Cement properties and barrier functions in repository environments, CEBAMA project

- Introduction to CEBAMA
- RD&D work performed
- Impact, Summary

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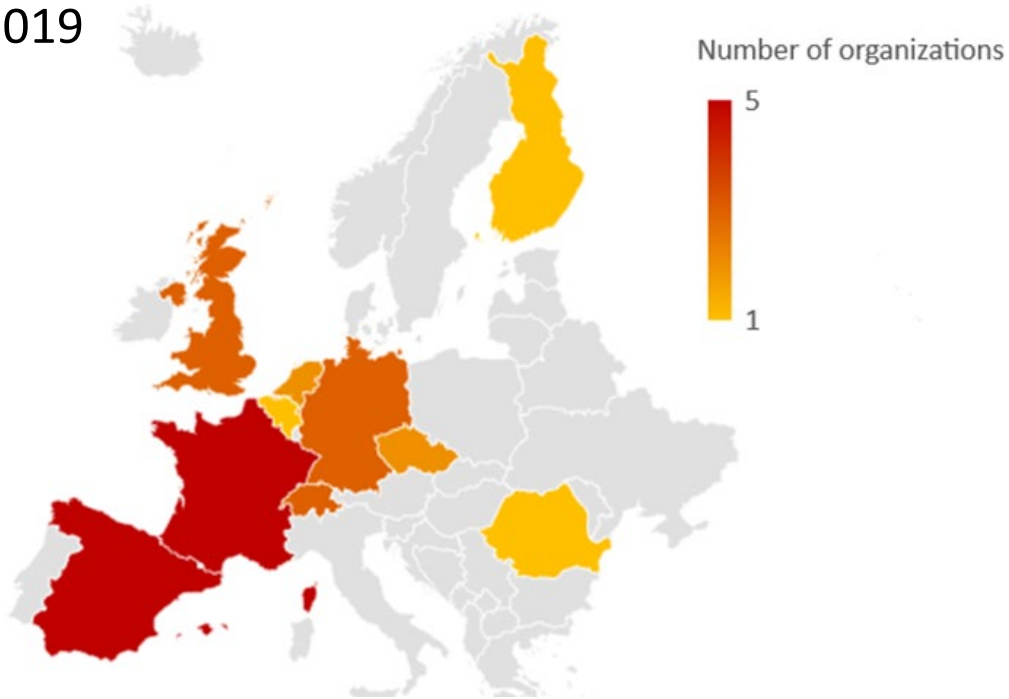
Cebama - key data

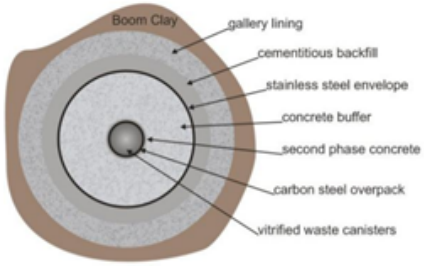
- **Grant agreement No:** 662147
- **Action full title:** Cement-based materials, properties, evolution, barrier functions
- **Estimated eligible costs:** 5,952,944.50 EUR
- **Maximum grant amount:** 3,868,607.25 EUR
- **Duration:** 1st June 2015 – 31st May 2019



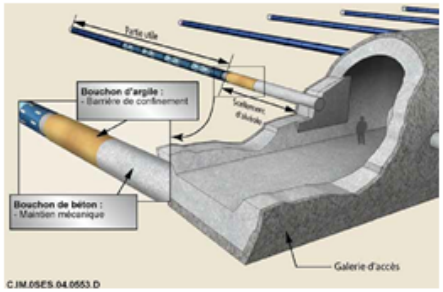
Project Aims

Cement-based materials are key components in the barrier system of repositories. These materials and their behaviour have to be addressed in the Safety Case.

High level radioactive wastes disposal: Cementitious materials are mainly used for the construction of the engineered barrier system (backfill, plugs, etc).

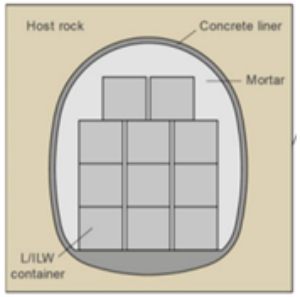


Belgian supercontainer concept for present high-level waste types (Cebama D1.03)

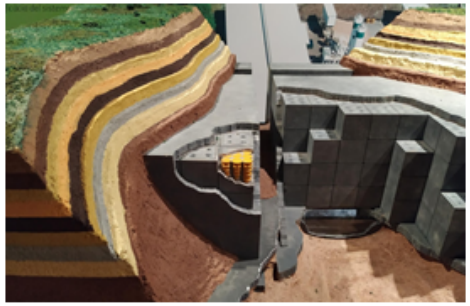


French concept of the HLW repository—Cigeo (Andra)

Low & Intermediate level radioactive wastes disposal: Cementitious materials are used for conditioning the waste and the construction of the engineered barrier system (container, backfill, plugs, etc).



Swiss concept for a L/ILW repository (Cebama D1.03)



Spanish repository for LILW— El Cabril

Project Aims

Cement-based materials are key components in the barrier system of repositories. These materials and their behaviour have to be addressed in the Safety Case.

CEBAMA:

- Experimental studies analysing interface processes between cement-based materials and potential host rocks (crystalline rock, Boom Clay, Opalinus Clay (OPA), Callovo-Oxfordian (COX), Toarcian mudstone, Borrowdale Volcanic Group) or bentonite backfill, and assessing the impact on physical/chemical properties.
- Investigation of radionuclide retention and migration processes in high pH cementitious environments, focusing on radionuclides which have high priority from the scientific and applied perspective.
- Improved validity of numerical methods to predict changes in transport processes as a result of chemical degradation, including advanced data interpretation and process modelling.

Consortium and bodies

CEBAMA: *consortium of 27 partners consisting of large Research Institutions, Universities, one TSO, one SME, from 9 EURATOM Signatory States, Switzerland and Japan.*

Consortium and bodies

European Commission

Individual Beneficiaries

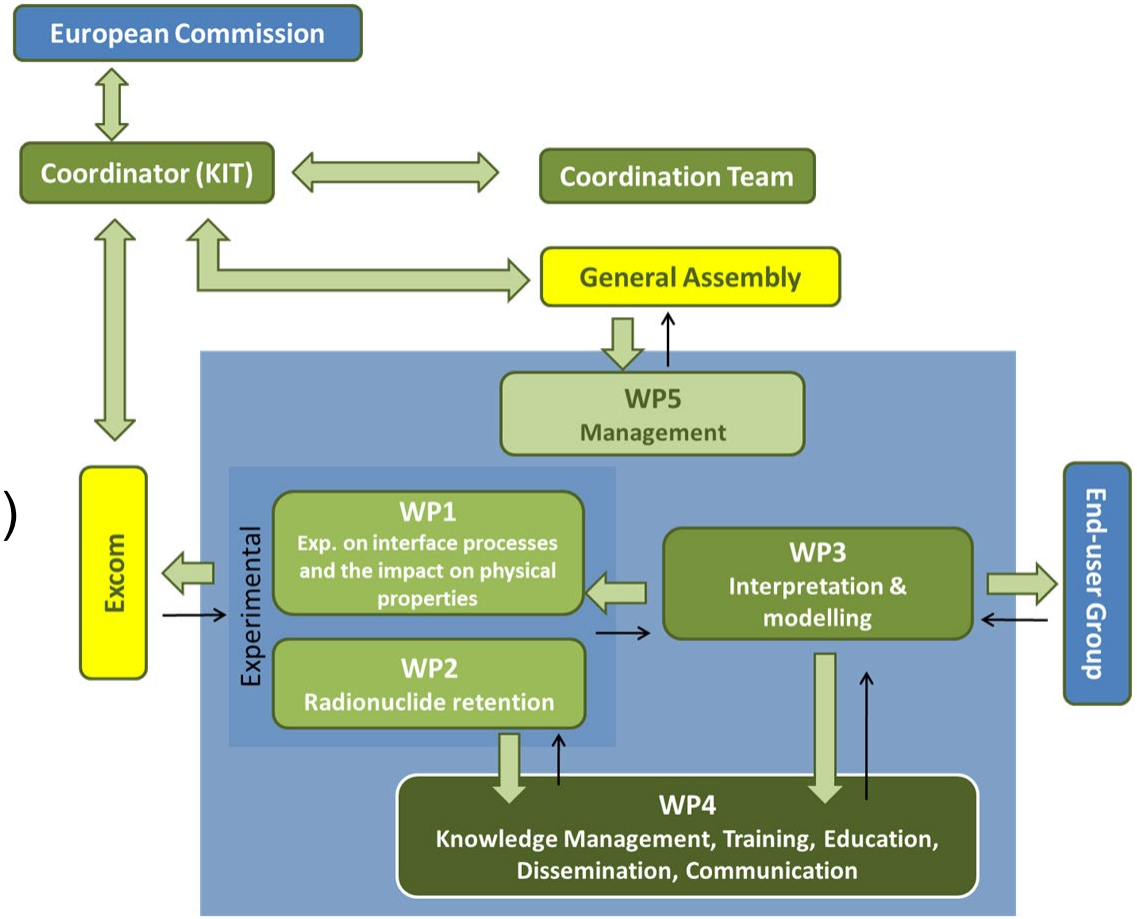
Coordination Team (CT)

Executive Committee (ExCom)

General Assembly (GA)

Associated Groups (AG)

End-User Group (EUG)



Executive Committee

WP 1 - Experiments on interface processes and the impact on physical properties

Erika Holt (VTT) “spokeswoman”, **Francis Claret** (BRGM), **Urs Mäder** (UNIBERN)

WP 2 - Radionuclide retention

Bernd Grambow (ARMINES)

WP 3 - Interpretation & Modelling

Andrés Idiart (AMPHOS21)

WP 4 Documentation, Knowledge Management, Dissemination and Training

Alba Valls (AMPHOS21)

WP 5 Management

Marcus Altmaier, **Vanessa Montoya** (KIT)

End User Group

ANDRA - Pierre Henocq

COVRA - Erika Neeft

ENRESA - Miguel Angel Cuñado

NAGRA - Nikitas Diomidis

ONDRAF/NIRAS - Seif Ben Hadj Hassine (*EUG chairperson*)

POSIVA - Marja Vuorio

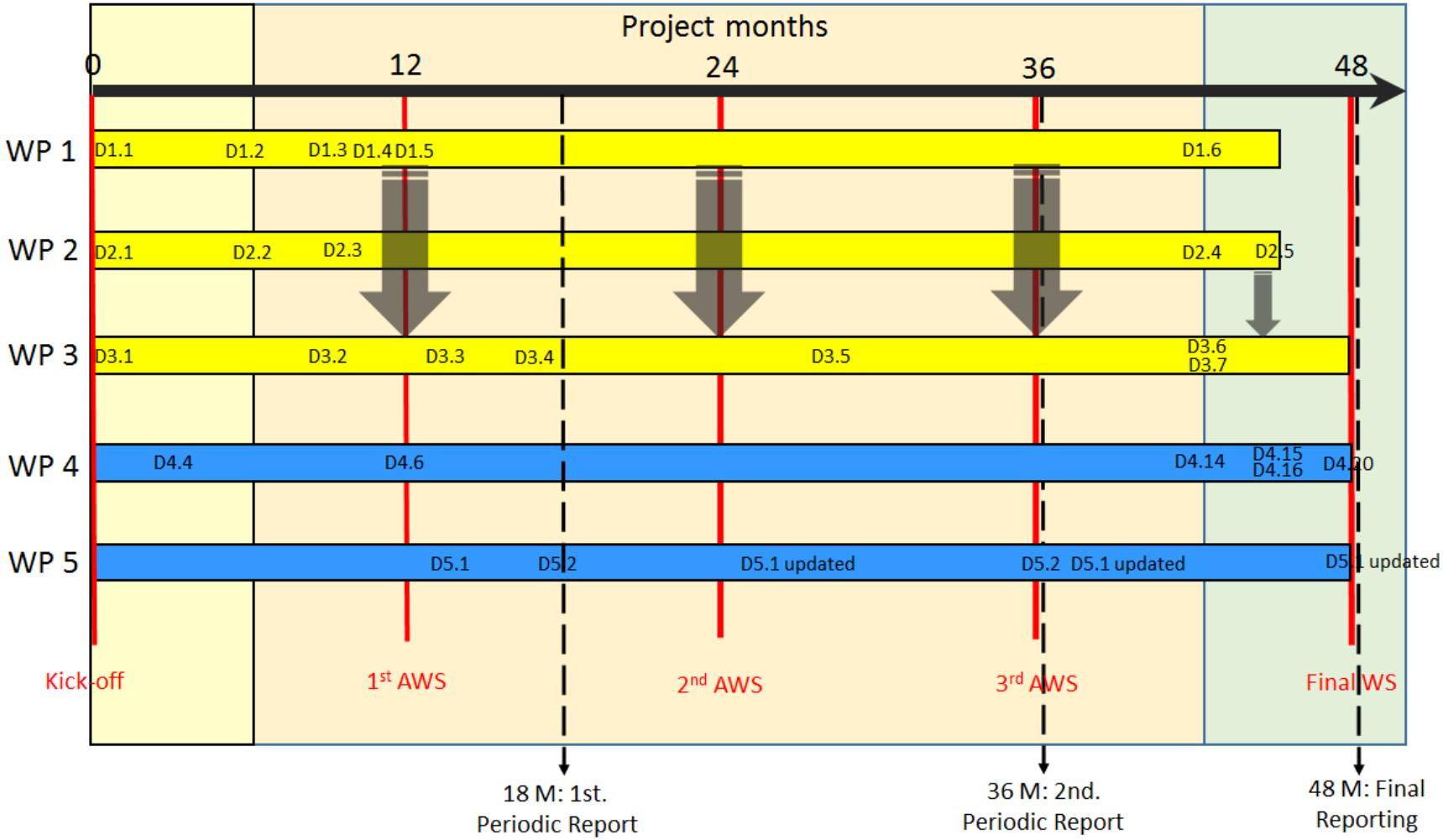
RWM - Amy Shelton

SKB - Per Martensson

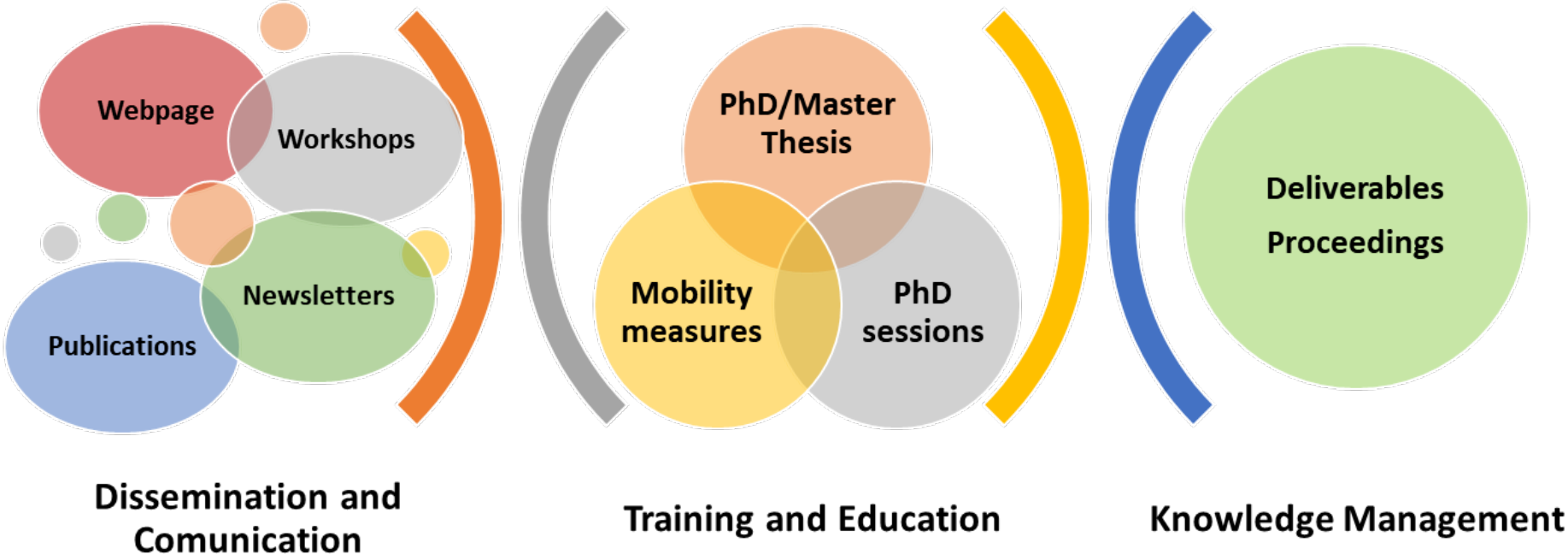
SURAO - Lucie Hausmannova (and Antonin Vokal)

Project Overview

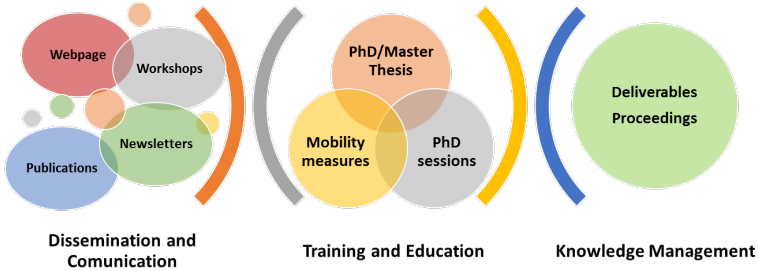
- **Start:** 01-06-2015
- **End:** 31-05-2019



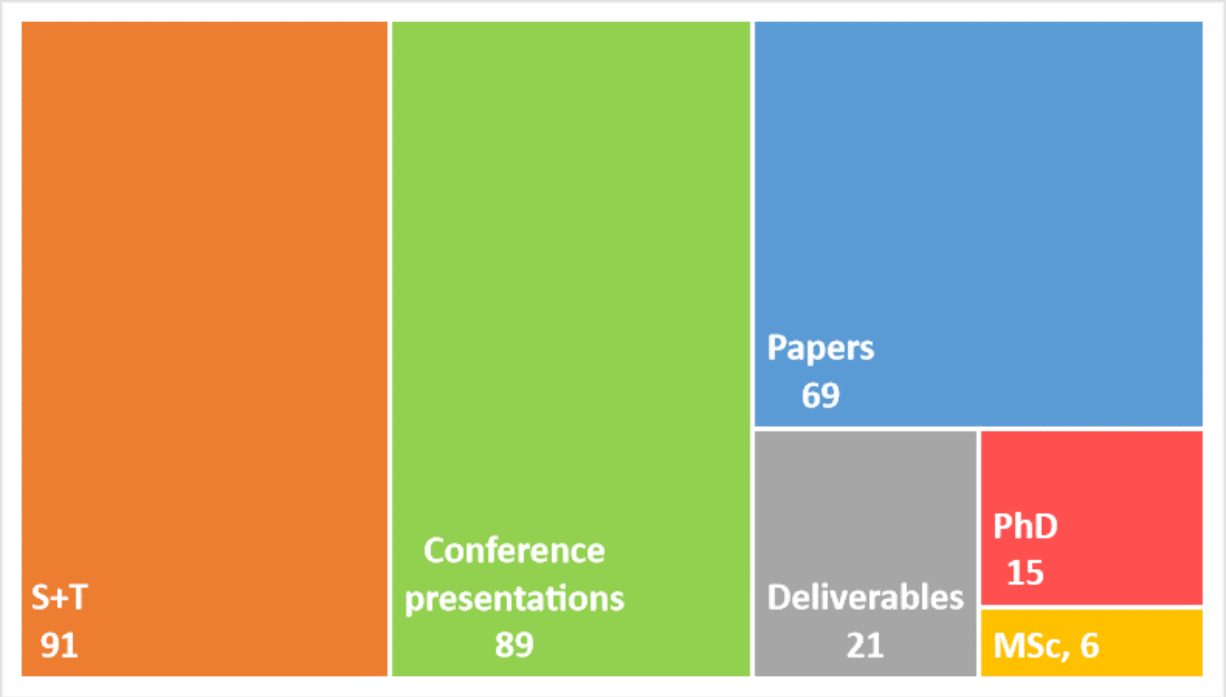
Dissemination, training, education, KM



Dissemination, training, education, KM



Project outcome summary



Where to find CEBAMA results

- *CEBAMA Newsletter, Website…*
- *S&T contributions to Annual CEBAMA Workshop Proceedings*

- **Individual peer-reviewed scientific publications**
  - Individual publications by beneficiaries in scientific journals
  - Contributions to Special Issue in Applied Geochemistry

- **Integrated Reports**
  - Three peer-reviewed publications on WP level
  - Application to the Safety Case
  - Final report (EURADWASTE paper)

CEBAMA contributions to EURADWASTE

- *Benchmark of reactive transport models within CEBAMA: application to a concrete/clay interface* (Idiart et al.)
- *Chemistry of beryllium in cementitious systems studied within CEBAMA: solubility, hydrolysis, carbonate complexation and sorption* (Gaona et al.)
- *Studies of Radium and Strontium uptake on Cementitious materials within CEBAMA project* (Jana Kittnerova et al.)
- *Radionuclide migration in low-pH cement / clay interfaces; derivation of reactive transport parameters within CEBAMA.* (Naila Ait Mouheb et al.)

WP1: Interface processes - impact on physical properties.

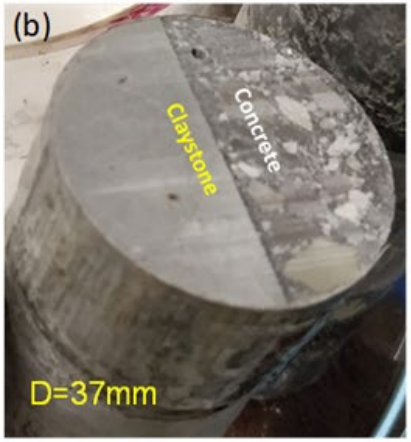
- Quantifying transport parameters of altered and unaltered cement-based samples by performing through- and in-diffusion experiments and development of new non-invasive techniques (i.e. GeoPET method).
- Study of hydro-mechanical processes in the interface cement - Callovo Oxfordian claystone, measuring the evolution of flow and strength properties of different cementitious-based materials (i.e. low-pH concrete).
- Study of thermo-hydro-geochemical processes in the interface cement-clay, measuring changes on transport properties due to mineralogical alteration and microstructure changes (e.g. Ca leaching, carbonation).
- Analyses of interface reactions, with respect to changes in mineralogy and porosity evolution, between different materials in contact with solutions with different compositions (i.e. pH, redox, carbonate, sulphate concentration, salinity) by percolation and leaching experiments.
- Manufacturing and characterisation of the CEBAMA reference materials as a benchmark to other studies by various partners.

WP1 – work performed

Preparation of samples

*Preparation of the reference **concrete** (VTT)*

*Preparation of a **bentonite** suspension (UJV)*



***Interface** between COx claystone and concrete (LML)*

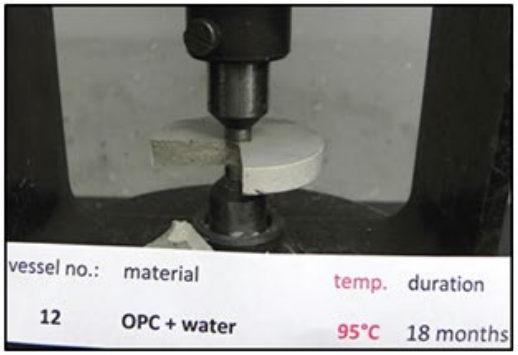
***Concrete** and **mortar** samples used for the experiments (CIEMAT)*

WP1 – work performed

Experimental set-up

Percolation experiment (SCK·CEN)

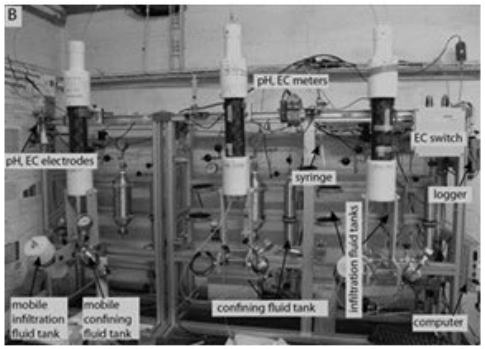
Experimental desing (UAM)



Punch test (UJV)

Experimental gallery of the concrete elements (ANDRA)

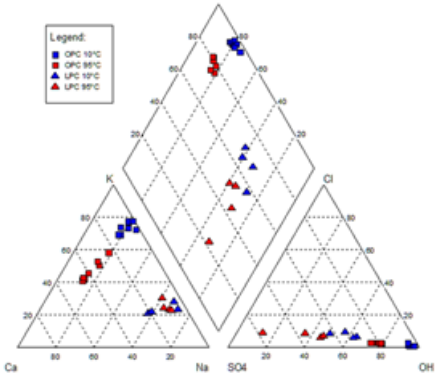
Analysis of tracer flow with GeoPET (HDZR)



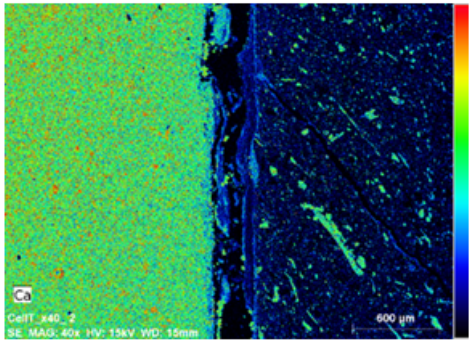
Infiltration devices (UNIBERN)

WP1 – data obtained

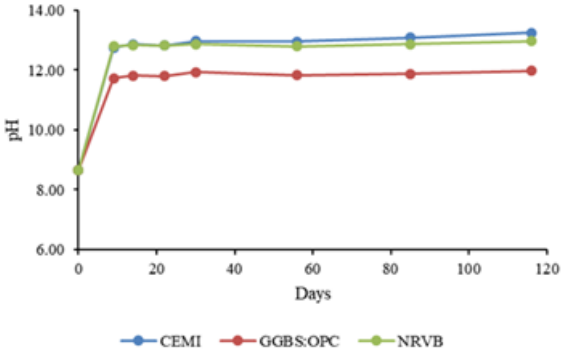
Chemical characterization and mineralogy



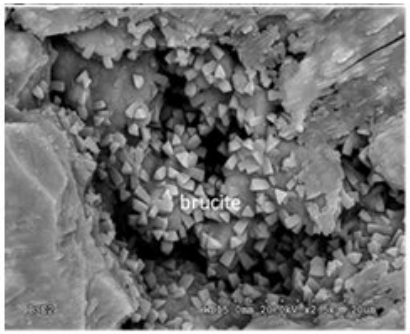
Piper diagram - Josef groundwater (UJV)



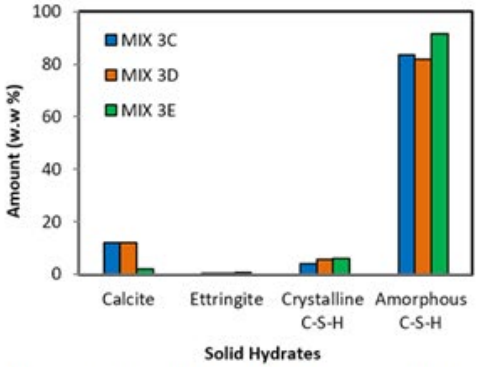
Map distribution of Ca - cement and argillite disks in contact (IRSN)



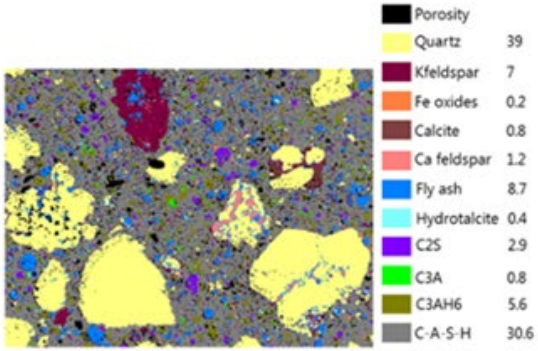
Changes in granitic GW pH due to interaction with cementitious materials (SURREY)



Mineral phases identified by GIXRD análisis (UAM)



Quantitative Rietveld phase analysis (KIT-INE)

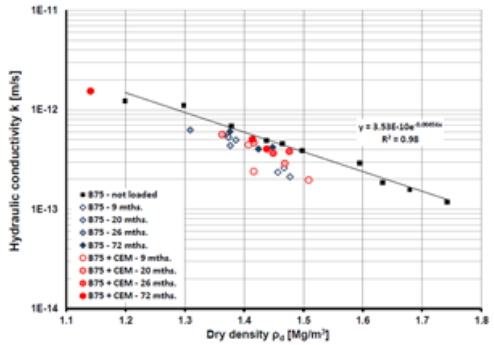


Quantitative mineralogical map for the concrete (SCK·CEN)

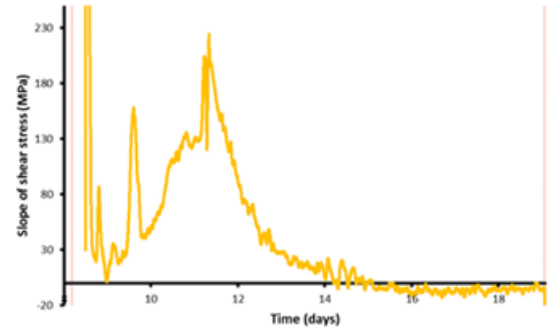
WP1 – data obtained

Physical and mechanical properties

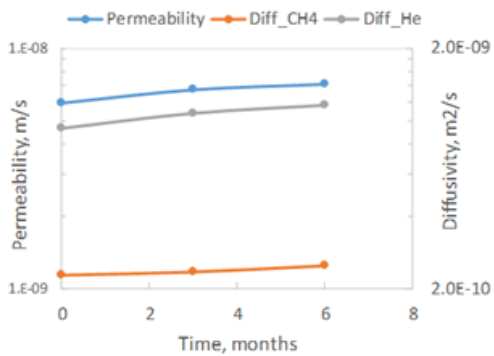
Fracture surface (HDZR)



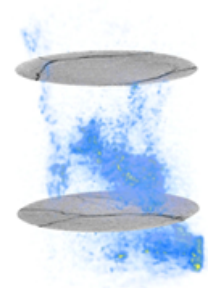
Hydraulic conductivity (UJV)



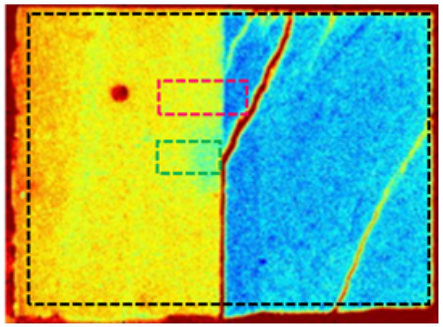
Slope of shear stress during shearing of the concrete/Cox interface (BGS)



Evolution of transport properties of backfill materials during batch experiment (BRGM)



Tracer concentration (HDZR)



Porosity (IRSN)

WP 1: main results

- At (25°C), whatever the concrete mixture formulation, both very little clay and concrete alterations were observed during the early phases (0-13 years) with respect to mineralogical changes being limited to the mm scale.
- The cement-internal extent of alteration in low-pH material was at least as extensive as in OPC (However: mineralogy is not the only driver to consider for cement-based materials formulation).
- Regarding porosity (and mass) re-distribution at small scale, an only partially coherent pattern was observed, indicating a potential tendency of permeability reduction.
- With specific focus on radionuclide mobility, low pH cementitious materials did not minimise the extent of reaction between bentonite and cementitious materials in the "high-performance" materials investigated (having dense paste structure). No significant reduction of anionic radionuclides mobility like $^{36}Cl^-$ and $^{129}I^-$ in cement.

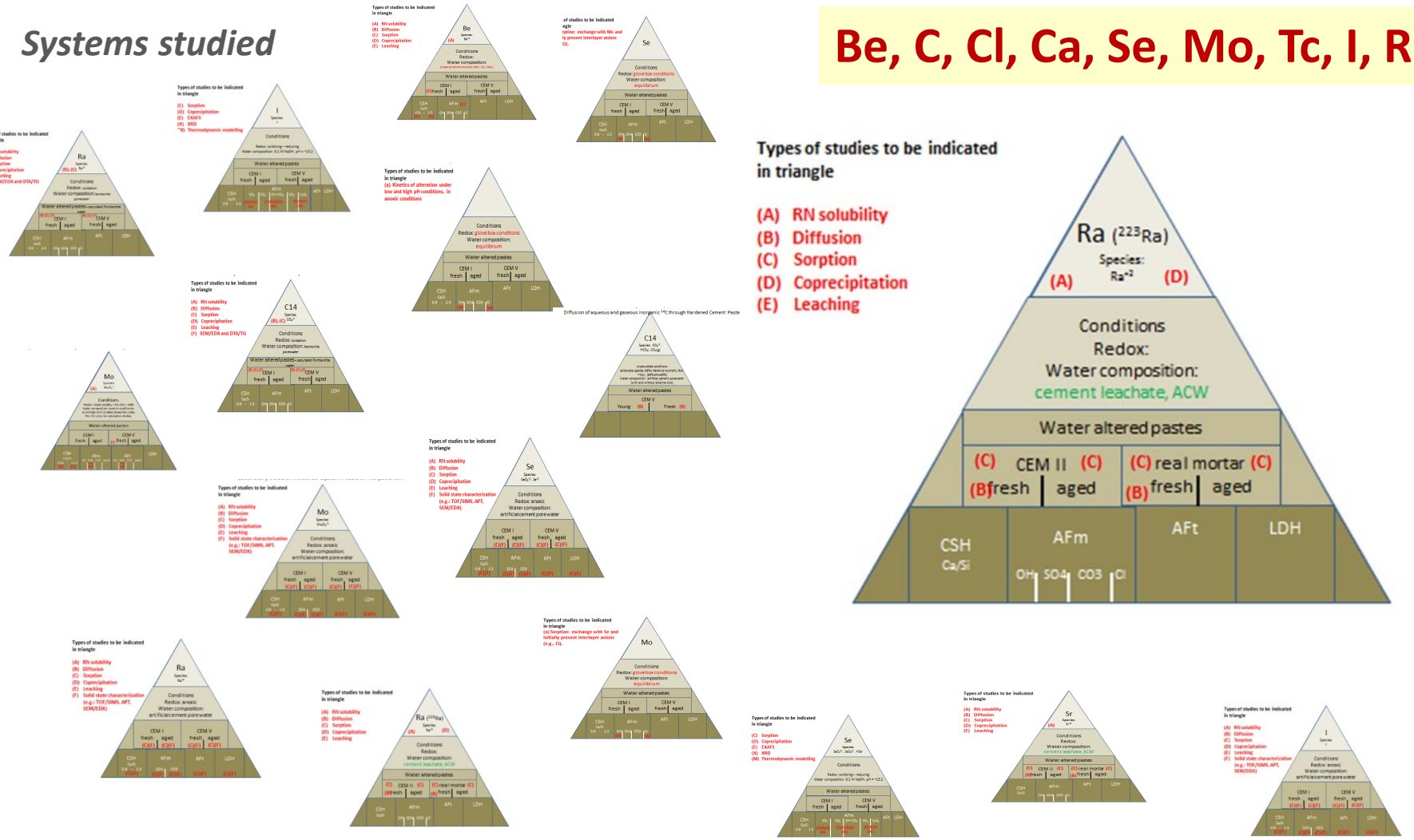
WP2: Radionuclide retention

- Solubility experiments with Be, Mo and Se under high pH conditions. Providing for realistic solubility limits and radionuclide speciation schemes as a prerequisite to derive advanced models on radionuclide retention.
- Sorption/desorption experiments using various radionuclides or toxic elements (i.e. Be, Mo, Ra, Tc, I-, IO_3^-, SeO_3^{2-}/SeO_4^{2-}, Cl^-, Ra, Sr and ^{14}C) and various hardened cement paste formulations as well as individual cement phases.
- Diffusion experiments performed with various anionic species ($^{36}Cl^-$, $^{99}TcO_4^-$, $^{125}I^-$, ^{14}C) or sorbing radionuclides (Ra, Sr) through saturated hardened cement pastes considering as well partially water saturated conditions.
- Solid solutions formation between radionuclides in a range of oxidation states (Se, I and Mo) and main components (OH, S, Cl…) in cementitious phases (AFm).
- Detailed characterisation performed on the experiments with radionuclides using several complementary analytical techniques. (e.g. XRD, XRF, BET, SEM/EDS, TG-DSC and ^{29}Si NMR for solid phases).

WP2 – work performed

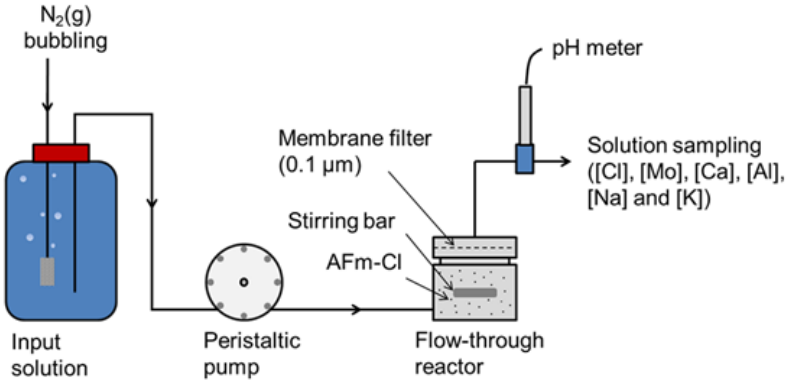
Systems studied

Be, C, Cl, Ca, Se, Mo, Tc, I, Ra



WP2 – work performed

Experimental set-up



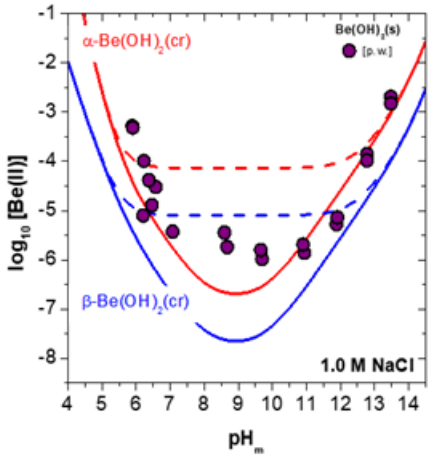
The experimental apparatus. Flow rates, pH as well as Cl, Mo, Ca, Al, Na and K concentrations were monitored as function of time (BRGM)

Synthesis of the (HS-) 2-AFm phase (PSI)

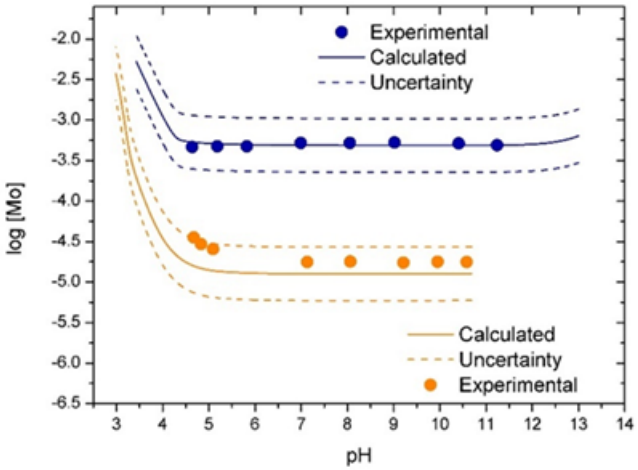
A21

WP2 – data obtained

Solubility data

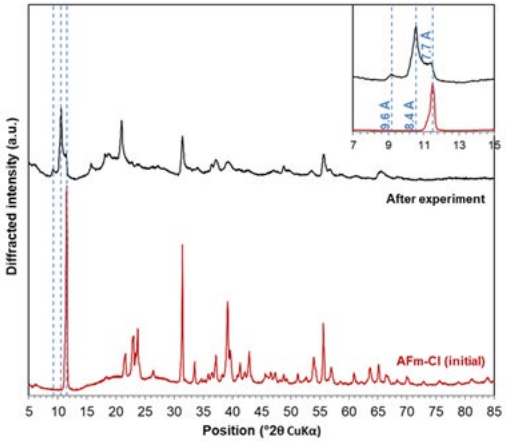


Berillium solubility (KIT-INE)

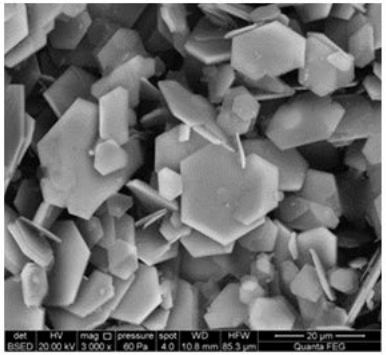


Molybdenum solubility (Amphos21)

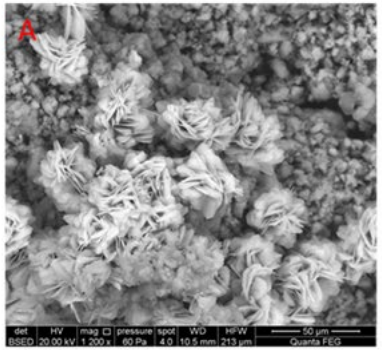
Mineral alteration



X-ray diffraction patterns before and after the experiment (BRGM)



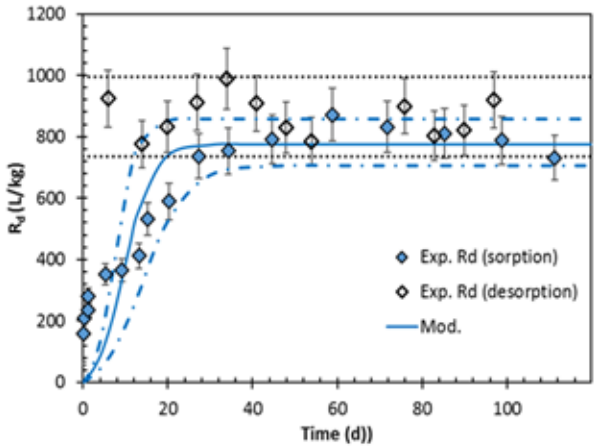
SEM picture of an AFm pase (JUELICH)



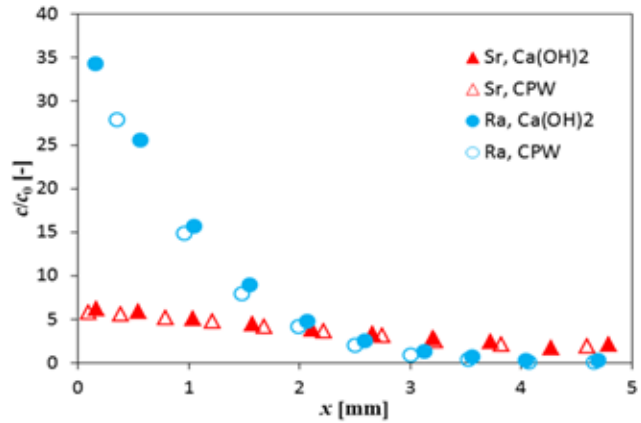
Selenium precipitation to CSH surface (SURREY)

WP2 – data obtained

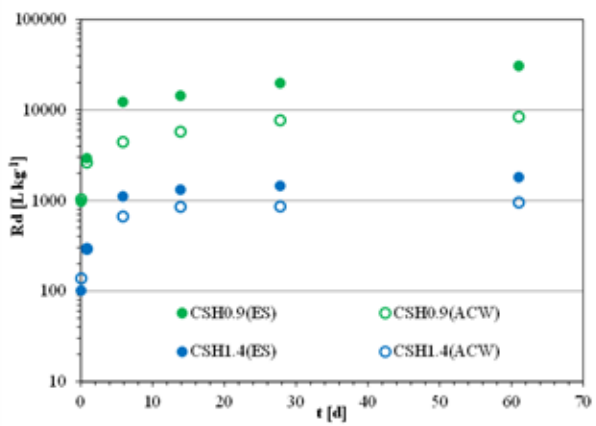
Sorption



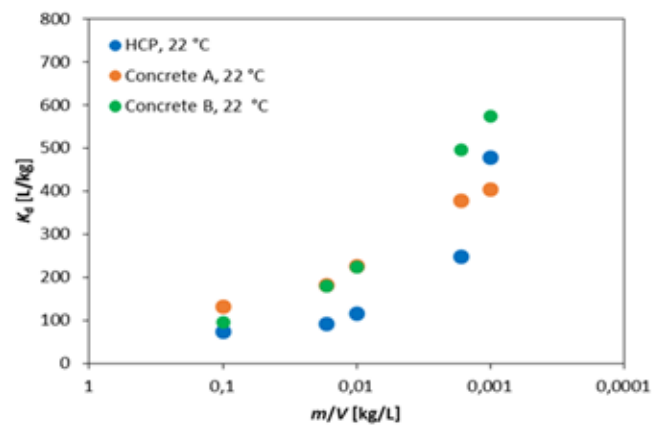
C-14 sorption (RATEN)



Strontium and radium sorption (CTU)



Radium uptake in CHS phases (JUELICH)



Dependence of radium sorptioon on the phase ratio mass solid phase/volume wáter (CTU)

WP 2: main results

- For the uptake of anions in AFm phases a continuous solid solution was found between the end members Se(IV)-AFm and S(VI)-Afm. Solid solution formation also observed between the pairs I-OH and I-OH_CO_3. The thermodynamic properties of each of the pure Se- and I-AFm phases and of AFm phases containing binary mixtures of Se and I with the common anions present in cement, were determined.
- Due to the higher amounts of aluminate phases in HCP based on CEM I, the retention capacity for the selenite and selenate is higher in this case compared to the low–pH CEBAMA reference paste.
- Flow-through studies showed that the Se(VI)/Cl exchange on AFm-Cl is rapid and reversible. The exchange can be modelled by 2 anion exchange sites. Exchange constants were obtained and accurate rate laws determined, implementable in reactive transport modelling.

WP 2: main results

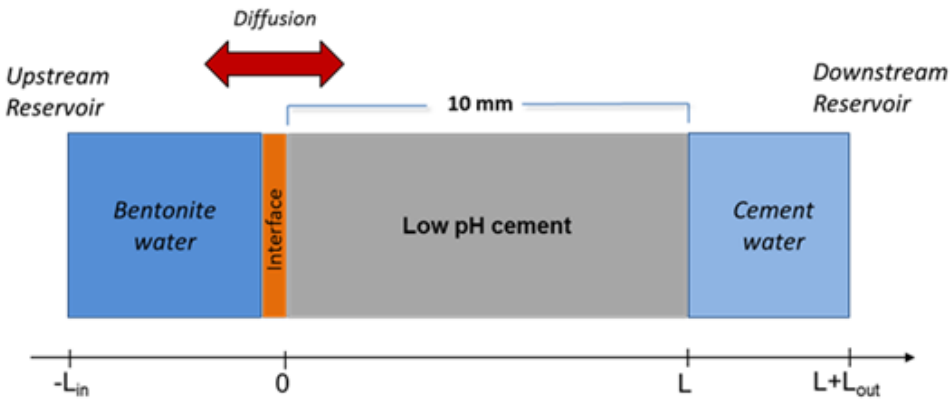
- CEBAMA has provided a first set of sorption parameters of Beryllium onto cementitious phases. In contrast to the traditional hypothesis of very weak Be sorption, assumed on the basis of the negative charge of the Be(II) species at high pH values, a strong uptake has been confirmed in the investigations.
- Sorption of molybdenum is not associated with ettringite in cementitious environments, in contrast to what has been traditionally assumed. This has important implications on sorption analogies - the project recommends not to use selenium as analogue for molybdenum in sorption estimations.
- Significantly higher retention of Ra than that of Sr onto cementitious materials. This again, decreases uncertainty and conservativism.
- Strong reduction of sorption of $^{14}C_{(inorg)}$ has been observed with the increased degradation of cement pastes in contrast to Ra sorption.

WP3: Modelling

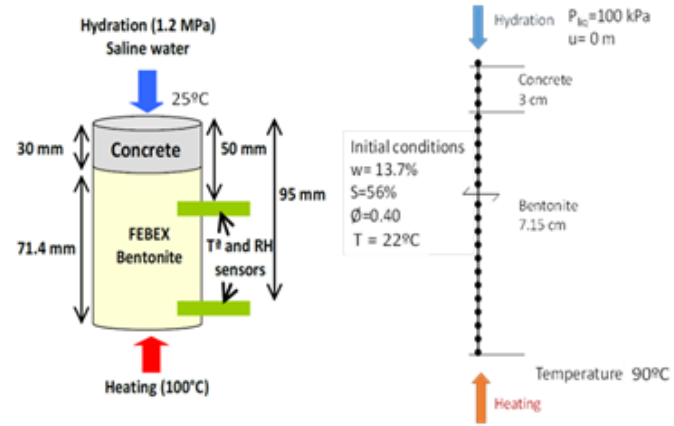
- <u>Development of modelling tools with pore- and continuum-scale applications</u> including new capabilities (i.e. Poisson-Nernst-Planck equations, Poisson-Boltzmann equations, coupling with geochemical solvers, coupling between chemistry and mechanics, etc.) in already existing or new codes (i.e. iCP, ORCHESTRA, MATLAB, iPP, Yantra, etc.).
- <u>Modelling work with application to WP1 and WP2 experiments</u> (i.e. through-diffusion tests, leaching tests, cement-clay interaction, etc.), including reactive and mass transport simulations, cement hydration models, solubility calculations and hydromechanical simulations.
- <u>Long-term modelling of concrete-clay interactions</u> including reactive transport and hydro-mechanical-chemical coupled analyses.

WP3 – work performed

Modelled systems

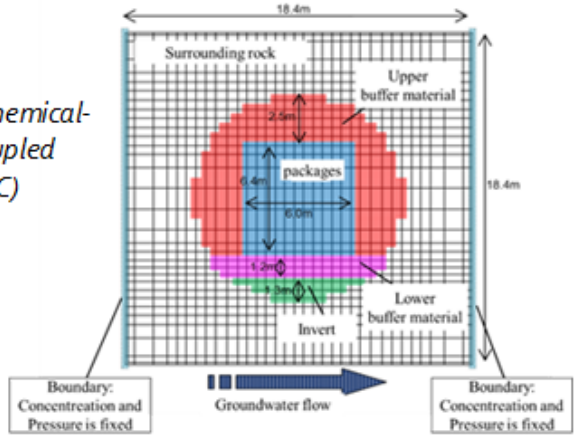


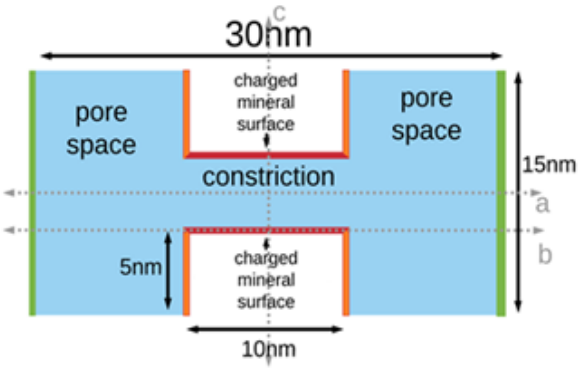
Schematic representation of the through diffusion experiments (KIT)



Setup of the concrete-bentonite HB column tests (left) and scheme for the numerical model (right). (UdC)

Geometry of the chemical-mass transport coupled calculation (RWMC)

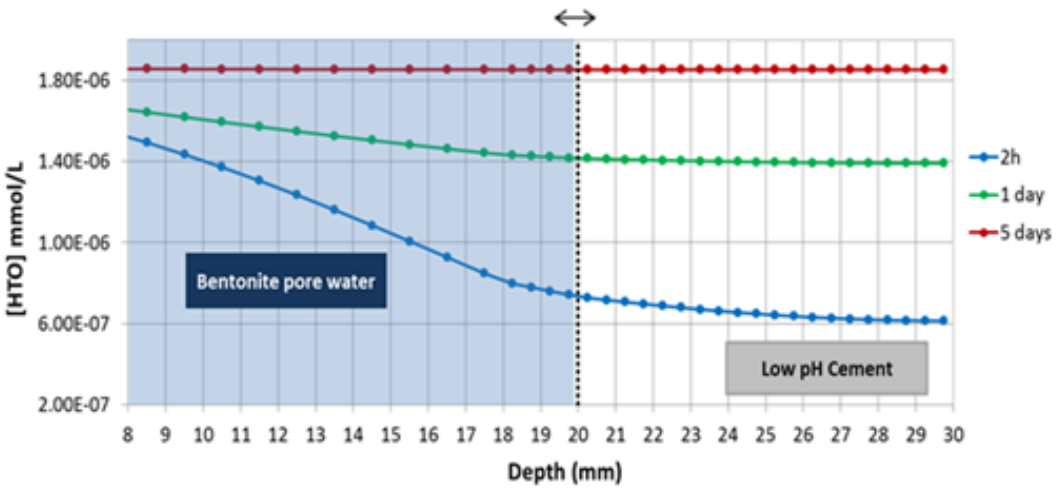




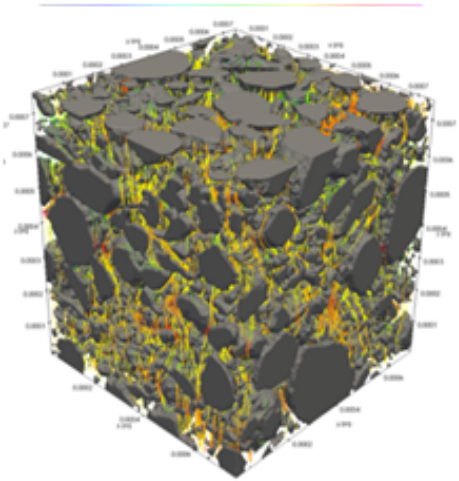
Scheme of the 2D model of the constricted pore and charged mineral surface (PSI)

WP3 – work performed

Modelling - Diffusion



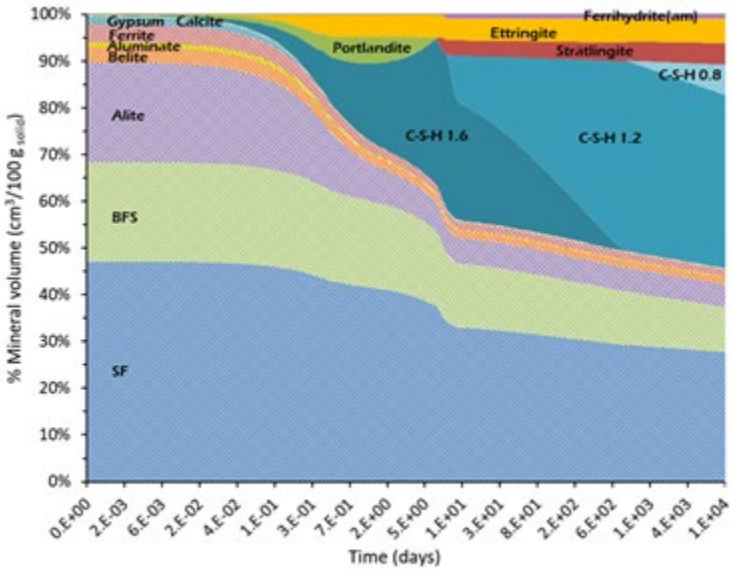
HTO diffusion in the low pH cement / bentonite interface (KIT-INE)



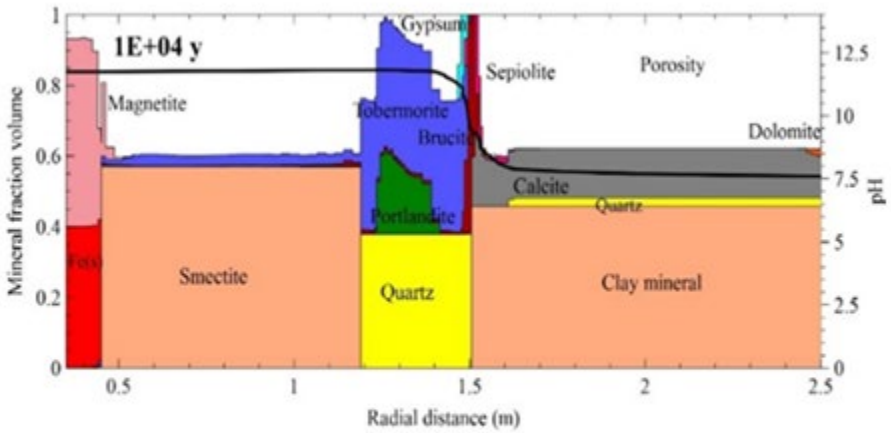
Diffusive flux streamlines of inert tracer (JUELIC)

WP3 – data obtained

Modelling - Mineralogy



Evolution of main cement hydrates as a function of hydration time (Amphos21)

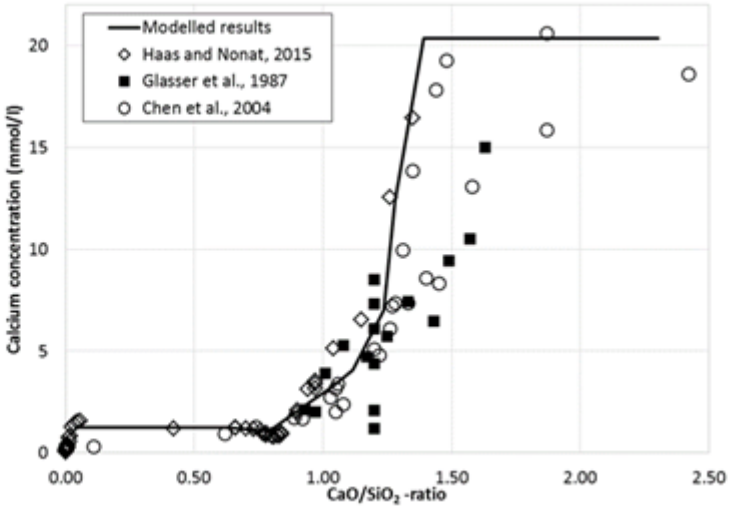


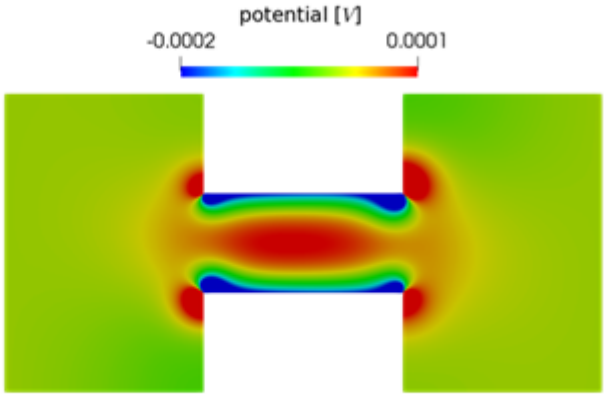
pH and mineral volume fractions (UdC)

WP3 – data obtained

Modelling – Chemical parameters

Calcium concentration as a function of CaO/ SiO2 -ratio (VTT)





Electric potential charges throughout the domain (PSI)

WP 3: main results

- THM models of clay-concrete interfaces, based on elasto-plasticity, have been developed that can now be used in future assessments of the behaviour and evolution of interfaces between concrete and different host rocks.
- New model features developed and implemented in WP3 include: diffusion-porosity changes couplings, electro-chemical multi-component diffusion capabilities, homogenization schemes for mechanical and transport properties, more efficient pore-scale reactive transport tools, and extended membrane polarization models for porosity and pore size distribution.
- CM models have been developed to predict the impact of chemical interaction of concrete with other materials in the repository on the mechanical integrity of cement-based barriers (i.e. strength, stiffness, pore space). New couplings were established regarding electrochemistry, diffusion-porosity couplings, CM models, HM coupling of clay/concrete interfaces, etc..

WP 3: main results

- New insights on low-pH cement and concrete were derived, including: hydration modelling in low-pH and low w/b ratio systems; assessment of diffusion properties from microscopic considerations; pore structure (pore-scale reactive transport models, homogenization models and membrane polarization models); assessment of thermodynamic data in low-pH systems: C-S-H, C-(A)-S-H, Fe speciation, alkali uptake, etc.; and hydro-mechanical behaviour of clay/concrete interfaces.
- For the first time, reactive transport models have explicitly considered the hydration of low-pH cement and how water consumption during hydration impacts the final mineralogical composition.
- Integrated Common Modelling Task built confidence on the modelling tools reactive transport tools used when simulating the long-term behaviour of an interface between low-pH concrete and a clayey host rock. Good agreement obtained with different codes, which is essential to demonstrate for the use of these tools in Safety Assessments.

Summary - Impact - 1

➢ CEBAMA and design issues

- impact optimisation of repository dimensioning.
- aid specification/selection of material parameters, material compatibility, evolution.
- aid specifications for experimental methods, i.e. for material quality control.

➢ CEBAMA and safety assessment issues

- evidence that interfaces (concrete-bentonite-host rock) can co-exist safely.
- better understanding of impacts from material interface processes for realistic description of the system performance affecting strength, flow properties, etc. and transport processes variation with time.
- evidenced porosity changes – if and when clogging occurs.
- improved accuracy in robustness and weighting of safety functions; increased modelling accuracy with new data and process understanding, accounting for evolution of the system.

Summary - Impact - 2

- **CEBAMA and radionuclide retention in cementitious repository near fields**

– decreased uncertainties and increased safety margins with respect to relevant radionuclide retention processes.

– substantiated and justified assumptions with respect to radionuclide migration behaviour in Safety Assessments.

– improved sorption databases for cementitious environments for so far less studied systems and different stages of system evolution .

– direct input to case studies like for the LLW-ILW repository Bratrství (Czech Republic) and the licensing process for the near surface repository in the proximity of Cernavoda NPP (Romania).

Summary - Impact - 3

➢ CEBAMA and modelling

- increased level of confidence in reactive transport models for further use in Safety Cases for near-field applications.
- improved reactive transport modelling tools to quantify how bentonite barrier or clayey host rocks could affect the integrity of normal and low-pH cementitious materials (tools available as open source or upon request).
- developed models can be used by to study the impact of reactive transport processes, but also other THMC coupled processes on the long-term performance of the near-field, including low-pH cement-based materials.
- Pore-scale reactive transport models can be used as process models to enhance understanding of the impact of alteration of cement-based materials on their transport properties.

Summary - Impact - 4

➢ Overarching aspects in CEBAMA

- ➢ Enhanced cooperation, exchange and knowledge transfer between different institutions and between different research fields (i.e. Geosciences, Environmental Engineering, Radiochemistry and Computational Sciences).
- ➢ Involvement from experts coming from countries at very different stages of implementation. Impact in view of sharing of expertise and resources.
- ➢ Cooperation and complementary competences as basis to tackle future challenges in a focused, cost-saving, collaborative approach.
- ➢ Experimental and modelling work to a significant extent performed by young researchers and within PhD theses - supporting and developing young talent.
- ➢ Ensure availability of highly trained specialists for implementers and regulators.

➢ **CEBAMA has contributed to European integration !!!**

Thank You !!!

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