CEMTEX Project – CEMent Temperature EXperiment: Physico-chemical evolution of concrete at high temperature in a high-level radioactive waste repository in deep clay formation

Dauzères A., Lalan P.*, Tang T.M.**, Van De Velde T.***

* IRSN/PRP-DGE/SRTG/LETIS, B.P. 17 – 92262 Fontenay aux Roses, France
** BEL V, Rue Walcourt 148, 1070 Brussels, Belgium

Abstract:
Geological disposal of radioactive waste in deep clay formation is the main option presently studied in France and Belgium, inducing the use of concretes. Alkaline perturbation will develop in clays, while concrete will be altered by the diffusion of chemical species present in the clay pore water. In addition, a high temperature is expected for High Level Waste cell (HLW). It could alter the reaction pathways observed at ambient temperature and also accelerate the propagation of the perturbations. However, these effects of high temperature on the concrete/clay interactions have never been investigated.
Original *in situ* (Tournemire URL, France) and laboratory (Fontenay aux Roses, France) experiments were developed as part of the CEMTEX project, coupled to a modelling approach. CEM I and low-pH cement pastes interact with argillite at 70 °C during 1, 2 and 5 years.
Preliminary results concerning the CEM I / argillite interface after one year in Tournemire, suggest strong variation compared to classical evolution at 20 or 50 °C. The main difference is the high carbonation in the cement paste associated to the formation of Al/Si-gel and Ca/Na Zeolite, reducing the alteration process. The temperature increasing seems positive in regard to the safety stakes.

1. INTRODUCTION

The creation of a disposal facility for radioactive waste in geological environment is a key issue addressed in the French and Belgium nuclear power industry. These two countries have been exploring for several decades the concept of disposal in clay natural environment, with favorable containment properties of radionuclides. The geological environment and disposal architectures must ensure a very long term containment of long-lived radionuclides that may be released to the biosphere. Such a configuration will inevitably create an alkaline plume, in which cementitious materials, (largely used in disposal cells and sealing plugs) will interact with clays. More importantly, in argilaceous materials (rocks and bentonite), these interactions are the main alteration sources of their swelling and retention properties.

The theme of concrete/clay interactions has been widely discussed in the literature in recent decades, both experimentally and by numerical simulation.
If recent years have seen a growing interest concerning the geochemical behavior of cementitious materials in clay environment, studies have focused mainly on the physico-chemical evolution of clay under alkaline conditions.

Several types of tests were carried out:
i) where pure clays, smectite type, were exposed to representative cementitious pore solutions [1-9], where argillaceous rocks, argillite type, Opalinus clays or altered sandstone, were exposed to alkaline or hyperalkaline solutions [10-21], where bentonites were exposed to alkaline solutions [22-28].

These tests describe extreme reactive systems that are not necessarily indicative of future contact area between cement and clay materials. However, this allow building a database where is listed all the reaction paths that may occur to concrete / clay interfaces. The major results of these studies are a systematic smectite illitisation [2;3;4;5;19;20;23], the formation of Na/K and Ca-zeolites in particular at high temperatures [3;11;18;20;23;24;25;27]. C-S-H (Calcium Silicates Hydrates) or C-A-S-H (Calcium-Silicates-Aluminium-Hydrates) formations were regularly observed [13;17;19;23;24;25;27].
The temperature increase in these extreme tests promotes the reactivity of clay minerals [3;6;23] and the quartz dissolution. Zeolites formations, minerals with very high retention properties of such cations, are mainly found for temperatures above 60°C.

ii) At the interface between cementitious materials and clay, studies are less common. They are divided into three main categories: (a) laboratory tests in well controlled conditions, (b) in situ tests in conditions more representative but less controlled, and finally (c) analogue sites allowing a longer term scale of reactivity (several hundreds of years), but however not representative for a future disposal facility..

(a) Laboratory tests are the most common. Study [29] on the interactions between a mortar disc and bentonite cylinder for 1, 6 and 12 months at 25, 60 and 120 °C is significant. At 25 and 60 °C, results show an alteration of a few millimeters in the cementitious material. C-S-H and brucite formations are observed in argillite. At 120 °C, which is not encountered in the disposal, C-S-H, Mg-clays and zeolites (analcime-type) are observed. Cuevas [24], with the same materials and in the same condition, observed more carbonation of cementitious material and confirms the formation of analcime. Dauzères [30] focused in the evolution of CEM I material in contact with the Callovo-Oxfordian with pure diffusive conditions at 25 °C. Portlandite dissolution, ettringite precipitation, low carbonation and C-S-H decalcification are identified, in parallel with a significant opening of the capillar porosity in the cementitious material.

(b) In situ tests are very scarce because of the cost and the difficulty of implementation. The only published study on the subject was made by Read [31] with interesting behaviors of cementitious materials in contact with clay in the Underground Research Laboratory (URL) of Mol in Belgium. Tests lasted between 12 and 18 months at 25 and 85 °C. Characterizations of these tests showed essentially the ionic species exchanges and a high cementitious material alteration. Precipitation of Si/Al gel and Si/Mg gel are the main conclusions.

(c) The study of engineered analogues was especially developed in recent years with the significant potential for samples that can be studied in the URL of IRSN in Tournemire in France. Three studies [32-34] focused on CEM II / Toarcian argillite interfaces after 15 and 20 years of contact in water saturated conditions. Results helped to highlight that the alteration depth in the argillite is about 12 mm against 4-5 mm in the cementitious material and that the extension of the front perturbation is not limited to the mineralogical reactions. Formation of C-S-H and illite have been highlighted in the clay material. A high capillary porosity opening was observed in the cementitious material in relation with the portlandite dissolution, also observed in [33;35].

Concrete / clay interactions have been widely discussed in the literature butrepresentative studies of these interactions in well controlled conditions, are rare.

The thermal transient in the futur disposal cells of High Level Waste and Intermediate Long-Lived Waste (HLW – ILLW) lead to an increase in temperature up to 70 °C at the interface areas between the cement and the surrounding clayey rock. Based on the literature, only one study [31] describes very briefly at the interface in in-situ conditions the evolution of materials at 85 °C. In conclusion we have no data describing the evolution of materials in these conditions.

Therefore to remedy this gap of knowledge, the CEMTEX project is jointly developed by IRSN and BEL V. The main objective is to test the durability of cementitious materials to be used in future geological disposal under thermal (65-70 °C), water (medium saturated with water), hydrodynamic (diffusive transport) and chemical (representative materials) conditions.

This project has no equivalent, mainly due to the difficulty of setting up the experiment.

for , Experimental conditions in situ testing are less well controlled than in a laboratory test. In order to control all the parameters, laboratory experiments started to follow the exchange of material between the different environments and to ensure that the physico-chemical behaviors between in situ and laboratory tests are the same.

This paper describes the experimental devices used in the CEMTEX laboratory and in situ project as well as preliminary results of the CEM I / argillite interaction after one year in the in situ experiment.

2. EXPERIMENTAL APPROACH

Two complementary experimental approaches were built to meet several objectives: i) characterize the mineralogical and chemical evolutions of interfaces (in situ and laboratory tests), ii) analyse the microstructural evolution of materials in the altered areas (in situ and laboratory tests), iii) identify the evolution of diffusive transport properties linked with the physico-chemical transformations (laboratory tests).

2.1 The CEMTEX in situ experiment

The technical objective of CEMTEX in situ experiments is one hand to create in each test argillite/cement paste interface and to consider transported in one dimension along a vertical axis perpendicular to the interface, and secondly to provide a heating system for controlling the temperature between 65 and 70 °C at any point of the device for multi-year period.

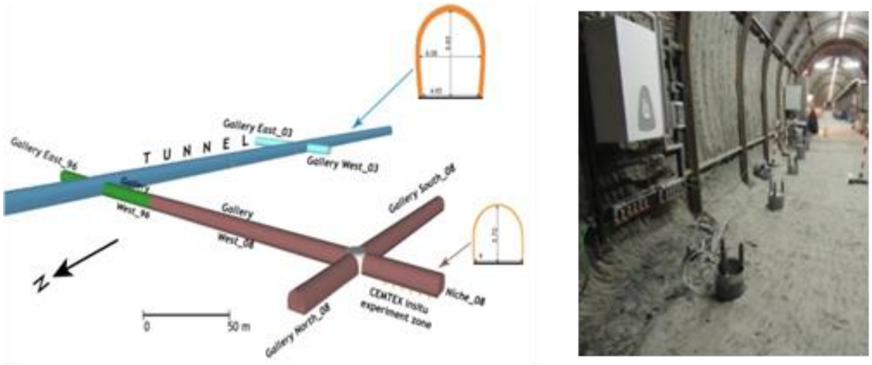


Figure 1 – Experimental device location (left) and picture (right)

All experimental devices of the in situ CEMTEX program is located in the termination of the West gallery 2008 in the URL of Tournemire (figure 1). Six vertical boreholes of 1.25 m depth and 250 mm in diameter were drilled in the argillite. Each borehole is spaced by 2.50 m. The bottom of each borehole was polished (relief <100 µm) with a cleaning reamer especially built of 250 mm diameter. Three of these boreholes are devoted to the study of argillite / CEM I cement paste and the last three in the study of argillite / low-pH cement paste interface. Each test corresponds to one period of experimental test: 1 year, 2 years and 5 years.

To generate a vertically exchange of matter in 1D between the two materials introduced, a PVC tubing is in place over the entire height of each borehole.

2.1.1 Rock resaturation process

To be certain of having a water-saturated rock, a hygrometer probe is placed at the interface, and two cups containing water are suspended in the borehole, one close to the interface, the other in the middle height.

Drilling is then held closed to resaturate argillite by vapor process. Results of the moisture evolution in the borehole are shown in the figure 2.
It is estimated that the rock is resaturated when the humidity at the interface reaches 99.5%, after a period of one to two months.

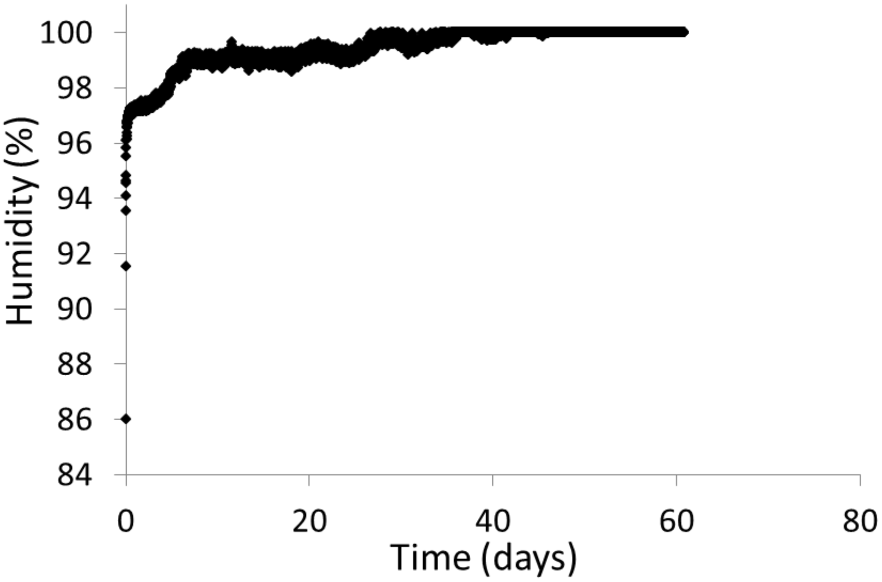


Figure 2 – Humidity evolution in the CEM-1 borehole during the ressaturation step by vapor phase.

2.1.2 Heating device

The heating system was designed in advance. Figure 3 shows the geometry and the mesh considered and Table 1 shows the thermal parameters used for these modellings.
A temperature of 13 °C was maintained permanently at the soil surface. Thermal exchange with the atmosphere will occur in the reality. This phenomenon has to be take into account in future interpretations.
The objective was to test by modelling several devices to select one that would provide the most homogeneous field temperature at the interface.

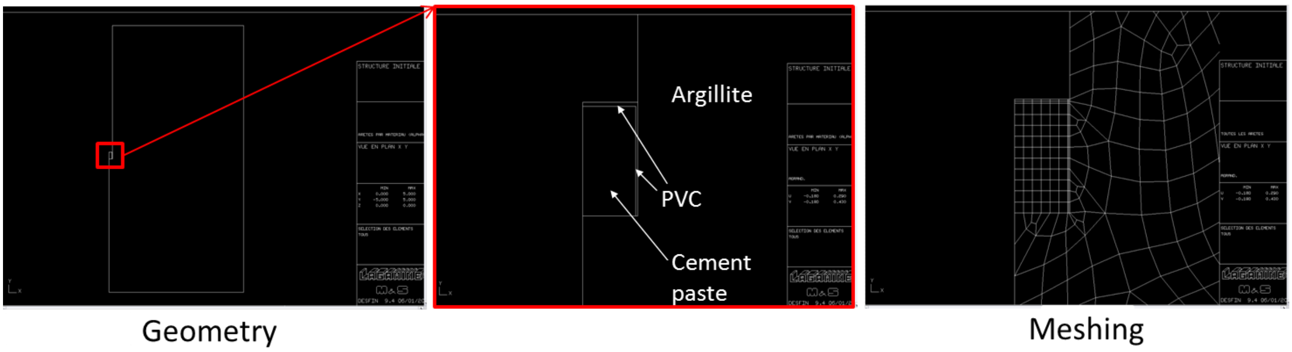


Figure 3 – Geometry and meshing used for modelling

Table 1- Thermic parameters used for modelling

	Unity	Cement	Argillite	PVC
Thermic conducitvity	$W.m^{-1}.K^{-1}$	0,9	1,4	0,17
Volumic specific heat	$J.m^{-3}.K^{-1}$	$0{,}69.10^{7}$	$0{,}19.10^{7}$	$0{,}14.10^{7}$
Initial temperature	°C	13	13	13

Two numerical simulations (2D axisymmetric) are presented for two different devices:

1 - The first device is the one that was eventually chosen for this project. It is a constant 70°C heating on the borehole wall with a central rod down the center of the interface (equivalent to a coil). By comparing results after 10 days and 1 year on figure 4, we found that the temperature at the interface varies very little. Temperature of 70°C is reached in the area close to the tube coil and the coldest point is about 60°C to the center of the interface due to heat flow to the solid.

2 - The second device simulated is a point heating source applied to the upper surface of the cement paste block. This kind of device would be easier to implement and indeed, the hot spot would be installed after the cementitious material hardening in the borehole. Results show that a significant temperature gradient moves in the cement paste after 10 days or 1 year, preventing the establishment of a uniform thermal regime close to 70 °C in the system (figure 4). The temperature after one year at the interface is only about 20 °C.

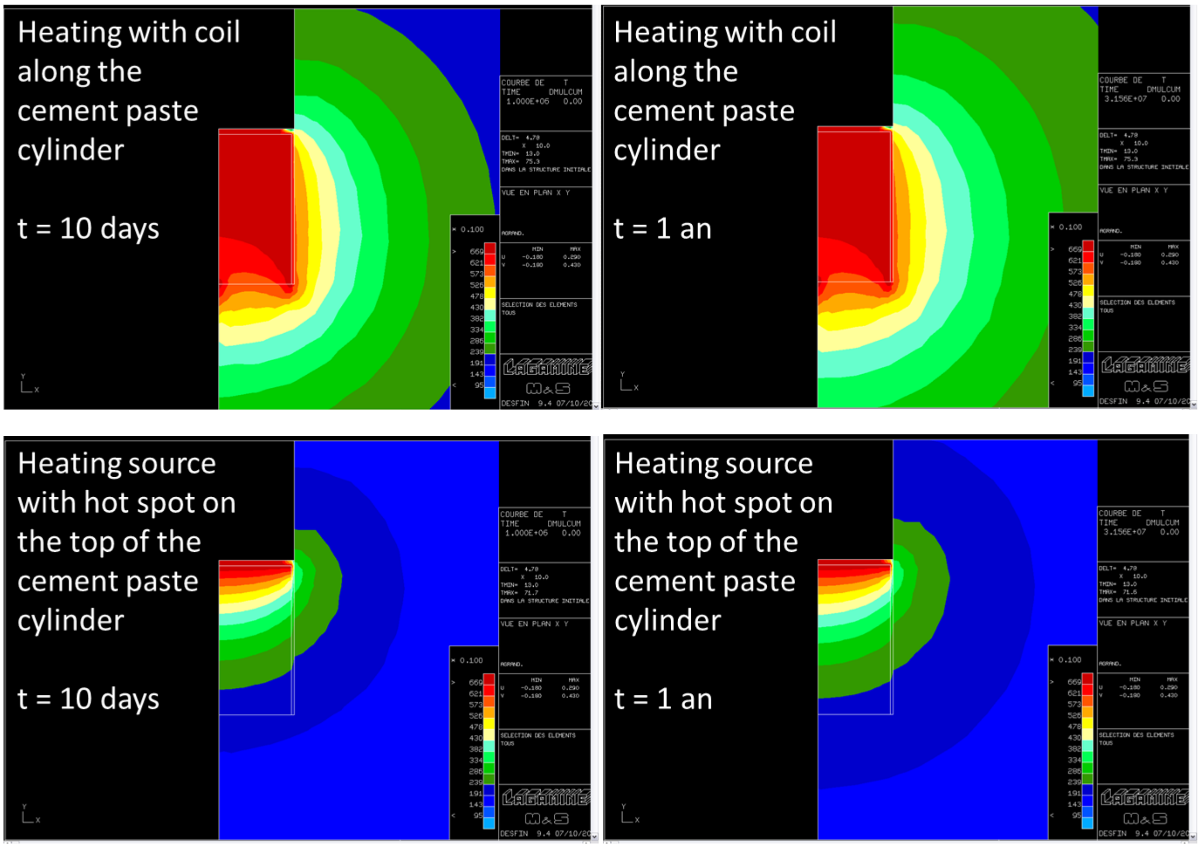


Figure 4 – Thermic numerical simulations in function of the heating option

These simulations validate the choice of the temperature control device with a coil and its central rod. The temperature sensors installed at the heart of the cylinder cement paste during the test will help validating these simulations.

2.1.3 Protocol and materials

The experimental device (figure 5) is composed of a nickel-plated copper coil (height 25 cm, width 180 cm, contiguous turns of 6 mm diameter) and plastic tube (PFA) connecting to an electric boiler where a fluid at 70 °C circulated in the whole device. Four temperature sensors were attached to a single support (M0: center interface, M1: top center of the device, M2: close to the circumference and M3 interface on top of the device near the circumference) connected to a ALMEMO PYROSYSTEM-acquisition system to register continuously the temperature changes in the cylinders of cement pastes. A PVC shell (inner diameter : 190mm, outer diameter : 200mm) with a PVC cover help to maintain the device and to isolate from the atmosphere. A rubber seal provides sealing between the argillite (downhole) and the PVC shell.

The entire device falls into the borehole after the argillite resaturation step and is connected to the boiler and to the acquisition system.

The cement paste is poured into the device covering the coil and the temperature sensors.

One month after the beginning of the cement hydration, the heating started and the device is held under a synthetic pore solution in equilibrium with the type of cementitious material considered to ensure saturation materials throughout the test.

Above the device, bubble wrap and polystyrene cap are in place, limiting water loss and heat loss. The system is closed by a tight PVC cover.

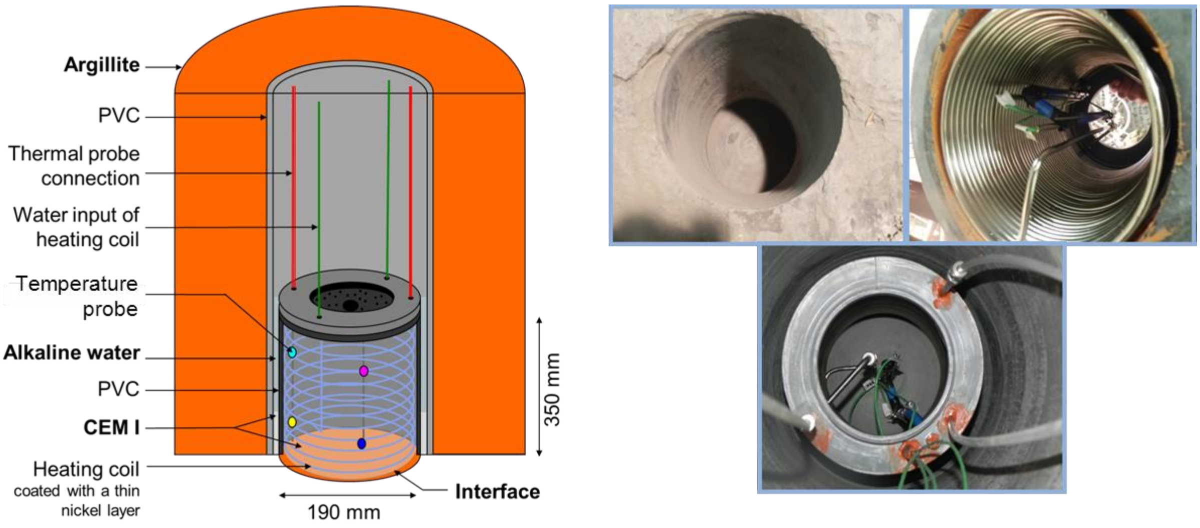


Figure 5 – CEMTEX in situ experimental device

2.1.4 Dismantling protocol

The successive steps in the dismantling of the test CEM I / argillite after one year of interaction are: (1) stop of the heating system ; (2) removal of thealkaline water that maintained the cement paste cylinder saturated ; (3) removal of the outer PVC tube from the borehole and the argillite upper annular by overcoring to a diameter of 400 mm and a depth of 600 mm. Then the hydration circuit as well as connectors between temperature sensors and recorders are cut close to the device. Three boreholes of 76 mm of diameters in peripherie of the coring of 400 mm are made in order to slide extract to retrieve the device during the ultimate step. Stainless steel rods are screwed into the holes and the epoxy resin is poured over the whole device for holding the entire system before the final steps. After polymerization of the resin, the coring with a 400 mm diameter continues to a depth of 300 mm below the interface with argillite. The drilling system is then removed and the extractor is inserted into the holes related to the same depth of 300 mm below the interface. These extractor was specifically designed for the CEMTEX project. It allows removing the whole system with 300 mm argillite more.

The sample (400 mm diameter and 650 mm height) is packaged immediately in insulating paper to keep it safe from the atmosphere.

The system is then cut into four pieces.. Several centimeter samples are extracted from the interface area in order to characterize the physico-chemical evolution between the two materials.

2.2 The CEMTEX Laboratory experiment

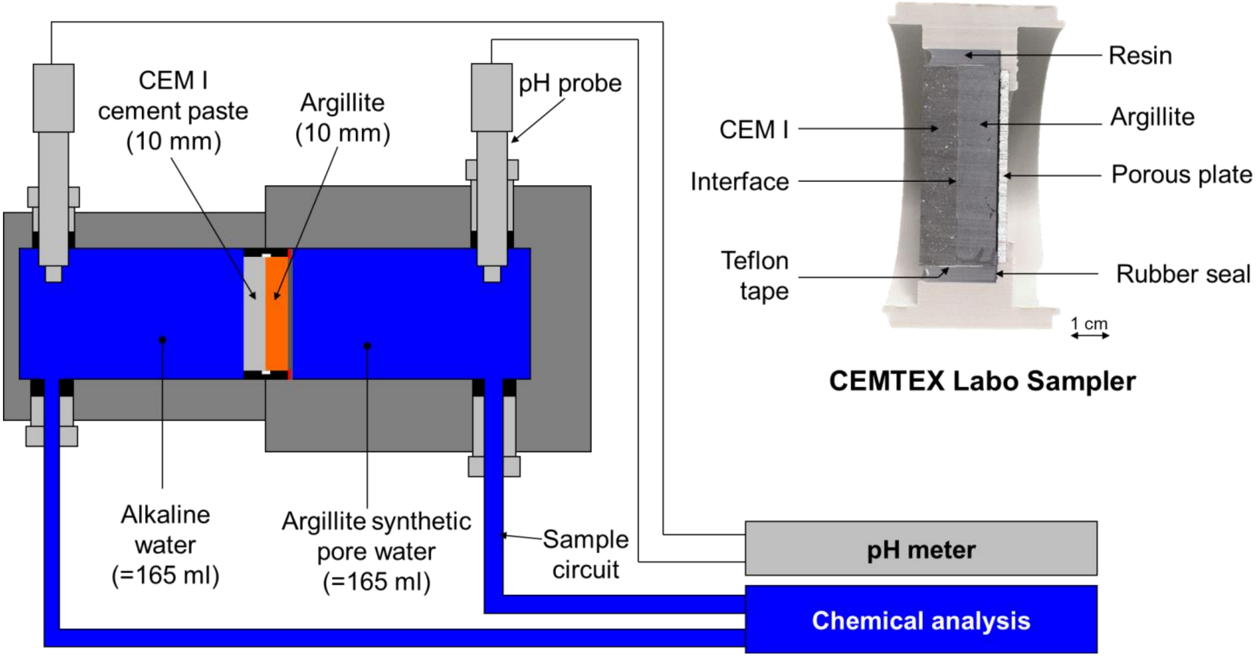
The technical objective of the CEMTEX Labo experiment is to generate CEM I cement paste/argillite interfaces in diffusion cells with tanks in contact, where solutions in equilibrium with each material are in place. The overall objective is to identify, in physico-chemical controlled conditions, the impact of mineralogical transformations on microstructure and deduce the impact on the diffusion properties of the interfaces after 2, 6 and 12 months of interaction. The tests are still ongoing and results for this part will not be presented in this paper. However, some comparisons will be made available already in the discussion to compare with in situ tests. Tests are performed in the laboratory of IRSN in Fontenay aux Roses (France).

2.2.1 Protocol and materials

The 25 cm long diffusion cells used are in polypropylene, and each tank has a capacity of 165 ml. The cap on the top of each tank is used to fill it and a valve is used to recover the solutions during the experiment. These solutions were analyzed by a pH meter, chromatography, a TOC-meter and UV/visible spectroscopy. The total duration of the experiment before dismantling the cell is two months. The figure 6 shows in detail the device used.

Before contacting, the argillite samples of 52 mm in diameter and 10 mm thick were stored in a water-saturated atmosphere.

The cement paste samples are cut with a saw wire after one month of hydration. The faces are polished to produce a perfect interface. Then, the resulting discs were placed in an alkaline solution to keep saturated conditions without inducing alkaline leaching.



CEMTEX Labo Sampler

Figure 6 – CEMTEX Labo experimental device

After the contacting of the disks in the sample holder, the periphery of the interface is surrounded with a Teflon paper. Argillite is in contact with a stainless steel porous plate to prevent it from disintegrating due to the swelling when contacted with water. The disk edge is put on a rubber seal to optimize sealing.

Epoxy resin, alkalin and thermo-resisting is poured around the cement paste / argillite composite to maintain and seal the device. After 12 hours of polymerisation, under 100% humidity conditions, the sample holder is placed in the diffusion cell and the solutions in equilibrium with each material are placed into tanks at 70 °C. The device is then placed in an oven between 68 and 70°C.

The pH is measured twice a week and every 15 days 60 ml are removed from each tank for measurments.

2.3 Geomaterials and synthetic solutions

2.3.1 Cementitious material

The cement is a Sulphate Resisting Portland Cement (SRPC) CEM I, provided by Lafarge Company (Val d'Azergues), whose chemical and normative phases compositions are detailed in Table 2. This cement is very poor in C_3A and rich in C_4AF. The chemical composition of the cement was determined by Bogue calculation (Table 2).

Cement pastes were prepared with a water/cement ratio of 0.42, and cured during one month before the starting of experiments in a solution in equilibrium with portlandite with KOH and NaOH (for laboratory experiments), in contact with the clayey rock (for in situ experiment).

The clinker phase, constituted of C_3S, C_2S, C_3A and C_4AF, is progressively hydrated. XRD analyses show that calcium, silicon and aluminium are released to precipitate as hydrated phases such as C-S-H, portlandite, ettringite (with the gypsum) and alumino carbonate. It remains Calcite in the final cement paste.

Table 2: Cement composition (CEM I 52.5 N)

Chemical phase analysis [g/100g]		Normative phase composition [g/100g]	
CaO	64.6	Alite	65.4
SiO_2	20.7	Belite	13.6
Al_2O_3	3.2	Aluminate	0.9
Fe_2O_3	4.6	Ferrite	13.5
CaO(free)	1.8	Clinker	93.4
MgO	0.6	Gypsum	3.9
K_2O	0.6	Filler	2.9
Na_2O	0.1		
CO_2	1.1		
SO_3	2.8		

Porosity measurements on 10 samples gives an homogeneous value around 35 % for the CEM I cement paste.

2.3.2 Clayey materials

Based on the XRD analyses and the very good knowledge of this material due to a lot of studies, the argillite is composed by illite, illite/smectite mixed-layer, calcite, pyrite, kaolinite, chlorite, K-feldspards and quartz [36].
The porosity is equal to 10%.

2.3.3 Synthetic solutions

The clayey synthetic solution used in the laboratory experiments and the hyperalcaline solution used in both experiments are described in the table 3.

Table 3: Synthetic pore solutions used in the CEMTEX project

[C] objectif (mmol/L)			
Clayey solution		Hyperalkaline solution	
$NaHCO_3$	3.6	NaOH	50
Na_2SO_4	8.1	KOH	350
NaCl	1.4		
KCl	0.7		
$CaCl_2$, $2H_2O$	1.7		
$MgCl_2$, $6H_2O$	0.8		

The hyperalkaline solution composition is based on previous work [30] where the solution was extracted by compression. The same concentration in sodium was chosen. The potassium concentration is lower compared to the previous study to reduce the pH to 13.4.

2.4 Analytical conditions

Multi-technical characterisations are used for solid analyses. First as part of the preliminary analyses, a part of the clay/cement paste interface is embedded with an epoxy resin to maintain the sample during cutting. Second, the sample is cut into two parts for XRD-characterisation and for SEM purposes. XRD is used to characterise qualitatively the mineralogical evolutions of the solids. Data were collected using a PANalytical X'Pert diffractometer with an X'Celerator detector relying on CuKa radiation (λ=1.5405 Å). The advantage of that detector is a reduction in the data-collection time by a factor of about 100 with no loss of resolution ([37;38]) compared to classical XRD detector. The working voltage and intensity are 40 kV and 35 mA. The acquisition time of the XRD patterns is about 25 min. The clay sample was scanned between 4 and 65° and the cement sample between 5 and 60° with a step degree of 0.02°. XRD analysis is performed directly on the solid sample [39]. The first XRD pattern is drawn on the surface in contact with the clayey rock. After, the surface is polished over a depth of 10 µm and the new surface is analysed. The abrasion is carried out with 350-grain abrasive paper.
SEM characterizations are carried out with a SEM HITACHI and two BRUCKER SDD detectors containing ESPRIT software, under a working voltage of 15 KeV and a working distance of 16 mm for local chemical analysis. Observations were performed on a thin section covered by a thin carbon layer.
As part of the CEMTEX labo experiment, solutions are analyzed by pH-meter, UV/visible spectrometer, ionic chromatography and TOC-Meter in the IRSN laboratory.

3. RESULTS AND DISCUSSION

Only the experimental results focusing on the one year experiment between CEM I paste and argillite in the in situ conditions will be presented. Some results already obtained in the laboratory tests for comparison will also be discussed.

3.1 Thermic regulation

The first important result to be highlighted and valid the experimental choices made, is temperatures regulation (figure 7) for a year in the heart of the concrete (near and away from the interface with the argillite). Regardeless of the location of the probes, a constant temperature control in the device between 65 and 73°C is clearly shown. This regulation, which is based on models produced before, is finally better than the simulation carried out where the coldest point was 60°C near the interface.

This result allows to interpret with serenity all the following results thanks to the very good thermic conditions in the experiment.
It was found that the coldest point is located at the interface with the argillite, mainly due to a loss of heat because the solid clay has a greater thermal conductivity.

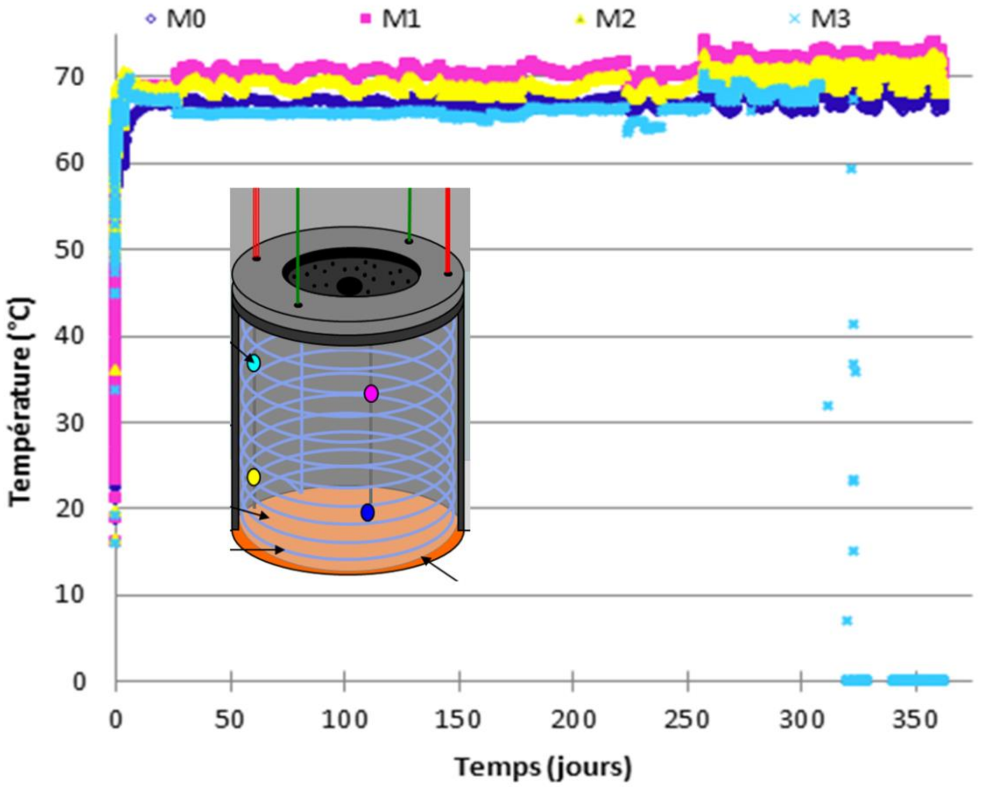


Figure 7: Continuous thermal monitoring on the CEMI/argillite in situ experiment during 1 year

3.2 Materials evolutions

After this first experiment, a set of very interesting and important results were highligted.

The figure 8 shows the macroscopic state of the surfaces of cementitious and clay materials that remained in contact for one year. Precipitates are observed on the surface of such cementitious material. It suggests first a carbonation (white phase) and second, a bluish phase recall C-S-H with very low CaO/SiO_2 ratio that have been observed in previous studies [32;34].

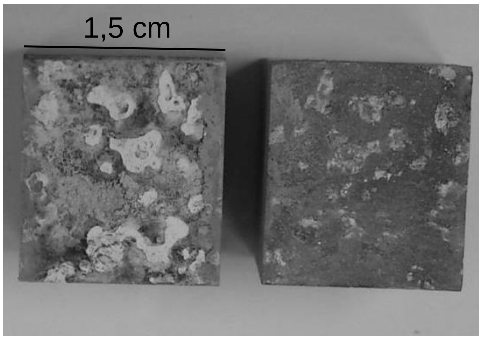


Figure 8: Cement paste and argillite surfaces in the in situ experiment after 1 year of interaction

The interface of the sample was separated to carry out diffraction patterns and reconstruct mineralogical changes in the depth of both sides of the interface.
All characterizations by SEM and XRD clearly show a set of reactive mechanisms.

The cementitious material is exposed to a decalcification resulting mainly by the portlandite dissolution (figure 9 and 10) to several tens of microns. Based on the EDS mappings performed (figure 11), this decalcification goes to a depth of 300 µm in the cementitious material. Calcium release is blocked to the interface and in the cementitious material but does not seem to have diffused in the argillite. This calcium is used to precipitate calcium carbonate type calcite (figure 9 and 10). The carbonation of the cementitious material extends up to 200 µm. The mechanism of portlandite dissolution and calcite precipitation is well known and has been observed in preliminary studies [30;32;34]. Precipitation of ettringite is also observed in the cementitious material behind the interface area.

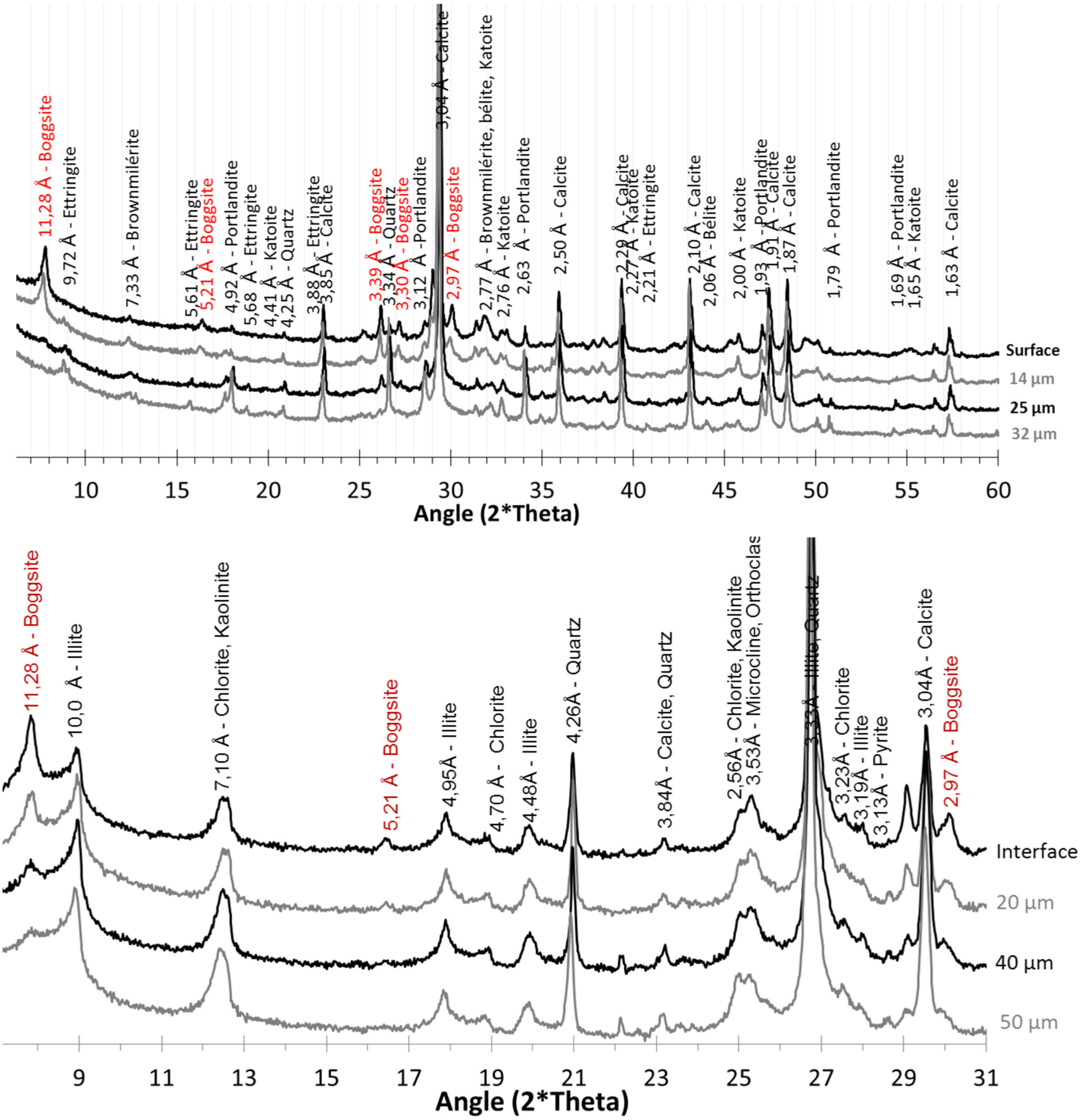


Figure 9: XRD diagrams profiles in the cement paste (top) and the argillite (down) in the in situ experiment after 1 year of interaction (Cu - Kα = 1.54056 Å)

Calcium is not only controlled by carbonation. Another phenomenon, even more pronounced, is observed macroscopically: the C-S-H formation. Beyond the very characteristic bluish tinge, this observation is supported by the SEM-EDS analysis.

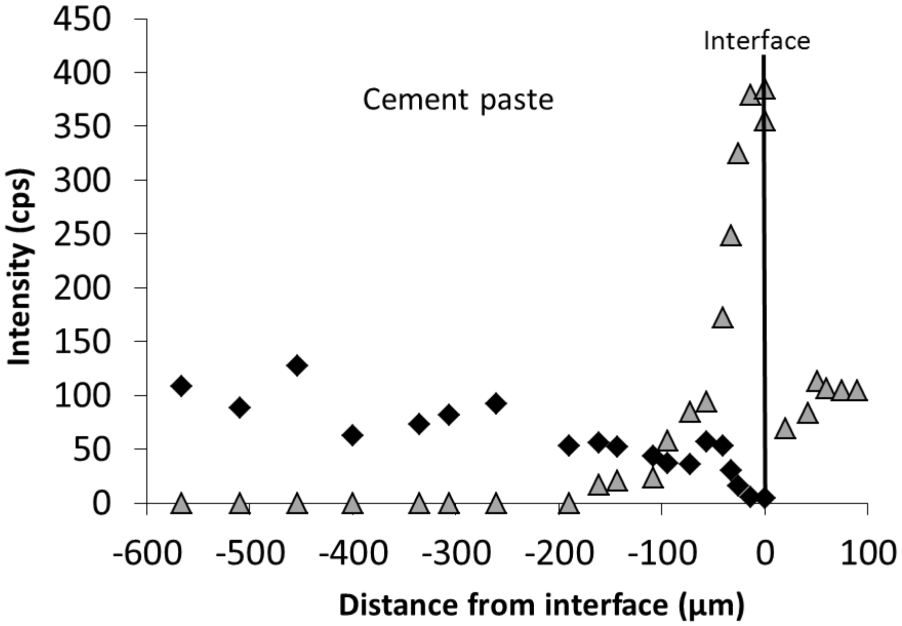


Figure 10: Mineralogical profiles of calcite (peak at 3.03) and portlandite (peak at 2.62) based on the XRD diagrams profiles in the cement paste and the argillite in the in situ experiment after 1 year of interaction (0 suggest the initial interface)

The figure 11 shows clearly from the left to the right (to the sound zone until the altered zone of the cementitious material and the interface with the argillite) a decrease in calcium content. It also shows an increase in calcium content in a texture area that greatly differs from the classical texture of the cement paste and the argillite. This increase in calcium, located at the ultimate surface of the cement paste, is associated with the silicon, and is exogenous to the material. It corresponds to the figures of precipitation observed macroscopically.

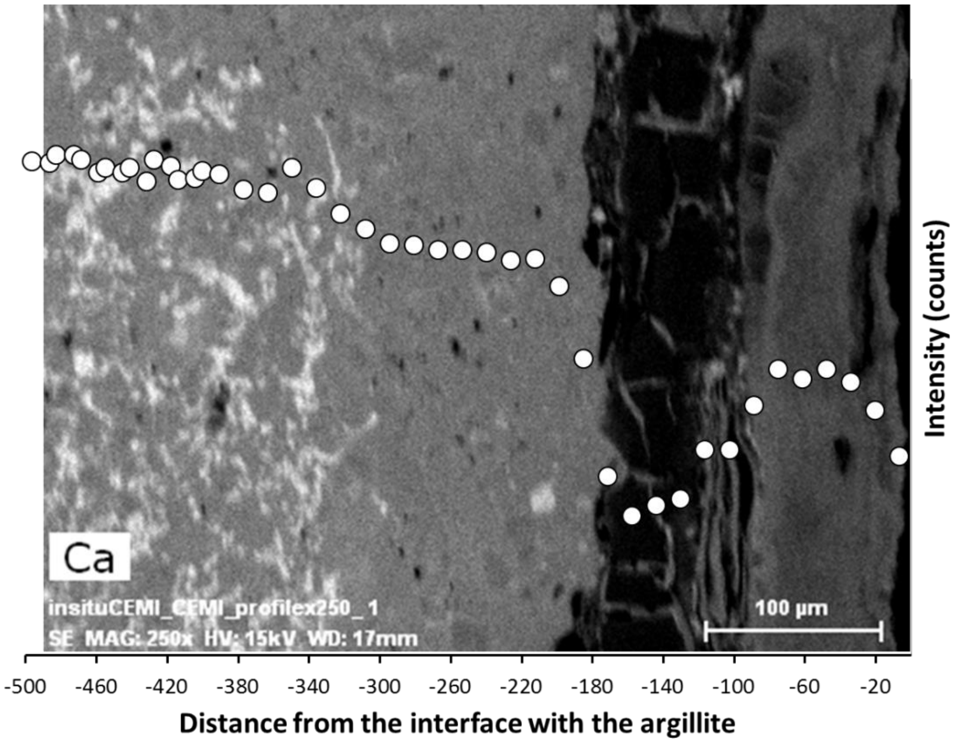


Figure 11: EDS mapping of the cement paste in the in situ experiment after 1 year of interaction with the argillite and profile of calcium evolution

Figure 12 identifies more precisely the texture of the constituents of this calcium enrichment area. The lamellar texture similar to the tobermorite texture [40] is clearly highlighted and finally validates the formation of C-S-H with a low CaO/SiO_2 ratio. This C-S-H formation is often described by the models but was never observed, especially on such short experimental times. The temperature increase has been a catalyst for its formation.

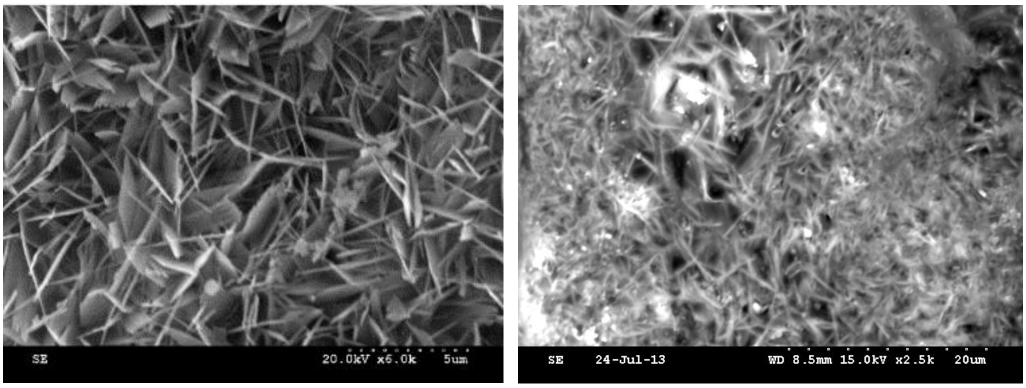


Figure 12: SEM picture (secondary electron) of the Ca-enrichment zone in the interface area in the in situ experiment after 1 year of interaction with the argillite (right); compared with a C-S-H picture [40] (left).

Between the well identified C-S-H layer measuring about 60 to 100 µm thick and the surface of the cementitious material, a second layer of similar thickness was observed (figure 13). This layer is mainly composed of silicon and aluminum, but also of alkaline and earth alkaline cations: potassium, calcium, magnesium and sodium.

By comparing these results with the XRD analyses of the cement paste surface (figure 9), it was possible to make the link between this layer and the formation of a zeolite, boggsite, analcime-Ca/Na type . The mineral identification is achieved through the identification of five peaks in the XRD pattern of the cement paste surface. This layer is also observed on the surface of the clay by XRD (figure 9) which shows three peaks corresponding to the boggsite.

Zeolites formation is very rarely observed in representative experiments with material interfaces, and much more with this very short experimental time. Calculation codes often provide the analcime Na-Ca-K-Mg formation but they have never been shown in experiments with interfaces as opposed to batch experiments. This proof of zeolites existence and also of C-S-H formation in the interface for a temperature of 70 °C are very interesting validation data for future modeling.

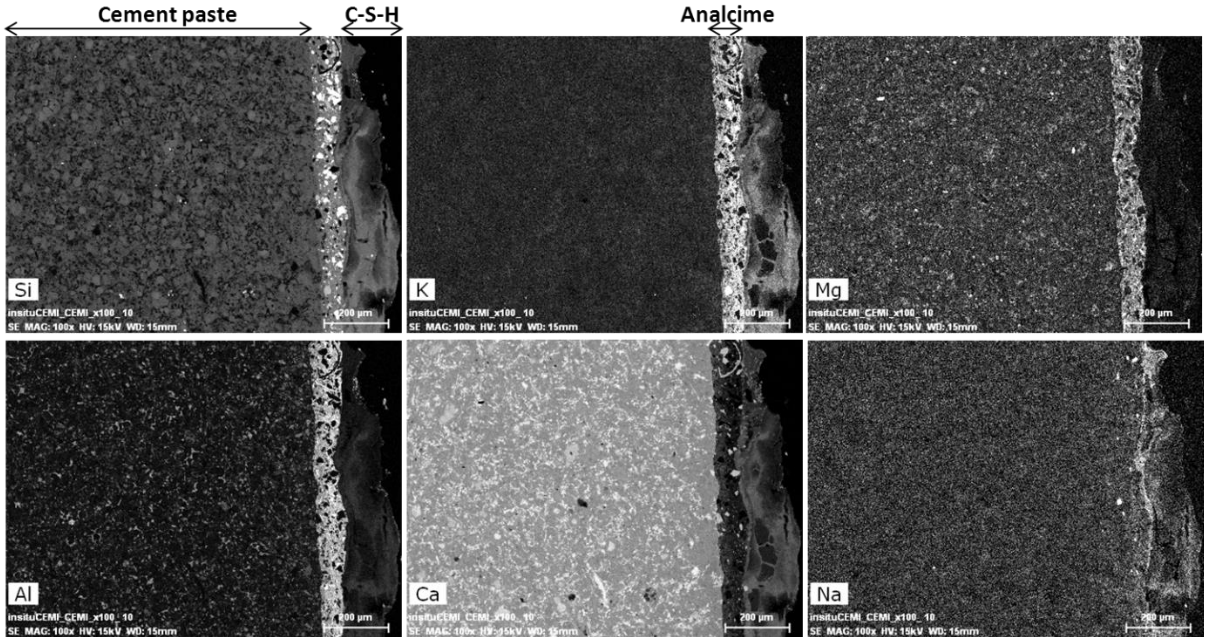


Figure 13: EDS mappings of the interface area in the in situ experiment after 1 year of interaction with the argillite

By studying the material exchange between the two environments, we observe that the sodium and calcium diffusing theoretically from the cementitious material to the clayey material did not get through the interface area. The main explanation for this phenomenon is the accumulation of these two elements in analcime (enrichment in Na and Ca in this area) as well as potassium and magnesium. This layer eventually would play a role of diffusive barrier for the cations.

In the argilite, except the zeolite and C-S-H formations in the interface area, the proportion of illite from the XRD patterns appears to have increased in parallel to the kaolinite decreasing. This reaction process already observed in batch is known but has never been proven in representative tests. Further analysis of the clay fraction of the rock are needed to confirm this suspected mechanism.

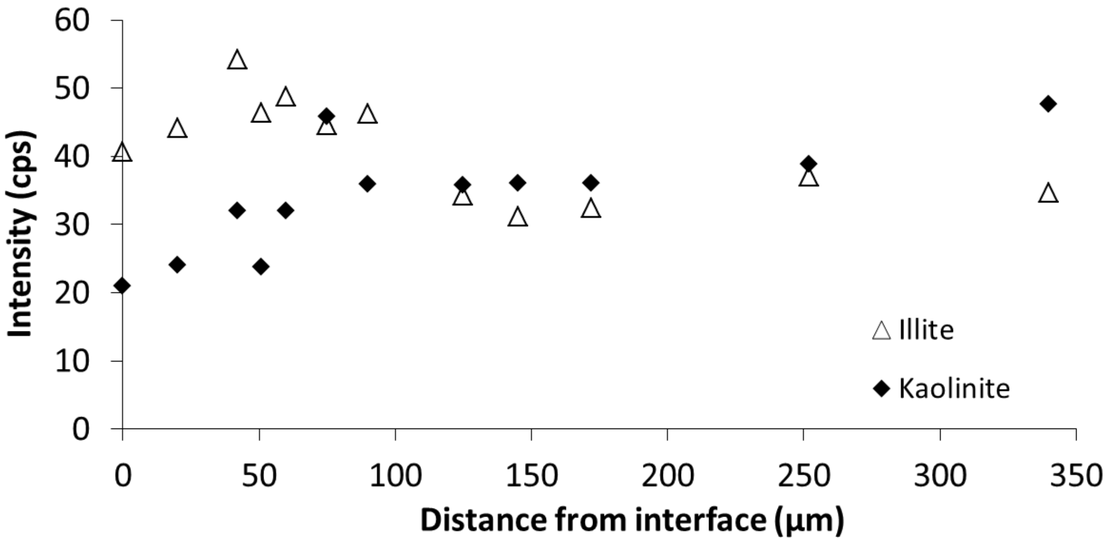


Figure 14: Mineralogical profiles of illite (peak at 10 Å) and kaolinite (peak at 7.13 Å) in the in situ experiment after 1 year of interaction with the CEM I cement paste

The interface area measures about 250-300 µm and is totally filled with zeolite, C-S-H and (in a lesser amount) with calcite. The textured appearance of these phases suggests that their formation was helped by the presence of an initial technology gap between the two materials.

For information, the first results on a two-month experiment in the diffusion cell have very similar reaction paths: decalcification, carbonation, C-S-H formation in the interface area and precipitation of ettringite. Only the formation of zeolite is not confirmed. However, the formation of Al/Si-gel was revealed, which is a possible precursor of zeolites. The future results after 6 and 12 months should confirm this hypothesis.

4- CONCLUSION

The CEMTEX project investigates interface reactions between cementitious materials and clay environment at high (70 °C) temperature. This project is a collaboration between two technical safety organizations: IRSN and BEL V. In situ tests are performed in the URL of Tournemire.

Preliminary results of CEMTEX do show good agreement with the existing literature:
- The carbonation of the cementitious material is observed both in the in situ and laboratory tests.
- The decalcification was demonstrated in all cases via the dissolution of portlandite.
- If ettringite is dissolved with the rise in temperature, experiments clearly show that it precipitates near the interface in the area of decalcification.
- The formation of C-S-H is provided for all models at the interface and in the argillite [13;17;19;23;24;25;27].
- The formation of zeolite, that was never been clearly demonstrated in representative experiments with interfaces, is proved in the in situ test. As well as the formation of C-S-H, the precipitation of zeolites as described in the literature [3;11;18;20;23;24;25;27] has been shown in extreme conditions in batch tests above 60 °C.

Remaining research is to identify the impact of the formation of such phases on the microstructure and hence on the extension of the disturbance in the CEM I and low-pH material.
From a purely safety point of view, these preliminary results are to be confirmed and better developed in the framework of the CEMTEX project. Preliminary results seems to highlight that an increase in temperature would have a positive effect on the durability of these interface due to the carbonation of cementitious material and to the formation of a band of zeolite. This band would trap part of the diffusive elements (and possibly radionuclides) between the two environments.

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