spectroscopic techniques

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Abstract

Repositories for low- and intermediate-level waste will contain large amounts of steel, which will slowly corrode under the alkaline conditions of the cementitious near field over time. The release of Fe(III) under oxidizing conditions or Fe(II) under reducing conditions, respectively, as a consequence of steel corrosion could influence mineral composition of hardened cement paste (HCP). At present, however, the impact of Fe species on the mineral omposition of HCP is poorly known. Replacement of Al(III) by Fe(III) in Alcontaining cement minerals and the formation of Al/Fe solid solutions was observed due to similar ionic radii in sixfold coordination of the two cations ($Al3+$: 0.54 Å; $Fe3+$: 0.65Å), e.g. [1]. In contrast, the replacement of $Ca2+$ by $Fe2+$ is uncertain due to the very different ionic radii in sixfold coordination ($Fe2+$: 0.78 Å; $Ca2+$: 1.00 Å). Micro-scale information on the impact of Fe species on the mineral composition of HCP will be essential with a view to long-term predictions of the effect of corroding steel on the barrier performance of HCP in a nuclear waste repository.

Synchrotron-based (micro-) spectroscopic studies on the Fe(III) speciation in HCP were carried out with the aim of determining the dominant Fe(III)-bearing minerals in cement paste. Synchrotron-based techniques were applied as the experimental identification of Fe-bearing hydrates in the complex matrix of hydrated cement pastes is difficult with techniques like X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy with micro-analysis (SEM/EDS) due to overlapping signals from the Al analogues. Earlier studies showed that the Fe K-edge absorption spectra of natural Febearing minerals differ from each other, which allows Fe-bearing minerals to be identified in complex mixtures [2].

Extended X-ray absorption fine structure (EXAFS) spectroscopy was used to determine the coordination environment of Fe(III) in crushed, hydrated cement samples. Bulk EXAFS spectra recorded on crushed HCP are composite spectra with contributions from several Fe(III) species. Factor analysis in combination with least-square fitting allowed the contribution of each Fe(III)-bearing cement mineral, for which the reference spectra had been recorded, to be quantified. Data analysis revealed that ferrite (C4AF), $Fe(OH)3$ and Fe-siliceous hydrogarnet are the dominant Fe(III)-bearing cement minerals in hydrated ordinary Portland cements. The results from the EXAFS study further agree with complementary measurements based on selective extraction of cement paste with salicylic acid and methanol (SAM) and subsequent characterization of the residual using XRD.

Micro X-ray fluorescence (micro-XRF), micro-X-ray absorption near edge spectroscopy (micro-XANES) and micro-EXAFS were used to determine the spatial distribution of Fe in the intact cement matrix and to further identify the Fe(III)-bearing species in reactive zones around ferrites. Micro-XRF maps revealing heterogeneous distribution of Fe in the cement matrix allowed points of interest to be identified for detailed micro-XANES/EXAFS

spectroscopic characterization of the mineral composition. The spectra from the micro-spectroscopic measurements on the intact samples could be interpreted consistently with the bulk EXAFS measurements on crushed materials, indicating that several Fe(III) species contributed to the composite spectra, and further suggesting that C4AF, Fe(OH)3 and Fe-siliceous hydrogarnet are the most abundant Fe(III)-bearing cement minerals formed in cement paste.

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Poster presentations

Stabilisation of polluted sediment in cementitious system

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Abstract

Large amounts of dredged sediment are made available as a result of the regular maintenance of waterways and harbours. In France, three million cubic metres of continental sediments are dredged every year to make navigation possible and to prevent flooding. In industrial regions, sediments are deeply impacted by metals and organic pollutants; their management is thus a major environmental concern. The common use of Ordinary Portland Cement (OPC) as a binder for sediment treatment is referred to as solidification/stabilisation. This technique uses cement and does not generate a valuable product.

In the present study, Portland cement clinker was synthesised using sediment in place of natural resources. The use of fluvial contaminated sediment to replace a portion of raw materials in conventional Portland cement manufacture produces a value-added product (cement) from wastes (sediment). The mineralogy of the synthetic cement was characterised using X-ray diffraction and scanning electron microscopy and its reactivity was followed by isothermal calorimetry. It was compared to a commercial ordinary Portland cement (CEM I 52.5). Compressive strength measurements were conducted on cement pastes at 1, 2, 4, 7, 14, 28 and 56 days to study the mechanical strength development. The results showed that Portland cement clinker can be successfully synthesised by using up to 39% sediment. The compressive strengths developed by the cement made from sediment were equivalent to those obtained with the reference at early ages and 20 % higher at long term.

Studies of the effect of organic materials and their degradation on radionuclide behaviour

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Abstract

UK Government policy is that geological disposal is the way higher activity radioactive wastes will be managed in the long term: this will be preceded by safe and secure interim storage until a geological disposal facility (GDF) is available and can receive waste.[1] Currently the UK has no site identified for a GDF and so the UK has a series of illustrative concepts which are considered in the generic Disposal System Safety Case (DSSC)[2]. The generic DSSC proposes approaches for the disposal of high level waste (HLW) and spent fuel as well as intermediate level waste (ILW) and longer-lived low level waste (LLW). This paper only considers ILW and LLW.

The generic DSSC considers the immobilisation of ILW and long lived LLW in cement-based grout which is packaged in standardised stainless steel, concretelined stainless steel containers or reinforced concrete disposal boxes. Organic material such as cellulose, halogenated and non-halogenated plastics, ion exchange resins and rubber would be present in ILW. Cement formulations may also contain organic additives. These materials may degrade over time to produce a range of degradation products, some of which might form aqueous complexes with radionuclides in the waste or possibly generate non-aqueous phase liquids (NAPLs). The formation of such complexes could stabilise radionuclides in solution, causing an increase in solubility and a reduction in sorption. The wastes may also contain 'as disposed' complexants.

This paper will give an overview of recent research in the UK programme to study the impact of the degradation of waste components under conditions relevant to grouted wastes. These include:
- the behaviour of selected radionuclides in cements in the presence and absence of a superplasticisers
- the effect of 'as disposed' complexants on the solubility of nickel, thorium and uranium (4+ and 6+)
- the characterisation of cellulose degradation products (CDP) and the behaviour of selected radionuclides in the presence of CDPs
- the potential for NAPLs to be generated and influence radionuclide migration.

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NEA TDBIV project: preparation of a state-of-the-art report on thermodynamic data for cements

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Abstract

The program of work of the fourth phase of the OECD NEA Thermochemical Database Project (TDB-IV) contemplates a line of activity on the preparation of a state of the art report on cements. The present work aims at presenting the project, its aims and its limits.

In the context of nuclear waste disposal, concrete is used both as a confinement and a building material. The safety of the repository has to be assessed over long period of times. Numerical simulations remain an important tool for such an assessment. For that purpose, the stability and more precisely, the solubilities of the mineral that compose the different containment barriers have to be defined with reliability, by taking into account the experimental data published on this topic. The present project aims to provide a consistent and reliable set of thermodynamic parameters especially for the minerals that form in cementitious materials. It consists in a review of the literature in order to establish what chemical thermodynamic data, models and numerical implementation tools exist for the thermodynamic treatment of cement systems. The chemical system considered contains $Na_2O-K_2O-CaO-SiO_2-Al_2O_3-MgO-Fe_2O_3-CO_2-SO_3-Cl-H_2O$ and includes nanocrystalline and crystalline phases. In addition, since highlevel long lived radwaste and some of the intermediate level wastes are exothermic (e.g. compacted hulls and endspecies), temperature exposure of the concrete backfill and packages must be considered. To describe the solubility at a range of temperatures, a complete set of thermodynamic parameters, including entropies and heat capacities functions, is needed.

The review itself covers the fields of:
- C-S-H minerals. This includes noncrystalline and crystalline phases, Al, Fe and Mg substitutions, the influence of relative humidity
- AFm, AFt, Hydrogarnet solid solutions
- Additional phases, hydroxides, zeolites

The work concerns basically the thermodynamics properties of minerals. Surface reactions or the influence of kinetics will not be treated.

Migration of acetate, formate and propionate species in cementitious materials

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Abstract

Carbon 14 is produced in the nuclear fuel cycle following neutron interactions with ^{13}C, ^{14}N, ^{15}N, ^{16}O and ^{17}O, which may be present in the nuclear fuels, as well as in primary and secondary coolant systems of nuclear reactors. In the framework of irradiated graphite waste from the first generation gas-cooled French reactors (UNGG) reprocessing and storage, ^{14}C, as a long-lived betta emitter ($T_{1/2}$= (5730 ± 30) years) is a radionuclide of interest and its behavior is still poorly known in cementitious system.

^{14}C can occur as inorganic and organic species in cementitious systems. The inorganic form $^{14}CO_3^{2-}$ reflects a low mobility due to high isotope exchange rates with carbonate species present in concrete materials. However, under the organic form (mainly composed of alkane and short-chain carboxylic acids), ^{14}C is less retained and is expected to be more mobile, particularly considering hydrocarbon form.

This research firstly focuses onto the interaction of the organic fraction (acetate, formate and propionate species) supposed to be released from graphite waste with cementitious matrices. Batch-sorption experiments are conducted using various cementitious materials (kinetics and isotherms of sorption and desorption) in order to investigate the effect of the alkane-chain length and the effect of cementitious materials compositions onto sorption properties. In parallel, diffusion experiments are conducted through cement paste materials and in mortar material, in order to determine diffusion parameters of the investigated organic species using ^{14}C-labelled organic tracers.

Experimental characterization of cement-bentonite interaction using core infiltration techniques and 4D computed tomography

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Abstract

Deep geological storage of radioactive waste foresees cementitious materials as reinforcement of tunnels, backfill, or as waste matrix. Bentonite, or sand-bentonite mixtures, are proposed as backfill material enclosing spent fuel drums, or as drift seals. The emplacement of cementitious material next to clay material generates an enormous chemical gradient in pore water, which drives diffusive transport. Laboratory studies and reactive transport modeling predict significant mineral alteration at and near interfaces, mainly resulting in a decrease of porosity in bentonite [1].

The goal of the project is to characterize and quantify the cement/bentonite skin effects spatially and temporally. The expected analytical data set will be amenable to interpretation by reactive transport modeling. The project focuses on the advective-diffusive transport domain, resolved at intermediate spatial scales. The experiment is carried out in a newly developed X-ray transparent core infiltration apparatus, which allow performing X-ray computed tomography scans (CT) [2] periodically without interrupting the running core infiltration experiment.

The experiment is performed on cylindrical bentonite samples, previously compacted and saturated. A sample is then subjected to a confining pressure in order to simulate underground repository conditions. The infiltration of high-pH cement pore-fluids into the bentonite plug is expected to alter the mineral assemblage over time as an advancing reaction front. The related change in phase densities, porosity and local bulk density is tracked over time periodically by non-destructive CT scans. The resulting micrographs describe the "density" distribution in three dimensions and as a function of time. "Densities" are actually different X-ray attenuations calibrated with reference samples mounted in an identical apparatus. After 1-2 years we will stop the experiment and subject the rock samples to post-mortem mineralogical and petrophysical analysis.

In the current experiment a compacted (ρwet 1.875 g/cm3) and saturated MX-80 bentonite is used as starting material. A confining pressure of 40 bar is applied. The infiltration fluid pressure is 20 bar, and the rate of discharge is on average 0.165 ml/day. The hydraulic conductivity of the bentonite is 2.56E-13 m/s at the beginning. The infiltrating fluid represents an ordinary Portland cement pore-water after a hydration time of 623 days (chemical composition after B. Lothenbach [3]).

First CT data show that X-ray computed tomography is a feasible tool to monitor ongoing infiltration experiments. A pore-scale resolution is not required to track changes in a relatively homogenous medium with a large porosity and significant changes in X-ray attenuation during formation of mineral precipitates.

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Solubility, hydrolysis and redox behaviour of Np(VI) in alkaline NaCl solutions

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Abstract

Solubility experiments with Np(VI) were conducted in NaCl solutions ($0.1\ M \leq I \leq 5.0\ M$) to assess the thermodynamic properties of the aqueous species and solid compounds forming under alkaline conditions. The solubility controlling solid phases were characterized by XRD, chemical analysis, thermogravimetric analysis and SEM–EDS, which indicated the prevalence of the anhydrous $Na_2Np_2O_7(cr)$ phase within the pH_m range 8–13.5 except for the system in 0.1 M NaCl, where the phase $NpO_2(OH)_{2 \cdot H2O}$ was shown to predominate under near–neutral pH conditions. XRD patterns of this newly identified solid phase showed a very good agreement with metaschoepite ($UO_3 \cdot 2H_2O$), thus highlighting the similarities between Np(VI) and U(VI) also in terms of solid phase formation.

Based on the slope analysis of the solubility data, solid phase characterization and chemical analogies with U(VI), the equilibrium reactions $0.5\ Na_2Np_2O_7(cr) + 1.5\ H_2O \Leftrightarrow Na^+ + NpO_2(OH)_3^-$ and $0.5\ Na_2Np_2O_7(cr) + 2.5\ H_2O \Leftrightarrow Na^+ + NpO_2(OH)_4^{2-} + H^+$ were shown to control Np(VI) solubility above $pH_m \sim 9.5$. The predominance of NpO_2^+ in the aqueous phase below this pH_m (quantified by UV–vis/NIR) indicated the reductive dissolution of Np(VI) (either as $Na_2Np_2O_7(cr)$ or $NpO_2(OH)_2 \cdot H_2O$) to $Np(V)_{aq}$.

The conditional equilibrium constants determined from the solubility experiments at different *I* were evaluated with the SIT and Pitzer approaches, and permitted to gain thermodynamic data for Np(VI) aqueous species ($NpO_2(OH)_3^-$ and $NpO_2(OH)_4^{2-}$) and solid compounds ($Na_2Np_2O_7(cr)$ and $NpO_2(OH)_2 \cdot H_2O$) relevant under alkaline conditions but not currently included in the NEA–TDB selection. The picture completed in this work indicates the need of accurately evaluate the behaviour of Np under particular scenarios, such as cement–based repositories in the presence of oxidizing waste forms, where the formation of the +VI redox state may enhance the mobilization of neptunium.

The effect of isotope exchange on the mobility of calcium in cementitious backfill

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Abstract

The UK radioactive waste inventory includes a significant quantity of material containing the long lived isotope ^{41}Ca ($t_{1/2}$ = 103000 a). This isotope arises from the neutron activation of calcium present in the concrete structures of nuclear reactors. It is important to understand the mechanism and rate of migration of radioactive calcium in the geological disposal facility environment where the non-active calcium concentration may be very high due to the use of cementitious media in packaging grouts and backfill.

The presentation describes a technique that uses a combination of radial diffusion and autoradiography to observe the movement of ^{45}Ca, a short half-life surrogate for ^{41}Ca, through the potential backfill material NRVB. The radial diffusion technique uses small pre-cast cylinders of NRVB. Approximately 10 kBq of ^{45}Ca is introduced into a cavity in the centre of the cylinder which is then sealed and placed in a solution previously equilibrated with the NRVB. As migration through the cement cylinder proceeds the increase in concentration of the radioisotope in the external solution can be determined at defined time intervals. It was anticipated that experimental timescales would be in the range of months to years and that diffusion constrained by isotope exchange with calcium containing phases would be the main mechanism. The autoradiographs and intensity plots presented, demonstrate that calcium migration of 10-15 mm can occur within a period of one year.

A series of advection experiments are currently underway to evaluate whether the isotope exchange observed in the diffusion experiments can be negated by forcing flow through a similar system. The results of this work are expected to provide an insight into the kinetics of calcium isotope exchange in cementitious media.

Processing of chemical data from phase mixtures: cement at interfaces

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Abstract

The identity of a crystalline phase can often be successfully derived from its chemical composition. Two major obstacles can complicate a straight-forward correlation: phase mixtures, and varying phase chemistry (e.g. solid solutions).

In cement science, elemental compositions of small regions located in a very fine-grained matrix of cement hydrates, are commonly measured by energy dispersive spectroscopy (EDX) in a scanning electron microscope (SEM). The chemical information of such measurements originates from a physically defined volume where the electron beam interacts with the sample, which generates the characteristic x-rays used for determination of elements present. This volume of approx. 1 µm in diameter is often larger than the grain size of the cement hydrates [1], and these are mostly present as solid solutions or gels with varying chemistry.

This complication is circumvent since the 1980's by measuring a large number of spots, and plotting the chemical data in appropriate mole ratio plots [2], along with the known chemical data of the phases expected to be present. Ideally, the measured data plots along linear trends between two phases for binary mixtures, or inside triangular regions spanned by three phases for ternary mixtures. Such discriminant diagrams prove to be very useful for simple systems where main phases involved differ in Ca, Si, and Al (plotting of Si/Ca against Al/Ca) [2, 3]. However, complex mixtures including more than two phases are hard to interpret, and if a common diagnostic element is absent, the two-dimensional plots (3 elements) are of limited value, and a generalised statistical approach is needed.

Samples from concrete-clay interfaces [4] show significant variations in Mg and S in addition to Ca, Si, and Al within the cement hydrate matrix. A statistical approach was developed and tested to identify the most probable phase assemblage for each EDX measurement in a 6-dimensional space (Mg, Al, Si, S, K, Ca).

1. Definition of phase assemblages: 6 phases with defined chemistry potentially present in the measurement area are proposed in order to obtain a 6x6 system of linear equations to satisfy element balance constraints. The vectors corresponding to the 6 phases have to be linearly independent. If phase chemistries are not well defined, several similar phases with varying chemistry are proposed (e.g., CSH is proposed as several CSH phases with different Ca/Si ratios). The number of phase assemblages proposed is arbitrary.
2. Exact solution: if the determinant of the equation system characterising a measurement with one of the proposed phase assemblages is nonzero and all coefficients are positive, this assemblage represents an exact solution. If several phase assemblages result in an exact solution, the measurement is discarded; if only one of the proposed phase assemblages results in an exact solution, this solution is taken as the characteristic phase assemblage for the measurement.

3. Best fit solution: if no exact solution exists with positive coefficients, the Generalized Reduced Gradient (GRG2) nonlinear optimisation code (Leon Lasdon, University of Texas at Austin, and Alan Waren, Cleveland State University) calculates the best solution for each phase assemblage. Of course, this routine also finds the exact solutions mentioned in 2. The assemblage showing the lowest difference to the measurement represents the most likely phase assemblage, if it is within the analytical error of the measurements.

This approach results in a likely phase assemblage for most of the EDX measurement points. An average phase composition can then be calculated. However, the number of measurement points successfully explained depends on the suggested phases and on how they are grouped into the 6x1 vectors. An increase of measurements and suggested vectors (phase assemblages) improves the result, but extends calculation time. In future work, statistical codes will be applied, that might also propose optimal phase compositions in an iterative process.

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Aluminum and alkali uptake in calcium silicate hydrate

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Abstract

The production of cement is responsible for 5-8% of global man-made CO_2. The replacement of Portland cement by supplementary cementitious materials (SCMs), such as fly ash or black furnace slag, offers the potential to reduce these CO_2 emissions. The industrial application of SCMs based materials is hindered by the fact that novel, low-CO_2 cementitious materials have different chemical compositions and will form other hydrates than present in Portland cements. High contents of silica and aluminium in SCMs may lead to dramatic changes in composition and structure of the C-S-H phase.

A series of experiments have been carried out to investigate the solubility, structure and composition of C(-A)-S-H gel as a function of different parameters such as Ca/Si ratio, pH, aluminium, alkali content and temperature in order to achieve a better understanding of the behaviour of aluminium and alkali in C-S-H.

In the presence of aluminium, C-S-H has been found to incorporate aluminium. For a C-S-H with Ca/Si ratio close to 1 and Al/Si ≤ 0.1, only C(-A)-S-H phase formed. At higher Al/Si ratios, C-S-H was intermixed with calcium aluminate phases such as stratlingite or hydrogarnet. However, even in the presence of additional solids, both the dissolved aluminium concentration and the uptake of aluminium in C-S-H increased. This increase of the aluminium uptake with increasing dissolved aluminium concentrations could suggest solid solution behaviour in C-A-S-H.

In the presence of potassium hydroxide, pH of the solution was higher which lead to (i) portlandite precipitation, (ii) higher dissolved aluminium concentrations and (iii) higher aluminium uptake by the C-S-H. Also in the presence of alkalis, the aluminium uptake in C-S-H correlated positively with the dissolved aluminium concentrations. While the alkali uptake decreased with increasing Ca/Si ratio, the presence of aluminium did not significantly influence the uptake of alkalis by the C-S-H.

Interactions of cationic exchange resins (saturated with Na⁺, K⁺, or Ca²⁺) with Portland cement during hydration

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Abstract

Ion exchange resins (IERs) are widely used by the nuclear industry to decontaminate radioactive effluents. Spent IERs have to be stabilized and solidified, that is placed under a solid, stable, monolithic and confining form. Calcium silicate cements offer many advantages for resins encapsulation: easy supply, simple process, good mechanical strength, compatibility with aqueous wastes, good self-shielding, and high alkalinity which allows precipitating and thus confining many radionuclides. However, several specificities of IERs must be taken into account to design a robust cement formula: *(i)* their ability to exchange ions with the cementitious medium, which may influence cement hydration, *(ii)* their low mechanical strength, which strongly weakens the strength of the solidified waste forms, and *(iii)* their strong dimensional variations which can, under severe conditions, induce swelling and cracking of the matrix.

These dimensional variations can result from two main processes in a saturated medium: osmotic pressure and ion exchange. The first objective of this work is to compare their influence in situations representative of a solidified waste form at different stages of its evolution. For that purpose, a particular attention is paid to the quantification of swelling pressures induced by resins in a confined environment, as it may be the case in the cementbased matrix. Two parameters are investigated: the nature of the ions fixed on the functional groups, and the ionic strength of the aqueous solution which is percolated through the resins. The second objective is to explain why a rapid expansion is observed at early age when Portland cement (OPC) is used to solidify cationic IERs saturated with sodium or potassium, whereas no swelling is observed for IERs in the calcium form. Evolution of the mineralogy, interstitial solution composition and microstructure is compared for various samples prepared with OPC and resins initially saturated with Na⁺, K⁺ or Ca²⁺. In the case of IERs in the Na⁺ or K⁺ form, ionic exchanges are observed with Ca²⁺ ions released by the dissolution of cement. These exchanges accelerate the dissolution process, leading to an accumulation of sulfate ionsin solution, and to a rapid increase in the ionic strength of the pore solution. As a consequence, the resins shrink. Then, in a second stage, the ionic strength decreases for two reasons:

- the exhaustion of gypsum, and the depletion of the sulfate ions from the interstitial solution due to the precipitation of ettringite,
- a second exchange between Ca²⁺ ions, released by the resins to precipitate cement hydrates, and Na⁺ or K⁺ ions previously released in the pore solution.

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

On the contrary, when IERs are in the Ca^{2+} form, the exchanges with cations released by the cement dissolution are very limited, and no expansion of the matrix is observed.

High temperature impact on geochemistry and diffusion at concrete/argillite interfaces in a radioactive waste disposal

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Abstract

The safe disposal of radioactive waste in geological environment is a key issue in the nuclear energy industry in France. Over an exceptionally long period of time for an industrial structure, the host-rock and the disposal architecture must ensure the containment of radionuclides that may be released from the wastes. The disposal multibarrier system induces interactions between natural (argillite) and industrial geo-materials (bentonite swelling clay, concrete). During the last decade, studies have been led on representative systems putting in contact cementitious and clayey materials, both in laboratory or under *in situ* conditions within Underground Research Laboratory (URL). 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.

To understand the impact of a high temperature on the physico-chemical behaviour of cement/clay interface, *in situ* (CEMTEX IN SITU, Tournemire, Aveyron, France) and laboratory experiments (CEMTEX LABO) are led simultaneously. In the straight line of previous experiments performed at 25°C [1], dedicated diffusion cells were developed to put into contact Tournemire argillite and CEM I hardened cement paste at 70°C under water saturated conditions. In a first step, the two materials interact from each side of the interface to the other, and in a second step tracers are injected in the back reservoir to quantify the material transformation impact on the overall transport parameters. The mineralogical and geochemical changes are characterised by different laboratory methods applied both to the lab and in situ samples (SEM, XRD-Rietveld, TEM, µRaman, ionic chromatography). Numerical modelling of the geochemical perturbations is initiated with the HYTEC code in order to better assess and quantify the materials physico-chemical evolutions at 70°C. The first experimental and modelling results will be given and discussed.

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Complexation of Nd(III)/Cm(III) with gluconate in dilute NaCl and CaCl$_2$ alkaline solutions: solubility and TRLFS studies

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Abstract

Gluconic acid (GLU) is a polyhydroxy carboxylic acid expected in repositories for low and intermediate–level radioactive waste as component of cementitious materials. The presence of this ligand can affect the solubility and sorption of radionuclides in cementitious and saline systems, which is of particular interest with regard to the safety of nuclear waste storage. The formation of very stable An(III)–GLU complexes has been reported in the literature, although in contrast to An(IV) no ternary species Ca-An(III)-GLU have been described so far. The latter may play a relevant role in cementitious and saline environments, where high Ca^{2+} concentrations are expected.

Undersaturation solubility studies with Nd(OH)$_3$(am) were conducted in inert gas (Ar) gloveboxes at 22 ± 2°C. Samples were prepared with 0.1 M NaCl and 0.25 M CaCl$_2$ as background electrolytes. Parallel experimental series were prepared with pH$_c$ = ctant ~12 and varying [GLU] (10^{-6} M to 10^{-2} M) and with [GLU] = ctant = 10^{-3} M and varying pH$_c$ (9 to 13).
The solubility of Nd(OH)$_3$(am) remained unaffected by GLU in 0.1 M NaCl solutions. XRD and TOC analyses confirmed that no new solid phases (Nd–GLU or Ca–GLU) were forming and that all GLU remained in solution under these conditions. On the other hand, solubility of Nd(OH)$_3$(am) in 0.25 M CaCl$_2$ solutions was clearly increased by GLU under hyperalkaline conditions. The species forming are pH–dependent and unequivocally involve the participation of Ca^{2+}.
TRLFS measurements were performed with ~10^{-7} Cm(III) per sample, with 0.1 M NaCl and 0.25 M CaCl$_2$ as background electrolytes. In the NaCl systems three different concentration levels of Ca^{2+} were considered: 0, 10^{-3} M and 10^{-2} M. The initial concentration of GLU in all samples (10^{-6} M) was increased to 3×10^{-3} M by step–wise additions of NaGLU-NaCl or Ca(GLU)$_2$-CaCl$_2$ solutions.
TRLFS indicates the formation of one main species in NaCl systems and 10^{-3} M ≤ [Ca] ≤ 10^{-2} M. Consistently with solubility data, TRLFS confirms the key role of Ca^{2+} in the process of complex formation, with the likely Ca:GLU ratio 1:1. Two to three Ca–Cm–GLU species were further identified in 0.1 M and 0.25 M CaCl$_2$ solutions.

In-situ X-Ray Micro-Diffraction Analysis of Heterogeneous Cementitious Materials

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Abstract

Synchrotron-based X-ray micro-diffraction (µ-XRD) techniques with a beam size focussed down to a few micrometres or less allow a variety of novel applications in the field of diffraction experiments on finestructured materials with a high spatial resolution. In contrast to traditional XRD analyses with typical X-ray beam cross-sections of a few hundred micrometres, µ-XRD experiments allow a spatial resolution improved by one to three magnitudes. Besides the state-of-the-art characterisation of pure, crystalline materials that are only available at very small sizes and at very low quantity, micro-diffraction experiments also allow local probing of heterogeneously composed materials that show chemical and structural zonation on a micrometre or even sub-micrometre scale, *e.g.* components in nanotechnology and samples of interest in environmental sciences, geochemistry and engineering. Scanning µ-XRD data acquisition technique generates highresolution 2D-maps of phase distributions on polycrystalline surfaces. A special application of this technique is, *e.g.*, the investigation of reaction products and structural alterations on a micrometre scale at phase contacts. Hardened cement paste typically shows a very fine-grained and complex polyphase composition. µ-XRD is therefore a suitable tool for phase characterization in cement chemistry. Two concrete systems using µ-XRD have been investigated. The corresponding experiments were carried out at different synchrotron facilities (SLS, Villigen (Switzerland); APS, Argonne (USA); ESRF, Grenoble (France)) with beam diameters between 30 µm and 0.3 µm. Samples were prepared as thin sections with a thickness of about 20 to 30 µm.

In the first system, reaction products formed during the alkali-silica-reaction (ASR) in concrete structures were investigated. The ASR is an important deterioration process in concrete, leading worldwide to severe damages in buildings and constructions. Reaction products formed due to interaction of amorphous or crystalline SiO_2 in aggregates with the alkaline pore solution of concrete produces expansive pressure and, as a consequence, give rise to damage of concrete structures. Even though appearances of ASR have been well documented, mineralogical knowledge of the ASR products and the mechanics leading to the expansion during the course of ASR is still limited. The expansion cracks in aggregates due to ASR have typically a cross-section in the range of a few tens of micrometres. Micro-diffraction data were collected *in-situ* along these veins, *i.e.* ASR products were probed within their original environment. Powder diffraction data analysis and analysis of single crystal diffraction patterns obtained from micrometer or sub-micrometer sized, microcrystallinegrains in the ASR zones were carried out. A

structural model of the reaction product will be presented based on the current status of data analysis.

In the second system, the phase assemblage of a cement/claystone interface was investigated. Such interfaces play an important role in multi-barrier concepts developed worldwide for the safe disposal of radioactive wastes in deep geological repositories. For instance, an approximately 180 million year old marine claystone formation (Opalinus clay) was identified and selected as the first-priority host-rock for the final disposal of radioactive waste in Switzerland. Both materials, *i.e.* natural claystone and cement used for construction of the engineered barrier, are heterogeneous mineral assemblages with discrete nano- to micro-scale particles. Micro-scale information on the chemical reactions and the secondary minerals formed at cement/clay interfaces with their large chemical gradients is almost completely lacking. SEM/EDX analyses that were performed on an about four-year-old cement/Opalinus clay interface taken from a borehole in the Mt. Terri Rock Laboratory, St. Ursanne (Switzerland) showed preferential accumulation of several chemical elements in an alteration zone, which expands over a few hundred µm into the concrete material. µ-XRD technique was used to characterise the complex heterogeneous phase assemblages in the disturbed zone at the cement/clay interface and to complement the information obtained from SEM/EDX with crystallographic information.

Speciation of C-14 during the anoxic corrosion of activated steel: Set-up of a long-term corrosion experiment

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Abstract

Carbon-14 was found to be an important contributor to the annual individual dose that would be released from a cement-based repository for low- and intermediate-level waste in Switzerland, although the calculated doses are still several orders of magnitude below the regulatory limit. Importance of ^{14}C in the assessment arises from the specific assumptions made regarding the speciation and mobility of the different forms of carbon. ^{14}C mainly contributes to dose in its organic form, e.g. ^{14}C labelled organic compounds, which are present or formed in the near field. Compilations of the activity inventories revealed that, in the already existing and future arising radioactive waste in Switzerland, the ^{14}C inventory mainly originates from activated metallic materials (~ 86.4 %), in particular activated steel (~ 85 %), while the ^{14}C inventory associated with activated zircaloy (hulls and ends) is much less (~ 1.4 %). In nuclear power plants ^{14}C is generated by the activation of nitrogen impurities in steel exposed to thermal neutron fluxes according to the reaction $^{14}N(n,p)14C$. While the ^{14}C inventory in the repository is known the chemical speciation of ^{14}C in the cementitious near field upon liberation from activated steel is hardly investigated. Earlier studies on the chemical form of carbon species generated during steel corrosion indicate formation of volatile and/or dissolved, low-molecular-weight organic compounds up to a maximum of five carbon atoms, such as alkanes and alkenes, alcohols and carboxylic acids.

In this study, first developments towards a long-term corrosion experiment with activated steel and preliminary results from batch-type corrosion experiments on non-activated steel will be presented. Determination of the chemical ^{14}C species formed during the anoxic corrosion of activated steel involves major challenges: First, the actual ^{14}C inventory of the activated steel foreseen for use is only approximately known from activation modelling of the $^{14}N(n,p)^{14}C$ reaction as the N content may range from 0.2 – 1 weight % in stainless steel. However, knowledge of the initial ^{14}C inventory of activated steel is important regarding to planned mass balance considerations on the amount of ^{14}C species released during steel corrosion. Therefore, it is foreseen to determine the ^{14}C inventory of the activated steel material used for the long-term corrosion study. Secondly, the corrosion rate of activated steel is extremely low under alkaline conditions (~ 10 - 100 nm/year) and further, the amount of material used in the corrosion experiments should be limited to minimize the costs of sample handling, sample preparation and the infrastructure required to enable safe operation of the long-term corrosion experiment (shielding, radiation protection). Hence, the ^{14}C concentrations to be determined in the long-term corrosion study are expected to be very low, which requires the development of a chromatographic separation technique coupled to a ^{14}C detection method with a very low detection limit,

such as compound-specific 14C accelerator mass spectrometry (AMS). As a first step towards the development of compound-specific ^{14}C AMS a series of batch-type corrosion experiments was carried out with the aim of determining the organic compounds formed during the course of the anoxic corrosion of non-activated steel, which was immersed in solutions with different chemical compositions (e.g. groundwater-type and cement pore water type). Dissolved carbon species were identified using highperformance ion exclusion chromatography coupled to conductivity detection and mass spectrometry while volatile carbon species were identified using gas chromatography coupled to mass spectrometry.

Cement/clay interfaces: evolution of structural and transport properties

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Abstract

Claystones are considered as suitable host rocks for nuclear waste disposal. Cement and concrete materials will be used as engineering material in the repositories. They will be directly in contact with clays, in different arrangements. The geochemical contrast between clay and cement leads to changes in their properties which need to be quantified in order to assess the long term safety of the disposal sites.

Our project is aimed at simultaneous monitoring of the mineralogical and structural evolution (dissolution/precipitation of minerals, porosity changes) expected to occur at the cement/clay interface. We are using different, complementary experimental techniques to characterize the changes and their relation to the transport parameters (diffusion coefficients, accessible porosities).

A diffusion cell has been developed to accommodate an interface sample consisting of a small (5 mm diameter, 5 mm length) clay plug (montmorillonite) and a small hardened cement plug (OPC) of the same size.

This cell allows to estimate bulk diffusion parameters from standard through-diffusion measurements with a tracer like HTO. At the same time, the cell can be transferred to the neutron tomography station ICON at PSI to image a tracer movement. This will possibly allow estimating local diffusion properties near the interfaces of the samples, which can be related to the observed structural changes. The cell is currently being tested and improved. Neutron images showed promising results with the current configuration. Specific challenges include improving the construction of the cell in order to bear the high swelling pressure of the clay without adversely affecting the neutron imaging capabilities. Several such optimized cells or sample holders will be built, which can then be charged with interface samples and be stored in parallel at an elevated temperature in order to speed up the mineralogical reactions.

Structural changes will be examined by X-ray diffraction and fluorescence studies, and interesting parts of the interface will be prepared for further investigations using micro-XRD and FIB/SEM methods. The obtained results will be implemented into a reactive transport model to improve the prediction of the repository's long-term behaviour.

A Local Sensitivity Analysis of the Influence of Mesoscale Components of Concrete on Effective Diffusivity

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Abstract

The mesoscale of concrete consists of aggregates of different sizes, bulk hardened cement paste and interfacial transition zone (ITZ). Interfaces between major components could play an important role in controlling the physical and mechanical properties and performance of composite materials. It is generally acknowledged that the ITZs in concrete are mechanically the weakest components. However, from the available experimental investigations the significance of the ITZs with regard to transport properties such as the effective diffusivity remains uncertain. The conflicting results from various sources reflect the inherent experimental difficulty in isolating the influence of the ITZs. Therefore, a better understanding of ITZ is important. Especially for long term degradation processes which also affect leaching of waste components, such as leaching of Ca, in which ITZ could play a relevant role because of its composition and transport properties.

In order to study transport processes in concrete, in particular, the long term (chemical) degradation mechanisms of concrete at different scales, a multiscale numerical model based on finite element analysis is currently being developed. This paper presents the initial steps, in this effort to study the factors that govern the effective diffusivity at the mesoscale via local sensitivity analyses.

The difficulty of mesoscale modelling is to handle the mesoscale structure computationally as both the millimeter aggregate length scale and the micrometer length scale of the ITZ must be dealt with simultaneously. This difficulty is overcome by the use of double noded interface elements which enables the modelling of the aforementioned spatial discontinuity with low computational cost. An efficient particle generation algorithm has been developed to achieve various shapes, volume fractions and distribution of aggregates. The paper further briefly describes the methods used to determine representative volume element which is useful in reducing the number of factors in the sensitivity analyses, in this instance, the distribution of aggregates.

Despite the ITZs having a higher porosity and diffusivity than the bulk paste, preliminary results suggest that the ITZs marginally affect the diffusivity as long as the ITZs are not percolated. It is further found that the effective diffusivity is mainly governed by the volume fraction and cement paste transport properties, not only by the ITZs. Further work is aiming to validate the mesoscale model by analytical approaches and experimental data.

Radionuclide sorption at high pH in calcite systems

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Abstract

Cement is ubiquitous in geological disposal facilities and carbonation will, over geological time, convert most of the portlandite components of cement into calcite. In addition, the UK's cementitious backfill material consists of a large calcite component. Thus, calcite may play an important role in the sequestration of radionuclides in any Geological Disposal Facility (GDF). The sorption behaviour of UO_2^{2+} in high pH conditions representative of a GDF (Young Cement Leachate, YCL, pH 13.3 and Old Cement Leachate, OCL, pH 10.5) were studied using modelling and batch techniques.

In batch sorption experiments at low concentrations of ^{232}U(VI) (5.27×10^{-11} M) in YCL, 5-70% was sorbed, whereas, in OCL it was 0-60% (depending on solid to solution ratio). These systems were successfully modelled with a simple, first order kinetic model that assumed sorption site concentration was proportional to mass of calcite. This successfully predicted U(VI) sorption behaviour in systems with different solid to solution ratios suggesting simple surface complexation.

At higher concentrations (1 to 10 ppm), ^{238}U(VI) showed little measurable sorption onto calcite in YCL. However, in OCL at ≤ 0.1 ppm, between 1 and 45% ^{238}U(VI) was removed and again, this was successfully modelled assuming a surface complexation mechanism. At ≥ 0.5 ppm, there is less dependence on calcite surface area, with 50-95% removal observed, which suggests removal being driven by the formation of a U(VI)-precipitate. This is supported by EXAFS data in which U-U backscatters were successfully identified and luminescence spectra which were shown to be a combination of a calciumuranate/ becquerelite like phase and a U(VI)-Calcite complex.

A discussion on simplification of the long-term modelling of chemical alteration of cement materials in radioactive waste repository environment

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Abstract

It has been suggested that precipitation of calcite on the surface of cement solid induces a reduction in the leach rate of components in groundwater by the result of a tank-leaching experiment in sodium bicarbonate solution, however, the modelling was complicated since the clogging by the precipitation of insoluble secondary phase depended on the feature of the near-surface layer of precipitates which was sensitive to the concentration of reactive ions in the solution and the mass transport property of the solid matrix [1]. In this paper, the alteration of cement material in contact with rock was observed under a condition in which reactive ions can attack cement solid only through rock as shown in Fig. 1. The rate of calcium leaching was decreased in sodium bicarbonate solution but calcium leaching continued after the period in which the calcium leaching was restricted in the case that cement solid contacted directly with sodium bicarbonate solution as shown in Fig. 2. This suggests that the clogging would not go strongly and would not produce a local thin layer of secondary precipitation to restrict the calcium leaching. On the basis of the experimental results, the reliability of the modelling will be discussed to describe actual chemical alteration of cement materials and to reduce uncertainty in the long-term performance assessment of radioactive waste repository.
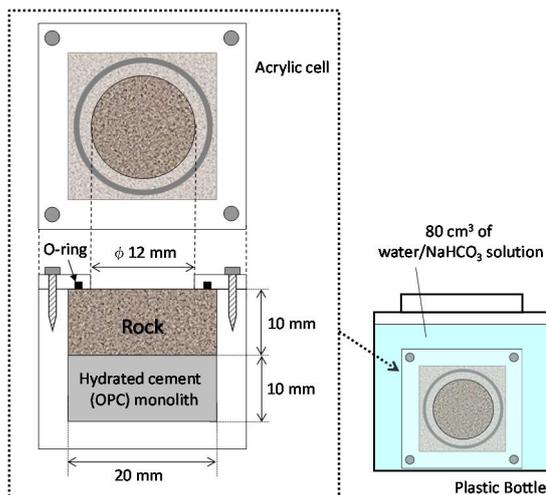
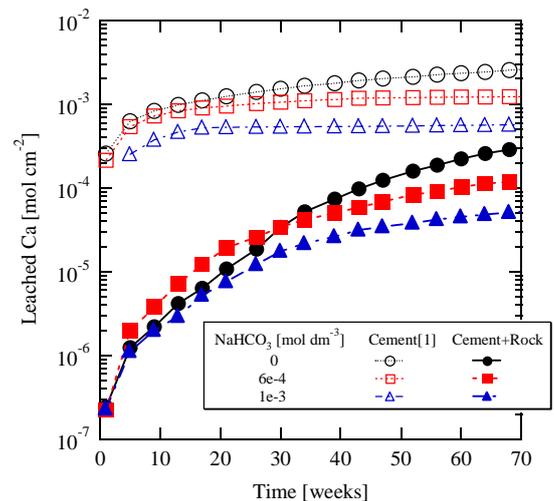**Fig. 1: Experimental design of alteration of cement monolith.**

Fig. 2: Leaching of calcium from cement monolith.

Reference

[1]   Daisuke Sugiyama, "Modelling of Chemical Alteration of Cement Materials in Radioactive Waste Repository Environment", Dr. Xiao-Ying Yu (Ed.), ISBN: 978-953-51-0501-5, InTech, 2012.

Development of Low-pH Cement Mixtures for Further Use in Radioactive Waste Disposal

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Abstract

In any concept of radioactive waste disposal the cementitious materials are envisaged. Interaction of cementitious materials with water produces high pH extracts (value ~ 12-13). These highly alkaline solutions may affect the barrier function of engineered barriers or host environment of deep waste repository. The most important interactions considered are concrete/bentonite or other clay material, used as a buffer. Alkaline front may cause significant changes of backfill material and also cause the formation of new mineral phases. In order to avoid as much as possible bentonite alteration, it is proposed to use the cementitious mixtures or concretes with a low pH of leachate.

At this stage of development the prior goal of presented study was to achieve such a cement mixture with the leachate values of pH < 11. Prepared cement mixtures were hardened for 28 days, then they were milled, and powdered samples were mixed with degassed distilled water. pH meter, calibrated by pH = 7, 9, 11 and 13 buffers, was used for determination of suspension pH and filtrate pH after interaction. Compressive strength tests on cubic samples were determined as additional information. This methodology is based on SKB R-12-02 report [1].

23 different mixtures were prepared and tested. Compositions of mixtures were progressively changed to achieve the lower pH values of suspension and leachate pH values. Value of compressive strength varied from 9 to 29 MPa. Three mixtures, based on cement type CEM II 42,5R or CEM III/B, silica fume and fine grained limestone, reached defined pH < 11. Prepared cement mixture composition will be the base for further development of cement mixtures and concretes for specific cases of use – matrix for waste fixation, for tunnel plug and seal purposes and for other construction elements etc.

Reference

[1] Alonso M. C.: Development of an accurate pH measurement methodology for the pore fluids of low pH cementitious materials, SKB R 12-02 report, ISSN 1402-3091, (2012)
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Reactive Transport Modeling of Organic Complexing Agents in Low and Intermediate Level Waste

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Abstract

The final repository for short-lived radioactive waste, the SFR, is located at Forsmark in Sweden. It holds low and intermediate-level operational waste from the Swedish nuclear power plants, as well as industrial, research-related and medical waste.

Operational waste commonly has a diverse origin and often includes organic material that can affect the long term safety of the repository. Classes of substances that are of special concern include:
- N,N- carboxylated-amino acids such as EDTA or NTA, which may be used in decontamination procedures.
- Polyhydroxycarboxylic acids such as gluconate and isosaccharinate, formed from the degradation of cellulose.
- Carboxylic acids such as citrate, used in decontamination procedures.

These organics can ligate to metal atoms forming stable complexes, thus affecting dissolution as well as transport properties. Determining the concentration distribution of complexing agents in different repository parts over time is important in order to understand how organics affect the release of radionuclides to the surroundings.

The work presented here is focused on the reactive transport modeling of isosaccharinate (ISA) in cementitious matrices. ISA is the dominant organic in the SFR produced by the degradation of cellulose. Waste conditioning as well as different storage concepts in the SFR have been considered. The model accounts for advection, diffusion, and sorption of solvated species to cement.

Results show an interplay between the ISA production rate, the sorption of ISA to cement, and the advective transport. For repository parts with expected modest groundwater flow rates, ISA sorption to cement is sufficiently strong to retain ISA over 1e5 years. This can be compared to non-sorbing species that for the same flow rate will be removed after approximately 1e4 years. As the groundwater flow increases sorption becomes less efficient, as only one of two available sorption site types forms strong enough bonds to ISA. In repository parts where relatively high flow rates coincide with a high cellulose loading, the advective removal of ISA is notable within the studied time frame.