Title: 2DNMR Maps for the characterization of the structural changes in cement pastes undergone to drying and wetting cycles.

Cement based materials, such as concrete and mortars, are widely used around the world in building industry, and due to the external environment they are subjected to repeated drying and wetting cycles. Water transport through solid matrix of concrete and mortars, and particularly, binder phase, cement, largely influences durability properties of the cement-based materials. The drying of cement-based materials may cause formation of cracks, which increase the permeability of the material and the durability of cement could be deteriorated by such processes as attack of acids, sulphates or alkalis, etc. [1]. The mechanisms involved in the drying and wetting process are complex and are often interrelated. This is mainly due to the wide range of the pore size distribution in standard cement mixes, which determines, to a large extent, the different transport mechanisms. Moisture transport within the porous solid involves liquid water and water vapor, and mechanisms such as permeation due to a pressure head, diffusion due to a concentration gradient, capillary suction due to surface tension acting in the capillaries, or adsorption-desorption phenomena, involving fixation and liberation of molecules on the solid surface due to mass forces. Evaporation and condensation within the porous solid are also important for determining the phase in which moisture is transported through the material. All these phenomena may act simultaneously and be predominant in different regions of the cement paste. During re-saturation cycles, reversible and irreversible changes of the structure were observed and reported in the literature, and it was proposed that irreversible changes mainly occur during the first drying process [2]. The experimental observation most frequently performed for sorption phenomenon is the adsorption isotherm: the measurement of the quantity of adsorbed material as a function of its vapor pressure at constant temperature. Hysteresis loop in sorption isotherms is a usual phenomenon for the cementitious materials. Although the sorption processes of cement materials have been widely studied for many years, and there are several interpretative models, there is still no agreement on a general theory of these phenomena.

Proton Nuclear Magnetic Resonance Relaxometry (^{1}H NMR) is a non-destructive powerful tool that has long been used in many fields to study the properties of materials. ^{1}H NMR of hydrogenous fluids confined in porous media provides a set of techniques exploited to study the pore space structure and fluids behavior in a wide range of systems, from sedimentary rocks to biological materials [3]. Parameters like the longitudinal (T_1) and the transverse (T_2) relaxation times, as well as the self-diffusion molecular coefficient (D), can be measured and associated to properties of the fluids and porous media. Therefore, ^{1}H NMR allows the measurement of water in the cement sample compartments, allowing one to distinguish different pores and voids inside the sample: “gel” pores, interlayer space, capillary pores and solid or crystalline water [4, 5]. Moreover, two-dimensional NMR (2DNMR) techniques to analyze porous media are gaining increasing importance [3]. When a hydrogenous fluid saturates a porous medium, T_1 and T_2

follow distributions of values and the problem is to correlate these two-dimensional distributions of relaxation times (2DNMR maps) with the two-dimensional experimental data. The problem of determining the relaxation times distribution from NMR data is a well- known ill-posed inverse problem. Therefore, an appropriate inversion algorithm of NMR relaxation data is a crucial requirement. The extension of the UPEN2D algorithm, UPEN2D-FISTA, has demonstrated to be a robust and flexible tool employing multi-parameter Tikhonov regularization, for the inversion of 2DNMR relaxation data [6].

Scope of the research

The scope of the research project is to attempt the characterization of effects induced by drying and wetting cycles on structure of WPC (White Portland Cement) samples by means of ^{1}H 2DNMR measurements. In particular, using the UPEN2D-FISTA tool on data measured with IRCPMG experiments to produce 2DNMR T_1-T_2 maps.

Activity plain

All the activities will be performed at the NMR laboratory of the LAGRIN, DICAM

WPC samples preparation, with different composition, and initial 1D NMR characterization during the first month of underwater hardening (1˚ months);

Tuning and calibration of both the IRCPMG NMR sequence used to acquire the cement 2DNMR T_1-T_2 relaxation data and of the UPEN2D-FISTA tool (2˚ month);

Using RH chambre to create sorption curves of WPC samples (from 2˚ to 11˚ month);

Using oven to create sorption curves of WPC samples (from 4˚ to 11˚ month);

Measurements of 2DNMR relaxation data from dried-wetted WPC samples and creation of the 2D T_1-T_2 maps using UPEN2D-FISTA (from 3˚ to 12˚ month);

Editing of the final report (12˚ month).

References

1. V.G. Papadakis et al. Physical and chemical characteristics affecting the durability of concrete. Aci Materials Journal, Vol. 88(2), pp: 186-196, 1991.
2. V. Baroghel-Bouny, Water Vapour Sorption Experiments on Hardened Cementitious Materials: Part I: Essential Tool for Analysis of Hygral Behaviour and its Relation to Pore Structure. Cement and Concrete Research, Vol. 37 (3), pp: 414-437, 2007.
3. J. Mitchell, L.F. Gladden, T.C Chandrasekera, E.J. Fordham. Low-field permanent magnets for industrial process and quality control. Progress in Nuclear Magnetic Resonance Spectroscopy, 76:1–60, 2014.
4. A.M. Gajewicz et al., A ^{1}H NMR relaxometry investigation of gel-pore drying shrinkage in cement pastes. Cement and Concrete Research, Vol. 86, pp:12-19, 2016.
5. V. Bortolotti, L. Brizi, R. J. S. Brown, P. Fantazzini, M. Mariani, Nano and Sub-nano Multiscale Porosity Formation and Other Features Revealed by ^{1}H NMR Relaxometry during Cement Hydration. Langmuir 30, 10871−10877, 2014.

6. V. Bortolotti, G. Landi, F. Zama, 2DNMR data inversion using locally adapted multi-penalty regularization, Computational Geosciences, 25:1215–1228, 2021.