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Deliverable D1.04

Report on WP1 established experimental boundary conditions, experimental methods. (M10 - March 2016)

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ABSTRACT:

CEBAMA deliverable D1.04 summarizes experimental boundary conditions and experimental methods employed by the 19 partners participating in WP1. It derives from original and updated project plans, follow-up information presented at the Project meeting in London (2015) and from surveys requested from all partners. Details about each project are listed in the appendices.

RESPONSIBLE PERSON(S):

WP1 co-leaders: Urs Mäder (UniBern), Erika Holt (VTT), Francis Claret (BRGM)

MAIN TEXT:

CEBAMA WP1 combines 19 partner projects that all study clay-cement systems by different experimental means. Deliverable D1.02 summarized the systems and materials that are being studied, with details about the clay material, the cementitious materials, and the types of interfaces. In this deliverable D1.04 the focus is on the experimental methods employed and the boundary conditions imposed. Detailed summaries provided by all partners are given in the appendices.

Table 1 lists all 19 projects of WP1 with information of the materials studied and the experimental methods chosen, as well as key objectives for the experiments. Table 2 details the experimental methods with respect to techniques and boundary conditions imposed on the experiments. “Boundary conditions” is used in a broad sense to include also geometry, confinement and some other relevant parameters.

Of the 19 partners, 10 are using some variant of column experiments or diffusion cells that use either mechanical or hydraulic confinement, and one is applying electro-migration techniques. 4 partners use some kind of immersion tests, with variable or no confinement. 5 partners use mechanical or combined hydraulic-mechanical devices to address also strength parameters. 3 projects rely on samples from existing experiments or those accessed by collaboration, and thus focus on characterisation.

Imposed boundary conditions depend on the equipment used. Almost all partners work at saturated conditions and at room temperature. Fluid pressure is either ambient, or elevated in case of tests where fluid is injected, or during some of the mechanical tests. Chemical boundary conditions include fluids of a specified composition, and monitoring during experiments (leaching tests, diffusion cells, columns).

Table 1: List of WP1 partners, materials, methods and focus

		Experiment	Focus	Materials		Interface
				clay	concrete	
1	KIT	diffusion in columns, interfae evolution in batch	Transport properties	Bentonite	LpH	bentonit groundwater
3	BRGM	Examination of existing interfaces	Transport properties, pore network	COX, Boom Clay	OPC, LPH	aged (URL, Mol)
4	BGS	1. Aging of concrete batch testing; 2. transport testing shear apparatus	Transport properties, seal performance	COX	LPH [CEM I/SF/BFS blend]	aged and fresh
5	CIEMAT	Column experiments, FEBEX in situ experiment	Transport properties	Bentonite (FEBEX)	OPC	OPC/FEBEX
6	TUDelft	Electromigration	Transport properties	Boom clay	Portland fly ash unreinforced cement	fresh, but fully set
10	RWMC	(1)Long term immersion test and/or structure (2)1D compression test	Transport, mechanical properties	Bentonitic (Kunigel)	OPC, Flyash mixed	5 to 10 years (lab / GTS)
11	SCK	diffusion, column, batch	Transport properties	Boom Clay	OPC (high strength/low por, low strength/high por)	aged (URL, Mol) + fresh
13	UJV	1/ lab-aged (CTU) 2/ URL Josef 3/ diffusion study after interaction	Mech., chemical, transport properties	Ca-Mg bentonite (CZ)	OPC, LPH (VTT)	fresh + aged (Josef)
15	ULOUGH	Diffusion & advection cells	Transport	COX & BVG	OPC (NRVB), LPH,	Interface with groundwater
16	CTU	1/ ageing - interaction in tests 2/ samples from Josef "cartridges"	Mechanical, hydrophys. properties	bentonite (CZ, Ca-Mg)	OPC, LPH (VTT)	fresh + aged (Josef)
17	USFD	Batch	Cement hydration, pH, transport	(None)	NRVB, PC - SF, PC - SF - FA	3 groundwater compositions
18	VTT	Batch	Transport properties	bentonite (MX80)	LPH	3 groundwaters / fresh samples
19	HZDR	confined column	Transport properties	Boom Clay and OPA	like SCK and like UniBE	like SCK and like UniBE
20	LML	direct shear in triaxial cell	Hydromechanical properties	COX	LPH	aged
21	UAM	*Core-interface *mm cell infiltration interface	Transport properties	FEBEX bentonite	OPC, LPH	Aged (GTS), Fresh(OPC or LPH)
22	CSIC	percolation test	Transport properties	FEBEX bentonite	OPC and LPH	aged (GTS) + fresh + groundwater
23	ANDRA	in situ	mechanical properties	COX	Low pH	fresh
25	UNIBERN	confined column	Transport properties	OPA	OPC, LPH	aged (Mont Terri)
26	IRSN	Tournemire 70°C (CEMTEX) - 1 D experiments	Transport properties	claystone (Tournemire)	LPH, OPC	aged: 1,2, 3 years
				1.2.1 claystone	OPC	aged interface claystone/cem.mat.
				1.2.2 bentonite	LPH	fresh interface claystone/cem.mat.
				no clay material		no interface clay/cem.mat.

Table 2: List of WP1 partners, experimental methods and boundary conditions

		Apparatus	Confinement	T	P	mechanical aspects
1	KIT	Diffusion cells, Batch sorption	Mechanical confinement; suspension	Ambient	Ambient	None
3	BRGM	None				
4	BGS	Hydromechanical apparatus	Load on solids, immersed	Ambient	Injection, ambient	Contolled load
5	CIEMAT	Column and diffusion experiments	Mechanical confinement	Ambient	Ambient	None
6	TUDelft	Diffusion cells with electro migration	Mechanical confinement	Ambient	Ambient	None
10	RWMC	Samples from immersion / compressions tests	Semi-confined	Ambient	Ambient	
11	SCK	Permeability tests, gas diffusion, constant-volume cells	Mechanical confinement	Ambient	Ambient	None
13	UJV	Diffusion cells	Mechanical confinement	Ambient	Ambient	None
15	ULOUGH	Diffusion cells	Semi-confined	Ambient	Ambient	None
16	CTU	Test cells for strength, hydr. Cond., swelling P, water retention	as required	Ambient	Ambient	as required
17	USFD	Batch immersion	Semi-confined	Ambient	Ambient	None
18	VTT	Btach immersion / leaching tests	Semi-confined	Ambient	Ambient	None
19	HZDR	Column/diffusion experiments from partners	Mechanical confinement	Ambient	Ambient	None
20	LML	Compression/shear tests, controlled pore pressure	Mechanical confinement	Ambient	up to 80 °C	Strength
21	UAM	Surface reactivity interface experiemnts	Mechanical confinement	Ambient	Ambient / injection	None
22	CSIC	Column experiments	Mechanical confinement	Ambient	Ambient / injection	None
23	ANDRA	Fieled test	Casting	Ambient	Ambient	Indirect
25	UNIBERN	Column experiments	Hydraulic confinement	Ambient	Injection, ambient	None
26	IRSN	Batch experiments; Option: mechanical properties		Elevated	Ambient	Optional

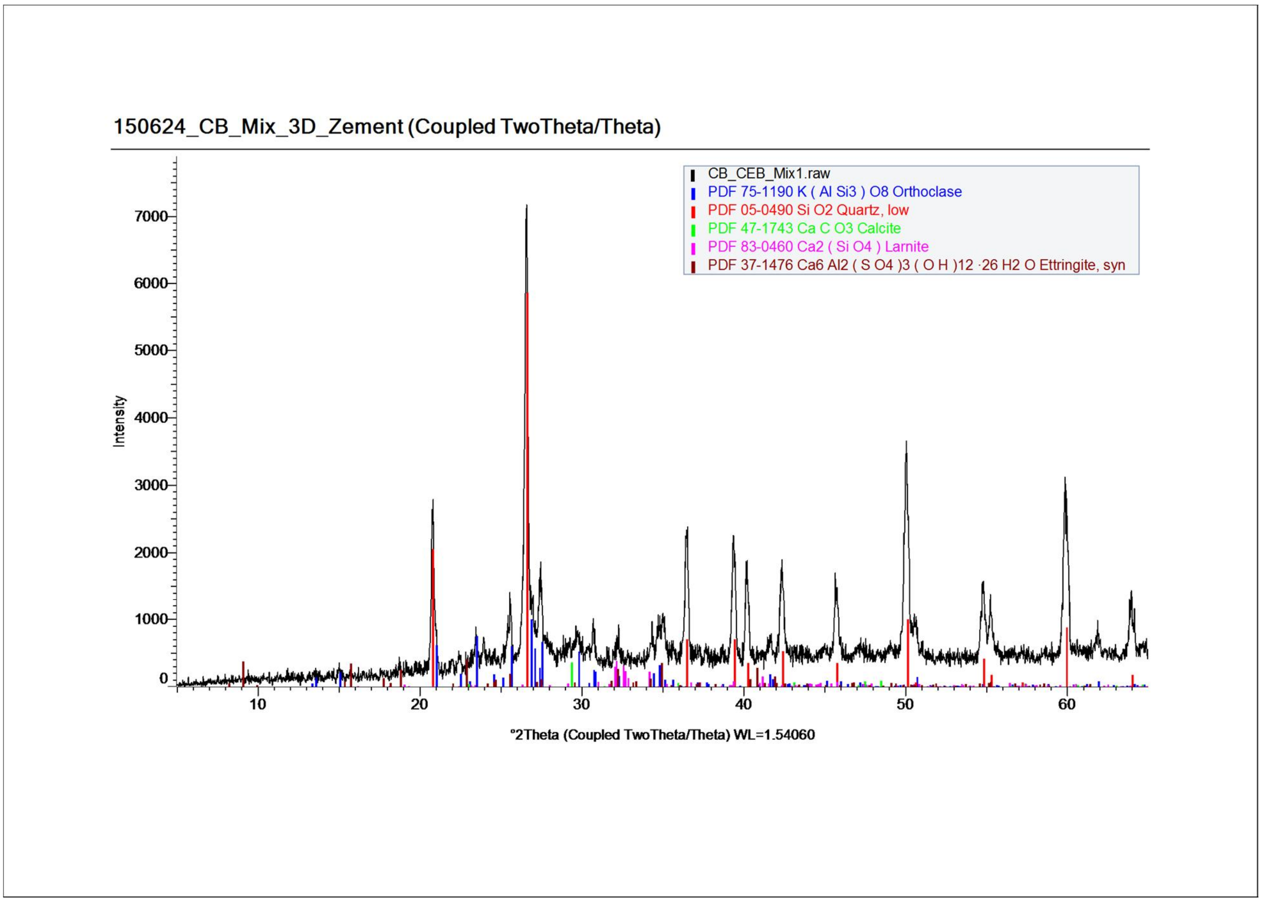
APPENDIX: Detailed Answers per Partner, regarding their experimental methods

1. KIT/Bernhard Kienzler, Vanessa Montoya

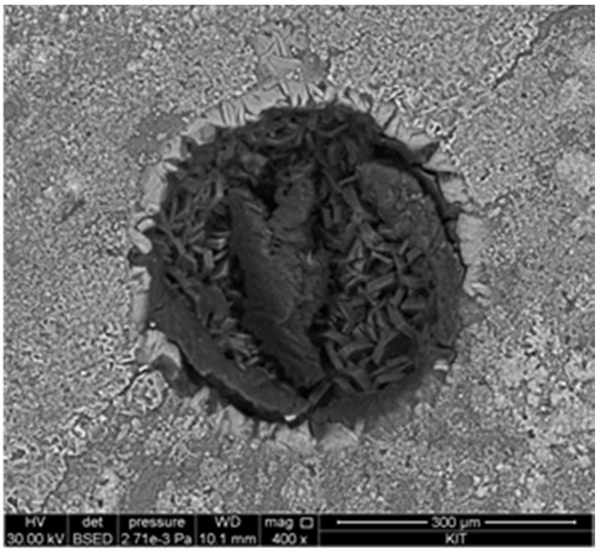
Task 1.1: Defining boundary conditions for experimental studies (0–12 months)
- Set-up of batch interaction experiments
- Set-up of samples, diffusion experiments
- Characterization of solids by SEM methods with respect to their porosity, the mineralogy will be analyzed by XRD and SEM-EDX.
- Determination of initial diffusion properties with radioactive inert tracers (HTO) by breakthrough measurements. Directly after the start of the diffusion experiments with clay pore water.

Task 1.2: Characterization & experimental studies
- Repetition of the breakthrough tests using the same samples after different interaction times with the clay pore water in order to determine changes and deviations in the diffusion parameters.
- Quantification of chemical degradation (carbonation of low pH concrete)

Example: XRD: Characterization of initial material



Example: SEM-EDX: Analysing the initial pore structure


HV
det
pressure
WD
mag
300 µm
30.00 kV
BSED
2.71e-3 Pa
10.1 mm
400 x
KIT

3. BRGM/F. Claret in very close collaboration with SCK-CEN (see their work description)

The aim of the multi-scale investigation that will be realized is really to **determine the pore-network distribution** at the clay/concrete induced by the mineralogical (precipitation, dissolution) changes observed at the interfaces.

Using an integrated downscaling approach, we aim to quantify and spatialize how the geochemical perturbation surrounding those interfaces will modify the microstructure of both engineered and natural barriers and therefore the effect on the transport properties. A multi-scale investigation methodology that has been developed on clay materials during the European FP7 CATCLAY project will be used to retrieve the µ-structural changes. The methodology integers several bulk macroscopic characterization techniques and imaging method to display quantitative data from macroscopic to nanoscopic scale. The association of several 2D/3D techniques (mineral cartography, autoradiography, µTomography-RX, SEM, FIB-nT and TEM) allow to reach a quantitative and spatial distribution of the mineralogy and the pore network, from nanometer to micrometer. Therefore, the influence of the mineralogical and chemical changes on the microstructure will be obtained by: a) 2D quantitative spatial distribution of the mineralogy and its evolution with the effect of the perturbation, b) 2D quantitative spatial distribution of the porosity to localize spatial heterogeneities and porosity evolution as regard to the interface, c) focus on localized area to reach 3D pore network.

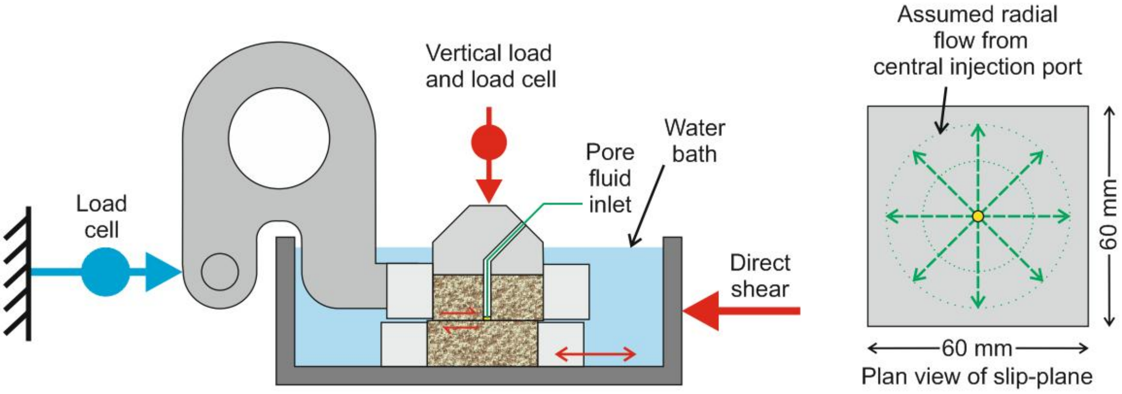
- This robust integrated methodology allows reaching the coherence of several geometric key parameters such as the pore size distribution and the associated mineral distributions. These quantitative data will be used to support lattice Boltzmann simulation to model the diffusion of radionuclides from the pore scale to the pore network
- The studied samples will be Boom Clay/cement interfaces of different ages either retrieved in the HADES URL or obtained after laboratory experiments.

- This will be available after the sampling

4. NERC-BGS/Rob Cuss

A bespoke experimental system (designed and built by BGS) will be used to simultaneously measure the hydromechanical and transport properties of repository interfaces (Figure 1). In this system, pore fluid is introduced into the middle of the top block of material directly to the interface and allowed to disperse through radial flow. Flow rate into the filter/interface is controlled or monitored[1] via a high precision syringe pump providing real-time pressure and flow rate data. Outflow, to the surrounding reservoir, cannot be directly monitored though this is not an issue given the accuracy of the inflow measurements. Experience has shown that the distribution and decay of pore pressure away from the central injection point is non-ideal and not radial. Experimental work undertaken as part of the FORGE project has shown that pore pressure within the fracture plane is very low/negligible compared with the injection pressure and therefore pressure at the outflow from the interface is expected to be close to atmospheric pressure[2]. The distribution of flow along the interface during hydraulic testing will be investigated by periodic tagging the pore fluid with fluorescein. Post-test fluorescence and optical microscopy measurements will be used to examine the distribution of flow.

Test samples of COx/concrete will be manufactured with a diameter of 60 mm and height of 50 mm (25 mm thickness for either side of the interface). Prior to testing, the COx side of the interface will have a 4 mm bore drilled directly to the interface. The top-block of the experimental apparatus has a 4 mm diameter bore that introduces fluid directly to the interface. A constant normal load will be established on the interface that will simulate in situ stress conditions. A constant pore pressure will be used and the flow rate will be monitored. A pore pressure will be selected that does not impose a high flow rate that would cause erosion of the interface. Once a stable flow rate has been achieved, the lower sample (concrete) will be sheared slowly and the changes in flow rate and shear properties will be measured.



This test program will give information on the interface between concrete and two types of COx and how these properties change with time. This will feed directly into modelling of the interface system.

[1] The syringe pump can be used in constant pressure or flow rate mode to provide a constant head or constant flow boundary condition. In previous tests a combination of these modes has been used to elicit the response and evolution of the interface.

[2] Unpublished work from FORGE work package 4.1.2 – Validation of critical stress theory applied to repository concepts; Cuss, R.J., Sathar, S. And Harrington, J.F.

5. CIEMAT/María Jesús Turrero / Elena Torres / Tiziana Missana

The main purpose of studying the real scale (aged shotcrete/bentonite samples coming from the *in situ* FEBEX experiment) and the small scale systems (aged concrete/bentonite samples coming from lab experiments) is the upscaling. The comparison between both experiments will give us certainty on the relevant parameters to be considered when modelling the transient state of a repository for performance assessment purposes (collaboration with UDC - WP3). For understanding aging and area of influence of processes at the different scales analysis at the concrete/bentonite interface and some centimetres further will be made including parameters such as chemical tracers, soluble salts, exchangeable cations, pore size distribution, specific surface area and gas and water permeability of specific samples.

Characterization of samples will be made following procedures already used in previous projects to study as much cementitious materials as bentonite (e.g. EU-Euratom PEBS project, Deliverable 2.3–6.1).

Transport (diffusion and column) experiments (details in refs 1, 2, 3 below) will be carried out with conservative tracers (HTO and Cl^-) to evaluate the modification of the transport properties due to changes of the chemical conditions of the system. The cement initially used will be CEM V and the tests will be eventually extended to CEM I. All the tests will be carried out under controlled conditions in a glow box (under N_2 or N_2+CO_2 atmosphere). Of special interest for this study is the evaluation of changes in porosity of the system during the aging of the cement. The conditions that will be analysed in details are the following: a) Stage I, i.e. fresh cement in contact with representative synthetic water (pH>13, high content in alkali, low Ca content); b) Stage II, i.e. degraded cement in contact with its representative synthetic water (pH around 12.4); Stage III, i.e. degraded and carbonated cement.

[1]M. García-Gutiérrez, Cormenzana J.L, Missana T., Mingarro M., Applied Clay Science 26 (2004) 65-73.
[2]M. García-Gutiérrez, Cormenzana J.L, Missana T., Mingarro M.,J. Molinero, Journal of Iberian Geology 32 (1), 2006, 37-53.
[3]U. Alonso, T. Missana, M. García-Guterrez, A. Patelli, D. Ceccato, V. Rigato, N. Albarran, H. Rojo, T. López (2009) Mater. Res. Soc. Symp. Proc. Vol.1124-Q5-08.

6. TUDelft/Denis Bykov

We are planning to use migration experiments in order to characterize transport properties linked to the associated microstructural changes. Diffusion cell is based on electromigration in order to speed up the diffusion process, but other set-ups could also be considered as well when necessary. For the characterisation of concentration profiles of elements and the porosity we have the following experimental techniques available:

- Instrumental Neutron Activation Analysis (determination of Ca and Mg content) to correlate with the observed changes in porosity,
- Neutron imaging of water penetration through the fresh and aged interfaces (or using an H-3 tracer),
- X-ray and neutron imaging for the visualization of changes of microporosity at the interfaces,
- Positron annihilation to study changes of nanoporosity at the interfaces.

The expected outcome of these experiments includes transport parameters and related microstructural characteristics.

10. RWMC/Hitoshi Owada

The expansion of the altered zone of bentonitic material will be obtained from long term coupled immersion test. The thickness of the altered zone will always be smaller than that in the results of geochemical and mass transport coupled calculation. The reason of the difference is thought that the clogging has occurred by the generation of secondary minerals. In RWMC's previous work, the secondary mineral around C-B interface is mainly C-S-H. So that, the quantitative and qualitative analysis of C-S-H around C-B interface is useful to understand and modelling of the change of mechanical and mass transport properties of bentonitic materials. Dissolution and growth ratio of primary and secondary minerals are also important to calculate such alteration.

Phase shift interferometry[1)] is the method for direct observation of the amount of dissolution or growth of minerals from the changes of the "height" of crystalline. To determine the growth and/or dissolution ratio, the effective surface area is required, which will be obtained by atomic force microscopy.

Since the thickness of the altered zone will be very small, the quantitative analysis of the secondary mineral might be difficult by usual chemical or spectroscopic way. Ca-XAFS analysis might be a good solution of such mineralogical analyses because the dominant secondary mineral generated by C-B interaction will be C-S-H gel. XAFS can qualitative and quantitative analyses at one time[2)]. The shape of specimen is not limited (but size of specimen is limited to few cm scale) a lamina or powdered sample is used in the RWMC's analyses.

The samples are described in Deliverable D1.05 and/or the drilled cores obtained from former GMT facility of GTS.

1) H.Sato, T. Ishii and H. Owada, "Dissolution of compacted montmorillonite at hyperalkaline pH and 70 ºC: in situ VSI and ex situ AFM measurements", Clay Mineral., Volume 48, Number 2, p285–p294, May (2013).

2) Hiroyuki SAKAMOTO, Kumi NEGISHI, Daisuke HAYASHI, Tomoko ISHII, Hitoshi OWADA, Hiroaki NITANI, Masaharu NOMURA, "Evaluation of long-term interaction between cement and bentonite for the geological disposal, (2) XAFS Analysis of Calcium-Silicate-Hydrate Precipitates at Cementitious and Bentonite Interface", AP/AP/6, Clays in natural and engineered barrier for geological disposal(Clay 2012) (2012).

11. SCK CEN/Norbert Maes; Quoc Tri Phung (with input from F. Claret, BRGM)

Hydraulic conductivity [m/s]; diffusivity [m^2/s]; porosity [-]; specific surface area [m^2/g]; Pore size distribution; mineralogical composition; pH.

- ✓ Permeability measurements: using controlled constant flow method (Phung et al., 2013); Sample size: cylinder 98 mm in diameter, 25 mm (cement paste) or 45 mm (concrete) in thickness
- ✓ Diffusivity measurements: measured diffusivity of 2 dissolved in a single experiment (Phung et al., 2015c); Sample size: cylinder 98 mm in diameter, 25 mm (cement paste) or 45 mm (concrete) in thickness
- ✓ Porosity and pore size distribution: combine mercury intrusion porosimetry (MIP) and N_2-adsorption (Phung et al., 2015b)
- ✓ Imaging analysis: SEM
- ✓ Mineralogical composition: TGA, XRD (Phung et al., 2015a), SEM-EDX
- ✓ Chemical composition of pore solution: Ion chromatography

Together with BRGM, the following methods will be applied:

- Using an integrated downscaling approach, we aim to quantify and spatialize how the geochemical perturbation surrounding those interfaces will modify the microstructure of both engineered and natural barriers and therefore the effect on the transport properties. A multi-scale investigation methodology that has been developed on clay materials during the European FP7 CATCLAY project will be used to retrieve the µ-structural changes. The methodology integers several bulk macroscopic characterization techniques and imaging method to display quantitative data from macroscopic to nanoscopic scale. The association of several 2D/3D techniques (mineral cartography, autoradiography, µTomography-RX, SEM, FIB-nT and TEM) allow to reach a quantitative and spatial distribution of the mineralogy and the pore network, from nanometer to micrometer. Therefore, the influence of the mineralogical and chemical changes on the microstructure will be obtained by: a) 2D quantitative spatial distribution of the mineralogy and its evolution with the effect of the perturbation, b) 2D quantitative spatial distribution of the porosity to localize spatial heterogeneities and porosity evolution as regard to the interface, c) focus on localized area to reach 3D pore network.
- This robust integrated methodology allows reaching the coherence of several geometric key parameters such as the pore size distribution and the associated mineral distributions. These quantitative data will be used to support lattice Boltzmann simulation (SCK•CEN, WP3) to model the diffusion of radionuclides from the pore scale to the pore network

References to the used test methods by SCK•CEN (see annexes):

Phung, Q. T., Maes, N., De Schutter, G., Jacques, D. & Ye, G. 2013. Determination of water permeability of cementitious materials using a controlled constant flow method. *Construction and Building Materials,* 47, 1488-1496.

Phung, Q. T., Maes, N., Jacques, D., Bruneel, E., Van Driessche, I., Ye, G. & De Schutter, G. 2015a. Effect of limestone fillers on microstructure and permeability due to carbonation of cement pastes under controlled CO2 pressure conditions. *Construction and Building Materials,* 82, 376-390.

Phung, Q. T., Maes, N., Jacques, D., De Schutter, G. & Ye, G. 2015b. Investigation of the changes in microstructure and transport properties of leached cement pastes accounting for mix composition. *Cement and Concrete Research.*

Phung, Q. T., Maes, N., Jacques, D., Jacop, E., Grade, A., Schutter, G. D. & Ye, G. 2015c. Determination of diffusivities of dissolved gases in saturated cement-based materials IN DEHN, F., BEUSHAUSEN, H.-D., ALEXANDER, M. G. & MOYO, P. (Eds.) *International Conference on Concrete Repair, Rehabilitation and Retrofitting IV*. Leipzig, Germany, CRC Press.

13. UJV/Petr Večerník, Radek Červinka, Václava Havlová

Cement/concrete material is considered as a barrier material in the Czech concept of deep geological disposal in case the HLW is considered to be disposed in the concrete containers.

Therefore, its retention properties and migration properties has to be determined in order to gain an input data for safety assessment models.

Furthermore, use of concrete material is expected to be used as a construction material. However, the amount of such a material in the repository cannot be neglected and the information about its behaviour in contact with other material and radionuclides has to be studied.

ÚJV will be focused mainly on bentonite and cement material characterisation and evaluation of diffusion parameters in relation with changes of material properties. Bentonite and cements themselves and mainly their interfaces and interaction products will be used as a materials for characterisation and migration experiments.

For material characterisation X-Ray Diffraction, Cation Exchange Capacity, chemical analysis of materials and leachates (Atomic Absorption Spectroscopy, pH, Eh, conductivity measurements) will be used. By these method it is possible to characterise the basic material properties, some of the physical/mechanical measurements will be also performed (uniaxial compressive strength).

For sorption/migration experiments with tracers following methods will be used:
- γ-spectrometry,
- Liquid Scintilation Counting,
- Atomic Absorption Spectroscopy.

Migration parameters of materials and their interaction with tracers will be studied and diffusion and sorption/ retardation coefficients will be evaluated. Migration parameters together with materials characteristics are the basic input data for performance and safety assessments. In CEBAMA we would like to focus mainly on migration of tracers at cement bentonite interfaces, but characterisation of pre-experiment input materials is also necessary.

For diffusion and sorption experiments commonly used through-diffusion experiments and batch sorption methods and procedures will be applied.

For materials characterisation commonly used methods and procedures will be used - see above.

15. ULough/Matthew Isaacs, Monica Felipe-Sotelo, David Read

Diffusion tests will be carried out by submerging a block of cement in synthetic groundwater spiked with a radioactive tracer under nitrogen atmosphere. The activity in solution will be monitored, to determine the rate of uptake of the tracer. The cement block will be sealed with wax on the top and bottom surfaces so that uptake of isotopes will be through a single plane. Once the diffusion tests have reached steady state, the blocks will be sawn in half for digital autoradiography to determine the extent of tracer migration through the block. The cement blocks will then be characterised via XRD, NMR, Raman, EXAFS, XANES, SEM-EDX and XRT to assess the mineralogical association(s) of each tracer.

Variables studied within the scope of this work include:

- The three cementitious systems mentioned in section 1.3
- The three groundwater formulations mentioned in section 1.1
- The radioactive tracers: ^{3}H, ^{14}C, ^{35}S, ^{36}Cl
- The presence of metallic iron in the ^{35}S diffusion experiments
- Three different cure times of the cement samples (28 days, 1 year, 2 years)

All experiments will be carried out in triplicate.

Samples will be small cylindrical cement blocks (30 mm diameter × 60 mm height), weighing approximately 50 g when cured.

This work will provide rate data for uptake of the tracers and diffusion depths that can be modelled in WP3.

16. CTU/Lucie Hausmannova

CTU-CEG will test changes of strength properties of cements depending on interaction periods and environment (mixtures compositions – see Table 1).

It is supposed that given limited interaction time only surface part of samples will be affected. Standard procedures for testing of strength properties require samples with prescribed shape which has low Surface Area/Volume ratio. That means that effect of interaction would be very difficult to study and alternative sample shape & methods have to be developed and used. An alternative method rock mechanics using thin plates is good candidate.

The results will be complementary to UJV and DNS data (chemical and geochemical) and will not be used for modelling in WP3.

Note: The alternative strength test method for thin samples is described in Rock Mechanics textbook (*Mechanika Hornin, Pauli and Holousova 1994*, *CTU in Prague*). It is used for rock. The usage of this method for cement samples will be verified.

Expected cement samples will have shape of thin plates (height around 8 mm and diameter around 50 mm). Samples will be made from cement paste with water content around 0.45. For one result 5–7 samples must be tested.

CTU-CEG will also perform complementary test on bentonite used for interaction with cement.

Following parameters will be evaluated:
- hydraulic conductivity (according to ASTM D5084)
- swelling pressure (according to internal procedure, constant volume sample)
- water absorption (spis according to DIN 18132 – Soil, testing procedures and testing equipment Determination of water absorption)
- retention curve (Villar et al 2008)

Table 1 – Combination of elements studied in defined loading procedures

	Ageing procedures	Bentonite 75	Josef water	Portland cement	LpH cement	95°C
new procedures: loading 9/18/27 months	suspension + OPC (LPH) 95°C	x	x	x	x	x
	suspension + OPC (LPH)	x	x	x	x	
	water + OPC (LPH?) 95°C		x	x	x	x
	water + OPC (LPH?)		x	x	x	
	suspension	x	x			
	OPC (LPH)			x	x	
aged samples 60 months	patrony	x	x			
	patrony + OPC	x	x	x		

17. USFD/Claire Corkhill

1. *Cement/solution interface analysis by batch methods*

In these experiments, cured samples of cement will be immersed in groundwater solution in:

- Anoxic conditions, and
- Anoxic conditions with added carbonate.

At several time points during the immersion, the cement samples will be removed and analysed for:

- Chemical changes: XRD (D2 Phaser, selected samples for analysis at Diamond Light Source, I11), TGA-MS, SEM/EDX (Hitachi TM3030), NMR (Durham EPSRC facility) will be used to understand how interaction with solution affects cement clinker and binder phase chemistry. This will provide information to input to reactive transport models (e.g. cement binder phase composition, pore solution composition);
- Physical changes: SEM (Hitachi TM3030), porosimetry (MIP, gas adsorption (Beckman Coulter SA3100) and XCT) will be used to determine changes to cement microstructure. This will provide information for input to physical transport models (e.g. porosity, tortuosity etc.).

2. *Cement/solution interface analysis by synchrotron methods*

As part of an ongoing experiment at the Diamond Light Source (to study the kinetics of cement hydration, in situ, for two years), selected samples will be prepared for analysis by synchrotron XRD. Cements listed in Table 1 will be prepared in kapton capillaries and cured for 6 months. Samples will be submerged in the different groundwater solutions specified in Table 1, and analysed over a prolonged period (ca. 1–6 months depending on availability) at the I11 beamline on the long duration experiment stage (Fig. 1).

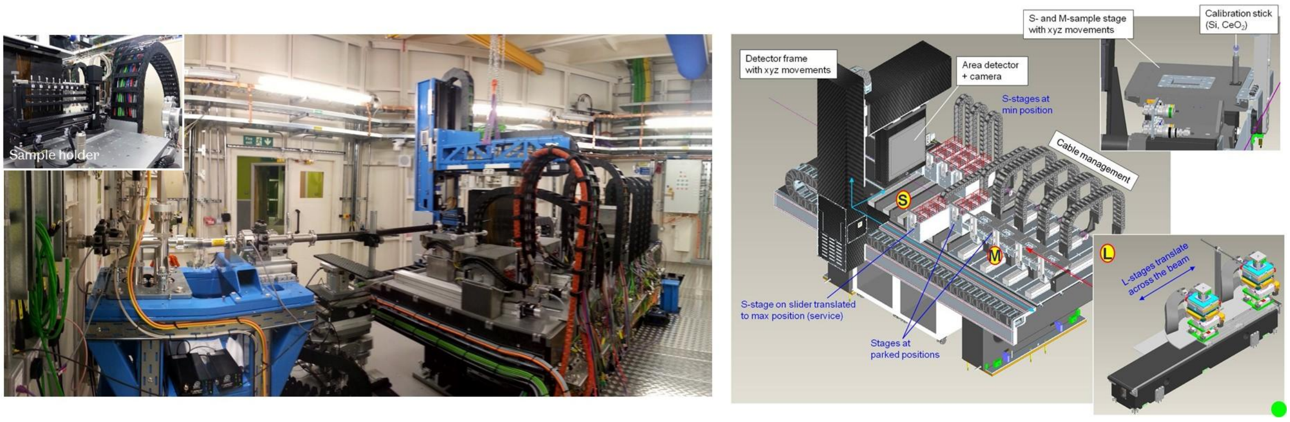


Figure 1. Photograph and schematic of the long duration beam line facility at the Diamond Light Source. Insert to left hand figure shows sample set up to be utilised for analysis of cement samples saturated with groundwater solutions.

This method of analysis will provide high resolution, in situ analysis of changes to cement chemistry as a function of groundwater composition. The advantages of using synchrotron XRD over laboratory based XRD methods are two-fold; the higher resolution allows determination of phases that may be present only in small concentrations and also allows for accurate analysis of amorphous content (by the Rietveld PONCKS method). The resulting data will be useful for input to thermodynamic models of cement chemistry following contact with groundwater, and for reactive transport models.

18. VTT/Tapio Vehmas

Equilibrium pH of the cement paste samples in various solutions, exposures and ages will be defined. PH values of various compositions, reaction- and leaching degrees can be compared to previously modelled data. Equilibrium pH will be defined according to “Development of an accurate pH measurement methodology for the pore fluids of low pH cementitious materials”(Alonso M., Garcia Calvo J., Walker C., Naito M., Pettersson S., Puigdomenech I., Cunado M., Vuorio M., Weber H., Ueda H., Fujisaki K., Svensk Kärnbränslehantering AB R-12-02). Solution analysis will be performed with inductive coupled plasma to complete the understanding of the equilibrium solution chemistry. Solid phase will be analysed with x-ray diffraction and SEM-EDX.

Kinetics of pozzolanic reaction will be defined with conduction calorimeter. Various pozzolans will be studied, nanosized silica, silica fume and grout aid. Kinetic parameters will be defined for pozzolanic materials with calcium hydroxide and various Ca/Si-ratio calcium-silicate-hydrates. Results will be compared to concrete, mortar and grout samples and comprehensive model of pozzolanic reactions time dependency will be generated. This model serves as an input to geochemical modelling in task 3.

Polymerisation degree of calcium-silicate-hydrates in various environment and exposure periods will be studied with NMR. Polymerisation degree of calcium-silicate-hydrates potentially alters the equilibrium composition of aqueous phase. Understanding of such parameter could have effect in long-term behaviour of concrete in repository environment. Attained data can be incorporated into geochemical models if needed.

Data obtained from the cement paste studies will be compared to concrete, mortar and grout samples to include effect of physical factors to kinetics. Physical factors such as low porosity can alter the reaction rate in the actual concrete, mortar and grout samples significantly when compared to cement paste samples. PH and solution composition analysis in various depths in the concrete, mortar and grout samples will give more detailed understanding of the reaction kinetics in repository environment. Microscopic methods (SEM-EDX and TEM) will be utilized to deepen the knowledge even further.

19. HZDR/Johannes Kulenkampff

We apply Positron Emission Tomography for quantitative observation of tracer transport. This non-destructive method yields the quantitative distribution of the tracer (time frames of activity concentration Bq/mm^3, or molar concentration) during its propagation through the material with a high sensitivity ("molecular imaging" with a sensitivity in the order of 10k tracer atoms/mm^3) during course of the process. Analysis of the temporal evolution of these tracer distribution patterns allows deriving local transport velocities, effective volumes, heterogeneity and alteration of transport pathways. Derived parameters will reflect heterogeneities, which are caused by structural inhomogeneities of the material and by process-related pattern formation. Heterogeneity effects should be parameterized and included in process simulations for performance assessment. The sample size (ca. 1000 cm^3) also allows direct comparisons of experimental data and process simulation for mutual verification of the results.

This method is not yet a standard for process observation in opaque material, but recently the number of reference applications is considerably growing.

Because of the application of radiotracers at high activities and the need for extensive instrumentation (radiochemical laboratory, cyclotron, PET-scanner), this method is rather expensive. We offer our facilities for the needs of the CEBAMA project partners.

The sample requirements and experimental conditions are readily to meet. The maximum diameter of the gantry (200 mm) limits the size of the experimental setup. The sample diameter should not exceed 20 cm, the length of the field of view is 10 cm, with the possibility to shift the specimen.

Preparation of samples is not our focus. We will investigate samples provided by the partners, namely SCK CEN and UNIBE.

20. LML/Jianfu Shao

Four groups of tests will be performed:

Group 1: Basic mechanical tests

In this group, two kinds of tests will be performed: normal compression test and direct shear test. All the tests will be conducted under room temperature (20 °C) and saturated condition (RH = 98%).

Normal compression test without fluid pressure:

The normal stress to the interface is increased until about 50 MPa without fluid pressure inside the interface with different values of fluid pressure in the interface. We measure the interface normal closure as function of normal stress. The date are used to identify the variation of normal stiffness of interface with closure deformation, which will used for constitutive modelling in Task 3.

Direct shear test without fluid pressure:

Using a specific device designed at the LML, direct shear tests will be performed on interface under shear strain controlled conditions with three different confining pressures (normal stresses), say 4MPa, 8MPa and 12MPa (possibly modified as function of in situ conditions), without fluid pressure inside the interface. The results of the tests include shear stress – shear strain curve, shear strain – normal strain curve. These curves allow the identification of shear strength, shearing indueced interface closure or opening (normal strain) for each confining pressure, which are the basic input data for constitutive modelling in Task 3.

Direct shear test with fluid pressure:

Direct shear tests will be realized under different confining pressures (5, 10 and 16MPa) with different fluid pressures inside the interface (1, 2 and 4MPa) so that the effective confining pressures are the same as those used in the tests without fluid pressure. The results of these tests also include shear stress – shear strain curve, shear strain – normal strain curve. The comparison between the tests respectively with and without fluid pressure is used to verify the validity of effective stress concept for interface.

Group 2: Hydromechanical tests

In this group, the objective is to study the evolution of permeability of interface with normal deformation. All the tests will be conducted under room temperature (20 °C) and saturated condition (RH = 100%).

Normal compression test with fluid flow:

A normal compression test will be performed until 50 MPa. At each 5 MPa, the permeability of interface will be determined using the permanent flow method with water as injection fluid, together with the measurement of normal closure. The variation of permeability with normal closure will be determined.

Direct shear tests with fluid flow:

Direct shear tests will be performed under different confining pressures (4, 8 and 12 MPa). At different levels of shear strain (to be determined from the results obtained from the direct shear tests without fluid pressure), the permeability of interface will be determined using the permanent flow method with water as injection fluid, together with the measurement of normal closure and shear strain. The variation of permeability with shearing induced normal closure or opening will be determined.

Group 3: Effects of RH and temperature

In this group, it is proposed to investigate influences of temperature and relative humidity on the mechanical behaviour of interface.

Direct shear tests with different temperature:

Three direct shear tests will be performed under 8MPa confining pressure and saturated condition (RH = 100%), but with different temperatures, say 40 °C, 60° and 80 °C.

Direct shear tests with different RH:

Three direct shear tests will be performed under 8 MPa confining pressure and saturated condition (RH = 100%), but with different RH, say 50%, 70% and 90%.

The date obtained from these tests will be used in constituting modelling in Task 3 to include effects of RH and temperature on the mechanical behaviour of interface.

Group 4: Effects of carbonation

In this group, we propose to investigate effects of carbonation on hydromechanical behaviours of interface.

A fluid solution enriched with CO2 will be used and injected into the interface to create an accelerated carbonation process of concrete.

A normal compression test will be realized until 50 MPa with measurement of permeability on the carbonated interface, to study effect of carbonation on the normal stiffness and permeability-closure relationship of the interface.

Three direct shear tests will be then performed on the carbonated interface with permeability measurement and with the same values of confining pressures as for the intact interface, to investigate effects of carbonation on the shear strength and permeability-normal deformation relationship of the interface.

21. UAM/Raúl Fernández Martín

Our objective is to focus at the interface between concrete and bentonite at small scale. We will examine samples from long-term experiments (#3 and #4) and we will execute short-term transport experiments (#1 and #2). We will measure changes in physic-chemical and mineralogical properties using valid methodology [BET, SEM, TEM (only in selected samples), XRD and FTIR]. These results should benefit from larger scale determinations performed by other groups to help the interpretation within the overall context. The results obtained by our group may serve to constrain results obtained by geochemical modelling. Results from experiment #3 will be used by the UDC group as their model input for the WP3.

Our group has experience running transport experiment in concrete-bentonite columns, e.g.:

- Fernández, R., Cuevas, J., Sánchez, L., Vigil de la Villa, R. and Leguey, S. (2006). Reactivity of the cement-bentonite interface with alkaline solutions using transport cells. *Appl. Geochem*., **21**, 6, 977–992.

However, for the proposed small transport experiment, the size scale is much lower than the former used. Specific techniques for the study of interface surfaces will be used and developed (small size XRDP) samples and GIXRD for examining surface precipitates.

Characterization of the overcoring samples described as experiment #4 will proceed as the standard characterization used in the previous experiments, however, preliminary discussion on how to manipulate the samples and subdivide them should be done with the Uni-Bern group.

22. CSIC/Maria Cruz Alonso/Jose Luis Garcia Calvo

Colum leaching tests will be considered to be very representative of field leaching conditions than other methods because of the continuous flux of the leaching solution through the monolithic material. There is an enormous concern on determining the material behaviour under the long-term action of water, in representative conditions of the real storage scenario. In practice, it is not possible to determine directly, from laboratory experiments, the degradation of the materials in real storage conditions for such a long time. Nevertheless, if the thermodynamic and kinetic processes at stake in the degradation are perfectly known, we could be able to modelling the material behaviour with the support of accelerated leaching tests. In these conditions it is possible to make very long-term predictions by means of numerical simulation. The objective in this test is to submit the fabricated concrete samples to the leaching by water, representative of natural aggressive conditions. The accelerated test helps to reproduce the sequence of degradation processes and its kinetics. Therefore, the appropriate test has to include the following characteristics: opened system, control of the inflow and outflow solutions (concentrations, flow, pH), temperature and pressure control.

Method: The leaching column method has been described in different papers published by the CSIC research group involved in CEBAMA project:

- Hidalgo, A., Llorente, I., Alonso, C., Andrade, C. (2004) Study of concrete/bentonite interaction using accelerated and natural leaching tests. OECD, 125–135
- García Calvo, J.L., Hidalgo, A., Alonso, C., Fernández Luco, L. (2010) Development of low-pH cementitious materials for HLRW repositories. Resistance against ground waters aggression. Cem. Concr. Res. 40, 1290–1297.
- García Calvo, J.L.; Alonso, M.C.; Hidalgo, A.; Fernández Luco, L.; Flor-Laguna, V. (2013) Development of low-pH cementitious materials based on CAC for HLW repositories: Long-term hydration and resistance against groundwater aggression. Cem. Concr. Res. 51, 67–77.

Sample: Cylindrical samples are placed between two cylinders of methacrylate containing holes for water inlet and outlet. The block is sealed with an epoxy-resin in order to be sure that water pass only through the sample and measured fluxes are correct. Once the samples are placed in contact, a water head of required bars pressure is maintained to pass water through the concrete after which, it is collected for analysis. The permeability of the samples and the pressure applied to the water regulate the water flow rate. The objective of this testing programme is to study the evolution of chemical and microstructural changes occurring when materials are subjected to a continuous flow of ground water.

The main characteristics of the test:

- Column leaching test (open system).
- Unidirectional flow.
- Control of the inflow and outflow solutions.
- Material shape: monolithic (usually cylinders 50 mm diameter and 50 mm length).
- Samples are water saturated for 24 hours, before the starting of the test.
- Water head of X bars (X depends on concrete permeability).
- Test period: over 1 year.

The variables measured continuously in the obtained leachates will be: effluent flux (to determine the hydraulic conductivity of the concretes and its possible evolution over time), chemical composition and pH of the leachates. At the end of experiments the concrete cylinders will be divided in three similar size portions (≈1.5 cm.); the upper part will be in direct contact with the water inlet. Each one of these three parts will be characterised by different microstructural techniques.

23. ANDRA/Xavier Bourbon

The main goal is a physical assessment of the two low pH formulations, to validate at a representative scale, the hydration model we developed the last few years. Linked to a mechanical model, it allows a description of the evolution of the physical properties.

Temperature measurements and physical evolution will be done. These physical measurements will be done with gauges, vibrating wires and optic fibers to give a large overview of the physical behaviour during setting and drying in operating conditions (endogenous and total shrinkage).

In relation to the physical evolution, the chemical reactivity of both cement and clay will be assessed through chemical analysis at the interface.

25. UNIBERN/Urs Mäder

Direct measurement of transport properties for water and dissolved components across aged interface: Bulk hydraulic conductivity (K) of compound material; advective-dispersive properties of water transport (D_2O); advective-dispersive properties of anion transport (Cl).

Advective-dispersive column experiment under confining pressure and subject to pre-select hydraulic gradient; collection of sample aliquots in syringes, in-line measurement of electric conductivity; fully protected from atmosphere.

Reference: Jenni, A., Mäder, U., Lerouge, C., Gaboreau, S. & Schwyn, B. (2014b). In situ interaction between different concretes and Opalinus Clay. Physics and Chemistry of the Earth, Parts A/B/C 70–71, 71–83.

Sample core of compound material containing aged interface, ca. 40-50 mm DM, 40–50 mm L; 2-3 experiments are planned. Comparing OPC/claystone and LPH/claystone (either mortar or paste). Details are provided in Deliverable D1.05.

26. IRSN/Alexandre Dauzeres

The aim of the set of experiments is to characterize the chemical, physical and microstructural evolution of cementitious materials exposed to such extreme environment. The following values are quantified in order to improve the models:

- Mineralogical changes?
- Extent of the perturbations?
- Microstructure (porosity, specific area) evolution?
- Mechanical properties evolution (in option - the mechanical behaviour of the cement could be investigated if the micro/nano indentation device is available).

To answer, a set of characterization tools were identified:

- Scanning electron microscopy
- X-ray diffraction
- X-ray micro-tomography
- Autoradiography
- BET
- Micro/nano indentation (option)