

## Neutron diffraction as a tool in the study of reinforced concrete. Compilation of some cases

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**Abstract.** Cementitious materials are much more complex than it seems at a first sight. On one hand, due to the excess of water needed to make the mix workable, a network of pores is generated, that puts in contact the material with the environment and allows their attack by aggressive agents that can be physical or chemical agents, producing the deterioration of the concrete itself and corrosion of the rebars. Then, it is necessary to study the transport properties and the chemical and physical interaction of aggressive agents with the solid and liquid phases of the cement paste, the corrosion of the rebars, and the repair processes. This is an approach concerning the service life of structures, however, we cannot forget an important chapter which is gaining much relevance in the last time: that of the special uses of concrete, for which, tailored concretes have to be designed. In order to undertake these problems, we need new analysis tools, different from the traditionally ones applied to study concrete, that allows the understanding of the mechanisms regulating the processes. One of these analysis tools is neutron diffraction that gives us the possibility of study the bulk of materials using a quite big specimen. In this work, 4 different problems undertaken with the help of neutrons in experiments carried out by the group of the author at the ILL, at the D1B and D20 instruments are presented.

### 1. Carbonation studies

Carbonation can be defined as the neutralisation of the cement paste due to reaction with acid atmospheric agents, mainly  $\text{CO}_2$ . When the neutral front arrives to the rebar in reinforced concrete, depassivation of the steel takes place and corrosion of the steel starts. Deepen in the knowledge of this process was undertaken by in-situ monitoring of the changes that take place in the phase composition of cement pastes during accelerated carbonation (100%  $\text{CO}_2$ ) at 65% HR for different binders (plain OPC and OPC with additions of fly ash and micro-silica) by taking Neutron Diffraction patterns in parallel with the carbonation experiments carried out at the D20 (a schema of the experiment is given in figure 1-a) [1]. The variation of the intensity of chosen reflections for each phase along the experiment was used to monitor concentration changes supplying data, in real time, for establishing the fractional conversion of different phases (Portlandite, Ettringite and CSH gel) of the hydrated cement pastes. Fitting of these results allowed to make a qualitative approach to the kinetics of the carbonation of the different phases deducing that all the phases consumed by the carbonation process disappear according to an exponential decay of first order, while formation of Calcite follows the trend of a sigmoid shape given by a Boltzmann function, as corresponds to a finite amount of reacting material (figure 1-b).



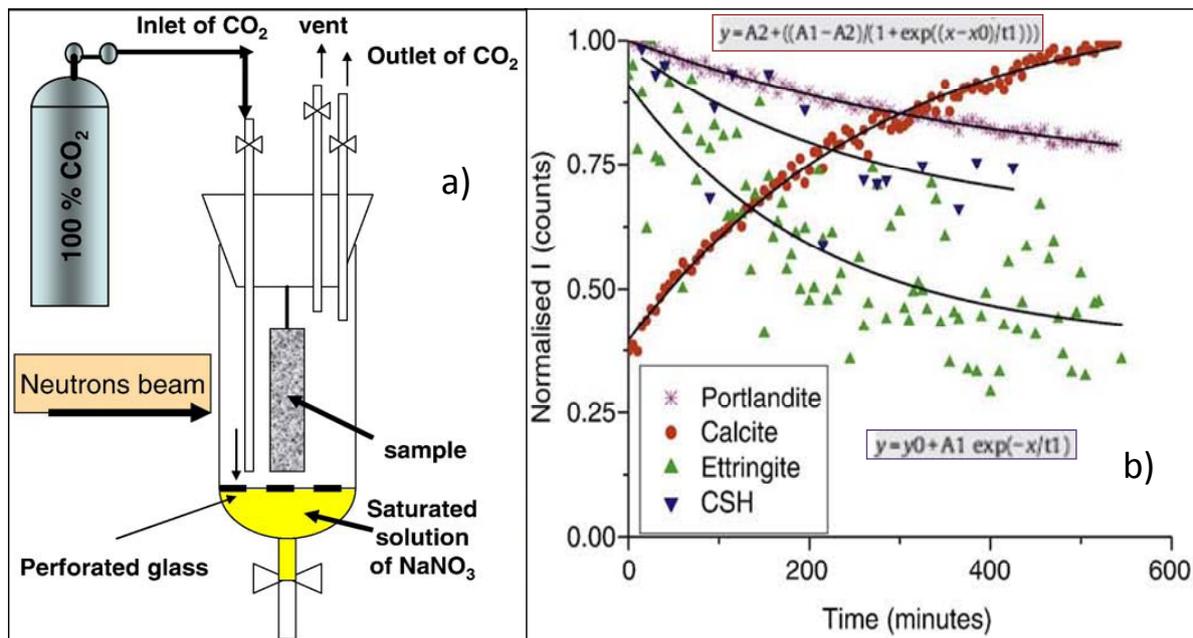


Fig. 1: a) Schema of the experiment. b) Example of fractional conversion of the different phases for the mix of OPC and fitting to the equations.

It could be deduced that the rate of decrease of each phase is different for the different mixes. For the same mix, the rate for the different phases is different, but maintaining the same proportionality between each phase in the different samples. Ettringite is the phase that reacts quicker, then, the crystalline fraction analysed of the CSH gel, being the consumption of Portlandite, the slowest persistent process. Additionally, interesting conclusions on the microstructural changes that takes place during the carbonation of cement pastes were extracted. Details on this experiment, treatment of the data and conclusions can be found in [1]. Additionally, the evolution of cement paste samples during accelerated carbonation was followed in situ, at the D1B instrument, at different RH, being able to find an optimum of the 53% of RH. In combination with other techniques, the presence of initial amorphous calcite was evidenced, as well as the crystalline character of the new calcite formed after carbonation [2].

## 2. Electro-osmosis and alkaline reserve restoration during realkalisation

Realkalisation is an electrochemical treatment for restoring to concrete, which surrounds reinforcing bars, a high pH value corresponding to sound-non carbonated concrete [3]. Even though the electroosmotic flux through hardened cementitious materials during laboratory realkalisation trials had been previously noticed, there was some controversy on either it was really an electrokinetic phenomena or just salvation water of  $\text{Na}^+$  ions. In-situ monitoring of the experiment, analysing at the same time the establishment of the electroosmotic flux and the microstructure changes in the surroundings of the rebar was possible through neutron diffraction experiments: two series of cement pastes, cast with CEM I and CEM I substituted in a 35% by fly ash, previously carbonated at 100%  $\text{CO}_2$ , were submitted to realkalisation treatments followed on line by simultaneous acquisition of neutron diffraction data [4]. A ponding was glued on the top of the cylinder of cement paste (prepared with deuterated water) and was filled with a solution of  $\text{Na}_2\text{CO}_3$  1M prepared with ordinary, non-deuterated, distilled water. The experiment was designed on the hypothesis that if electroosmotic flux took place, an abrupt increase in the background of the diffraction patterns should occur due to incoherent scattering of the hydrogen of the plain water.

In order to determine the exact moment, and therefore the conditions in the experiment in which the electroosmotic flux starts to develop, the derivative of the curve of the background in function of time has been calculated for both experiments. Therefore, in the inflexion points of the original curve towards higher slopes, a maximum appears in the derivative curve. The positions of these maximums give the points of establishment of the electroosmotic flux.

The averaged values of zeta-potential, calculated from the averaged electroosmotic flux, for mixes A and B were also calculated, being of -1.2 and -4 mV, respectively. Therefore, the zeta potential of the electrical double layer in the walls of the pores of cement paste is more negative when adding fly ashes to the clinker than when using plain CEM I. Concerning the evolution of phases, it could be directly observed the precipitation of portlandite on the rebar and on the zone close to the negative electrode as far as the pH was high enough. The provision of  $\text{Ca}^{2+}$  ions come from the dissolution of calcite and vaterite. So, for the first time, it could be said that it is possible to restore the alkaline reserve if passing enough amount of charge during a realkalisation treatment.

### **3. Resistance in case of fire**

Other important aspect is the resistance of the structures in case of fire. In this framework, composition and microstructure changes of cement pastes when heating until 620 °C and cooling afterwards were monitored on site by neutron diffraction at the D1B (ILL). The parameters involved in the study were the heating ramp, the state of the sample (in block or ground) and the type of cement. The residual state of the samples was complemented by mercury intrusion porosimetry (MIP) and thermogravimetry analysis (TGA) [5]. The use of neutron diffraction allowed monitoring the major features of the experiments, i.e., the phases existence domains and their growing and decaying: portlandite, Ettringite, CSH, calcite and larnite. Additionally, it could be stated that Portlandite that was formed when cooling is less crystalline than the original one, and its temperature of thermal decomposition gets lower. On the contrary, calcite that precipitates decomposed thermally at higher temperature than the original one. The monitoring of the loss of free and combined water, by integration of diffraction patterns backgrounds as a function of the internal temperature of the samples could be related to the resulting microstructure. Finally, changing the heating rate, from 60 to 120 °C/h had no significant influence neither in the composition nor in the resulting microstructure of the cement paste; however, the type of cement or the state of the sample (powder or block) was a significant parameter, leading to different residual phases (free lime content), which might have a significant influence in the durability of a concrete after a fire.

### **4. Hydrogen embrittlement of high strength steel**

Embrittlement of high-strength steel is known to be caused by hydrogen penetration into the network of the metal that could lead to disastrous failures of pre and post tensioned structures. However, the penetration mechanism of hydrogen into the steel is still under discussion, as it is not so easy to detect and measure the hydrogen in steels. To undertake this subject, relatively large commercial cold drawn pearlitic steel wires were submitted to stress corrosion cracking under different environments: inert (air) environment; at a controlled anodic potential of -300 mV (SCE) in 0.05 M aqueous solution of  $\text{NaHCO}_3$  and at a controlled cathodic potential of -1200 mV (SCE) in 0.05 M aqueous solution of  $\text{NaHCO}_3$ . From the slow strain rate testing (SSRT) of the steels it was shown that both samples in aggressive environment, exhibited brittle fracture, while the inert sample did not. The steel tested at -300 mV (SCE) was the one that presented a higher embrittlement degree. Neutron Diffraction Technique was used to analyze the samples. The data acquisition was performed at the D20 instrument of the (ILL), in Grenoble, France [6]. The wavelength used was 1.3 Å, exploring an angular domain in  $2\theta$  from 10° to 150°. Cell parameter variations of the different phases were measured using pseudo-Voigt functions and by Rietveld refinement using the Fullprof software. The penetration of the

hydrogen into the unit cell of the ferrite was deduced from the shift of the d-spacing after the experiments. The increase of volume in the ferrite unit cell was quantified and correlated with the degree of embrittlement of the steels in aggressive environment (see figure 2).

Other examples of application of neutron techniques to the study of concrete can be found in [7-14].

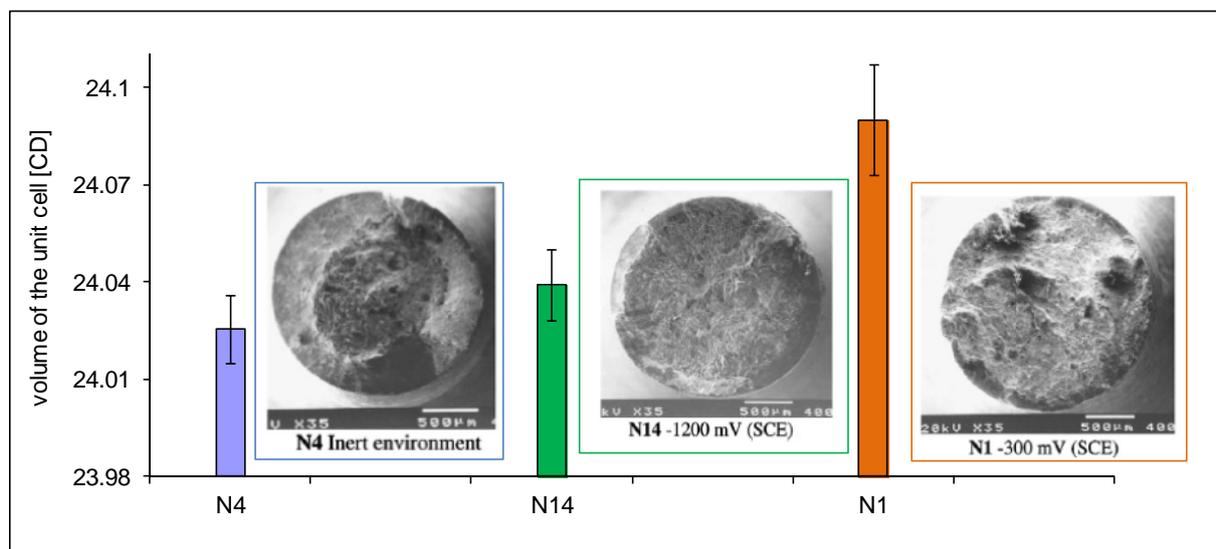


Fig. 2. Volume of the unit cell of Ferrite for the three samples studied, calculated by fitting isolated peaks to pseudo-Voigt functions, and micrograph of the surface of fracture after the tests.

### Acknowledgements:

The author is grateful to the ILL, especially to the staff of D1B and D20.

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