P9: NMR Imaging and Relaxation Analysis of Cement Based Material

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A native of Poland, Agata Gajewicz got her MS in Building Materials at the University of Science and Technology AGH in Cracow, Poland, in 2010. She started to work at University of Surrey on the 1st of October 2010.

Project description

Project number 9 was design to utilize proton (^{1}H) Nuclear Magnetic Resonance (NMR) techniques to study cement based materials.

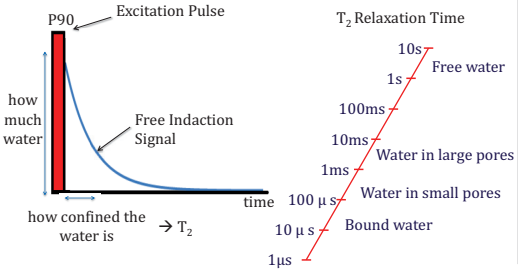
NMR relaxometry is proving to be an excellent non-invasive and non-destructive tool for the characterization of pore size distribution and pore-water interactions in cement without drying and hence without damaging the delicate C-S-H nanostructure.

Aims: To characterise water in the nanoporosity of cement to provide input data to support modelling projects.

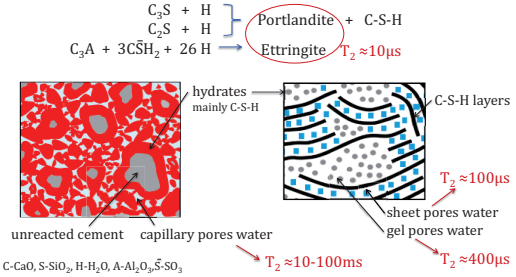
Objectives: Define pore size distribution of; pore connectivity in; and state of water within cements.

The understanding of the nano-meter scale structure of cement paste, including porosity, size distribution and connectivity of pores as well as the role of water is essential for prediction of macro properties of building materials.

NMR technique:



Cement porosity by NMR:

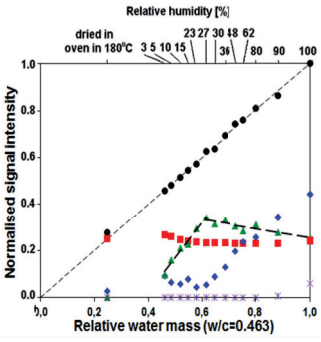


Project results

First Desorption

Measurements were made on white cement paste (w/c = 0.4) cured under water for 28 days and then equilibrated to constant mass at reduced relative humidity.

The total signal intensity comprises of components for *bound* water and water in: *sheet, gel and capillary pores*.



The total NMR signal (●), solid (■), sheet (▲), gel (◆) and capillary (✕) pore water signal as a function of relative water mass and humidity for first desorption.

The capillary pore water dries above 90% RH.

The gel pore water decreseas between 100 and 25% RH.

Above 25% RH, sheet pore water intensity increases.

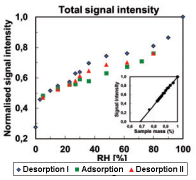
Below this humidity, sheet pore intensity decreases in sympathy with a growth in solid signal intensity.

$Ca(OH)_2$ and ettringite (Solid) water mass fraction
- by NMR – 24.3%
- by XRD – 26.4%
- by TGA – 25.5%

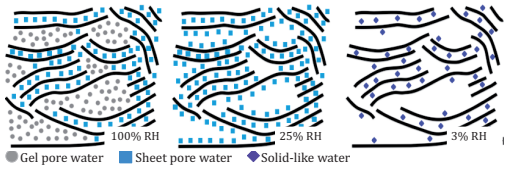
Isotherm Loop

The normalised total signal intensity presents a normal gravimetric isotherm loop.

Loss of total signal intensity with mass is linear and implies an effective water to cement ratio - 0.463.
It proves that 'all' water is seen by NMR.



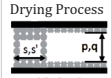
Schematic Morphology of C-S-H



Pore Sizes

• Amplitudes Model

Drying Process



$p = -\frac{2}{a_1}; q = \frac{2}{a_2 - 1}$

a_1, a_2 - slopes of fitting lines in first desorption plot (left)

• Relaxation Model

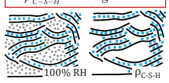
$r = \frac{2 \cdot \varepsilon \cdot T_2}{T_{2Surf}}$ ε - monolayer of water; T_{2surf} – sheet water T_2 at 3%RH

Model	Amplitudes	Relaxation
Gel pore size	3.4 nm	3.1 nm
Sheet pore size	1.6 nm	0.96 nm

C-S-H Density And Composition

These follow from solution of *mass, volume* and *oxide content* balance *equations* written in terms of:
- signals intensities → NMR
- degree of hydration + ettringite fraction + anhydrous cement composition } XRD

$(Ca)_{1.53}(Si,Al)O_{3.51}(H_2O)_{1.92}$
$\rho_{C-S-H} = 2.68\ g/cm^3$

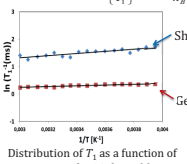


Activation Energies

$\ln\left\{\frac{1}{T_1}\right\} = C + \frac{E_A}{k_B \cdot T}$ [?]

Activation energy: $E_A = -\frac{a}{k_B}$

where: a – intercept of fitting line
k_B – Boltzman constant



Distribution of T_1 as a function of temperature for 28 days old paste.

Activation energies:

@ 28days $E_A^{SHEET} = 0.034 \pm 0.005 eV$; $E_A^{GEL} = 0.012 \pm 0.001 eV$

@ 90days $E_A^{SHEET} = 0.032 \pm 0.005 eV$; $E_A^{GEL} = 0.009 \pm 0.003 eV$

Achivements

- established that the 'mobile' signal can be decomposed into three components – *sheet, gel and capillary pore water*
- calculated *density, water fraction* and *composition* of *C-S-H* in situ
- estimated the *width* of C-S-H *gel* and *sheet pores*
- measured *pore size resolved sorption isotherm*
- provided a picture of *C-S-H morphology*
- *measured activation energies for water dynamics*

✓ NMR is a powerful method of characterising cement pastes without drying and hence damaging the delicate C-S-H nanostructure.

What I am planning to do for the remaining time

Evolution of T_2 / pore size distribution

T_2 relaxation measurement will be performed by applying two NMR pulse sequence: *quad echo* and *CPMG sequence*.

The NMR signal will be decomposed into relaxation fractions corresponding to chemically combined water and water in C-S-H sheet, gel and capillary pores.

Obtained data will allow to follow the grown of hydration products, pore size evolution and calculate of C-S-H density and composition.

Evolution of T_2 relaxation components / pore size distribution as a function of:
- hydration time
- cement composition ⇒ white OPC and white OPC + 10% silica fume
- temperature ⇒ 20, 40 and 60°C

Measurements will be made on cement paste (w/c = 0.4) cured under water.

Note: Measurements have already started but have been halted due to problems with the Maran Bench top spectrometer.

$T_2 - T_2$ experiments for pore connectivity

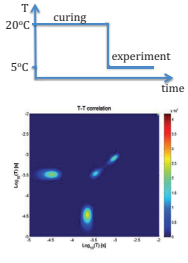
NMR 2-dimensional exchange experiments to:
- quantitatively investigate the loss of pore connectivity
- explore loss of water path connectivity with reduced relative humidity.

Different approaches will be tried:
✓ $T_2 - T_2$ exchange experiments as a function of sample age (till 10 days)
✓ $T_2 - T_2$ exchange experiments at fixed age and variable humidities

Specimens will be prepared with OPC and OPC + 10% silica fume.

Collaboration with Vadim who will freeze the pore connectivity and use cryoporometry.

Note: Measurements are postponed due to problems with Maran Bench top spectrometer.



Recent T_2-T_2 results at 10°C

MRI maps of wetting and drying cycles.

The NMR imaging experiments will be performed to:
- measure macroscopic ingress and cracks in concrete,
- visualise the pore network and water propagation in cement paste and concrete exposed to wetting and drying cycles,
- measure water diffusion coefficient in macroscopic scale – transport diffusion.

The exact plan of NMR Imaging experiments will be arranged after consultation with other members of NMR Group at University of Surrey who are currently performing experiments using this method.

Their results, problems and solutions will help to organize future work.

Secondment at Heidelberg Cement.

Secondment at Heidelberg is planned for April/May 2013.

Collaboration with Noemi who works with portable Surface GARField. Help with validation on *in situ* magnet if it is needed.

Outstanding questions

- Can we solve the problem of Maran Bench top spectrometer?
- Will it be possible to perform the experiments according to the plan?

Systematic study has been pursued to try and track back the problem. Possibilities were successively eliminated leading to the conclusion that spectrometer does not work properly.

The coil was upgraded but the problem is still there. The study showed that homogeneity of the magnetic filed has changed.
- Is the magnetic field the problem?

→ Peter Aptaker will come from Laplacian next week to re-shim and try and fix magnet.

→ We have money for new spectrometer and gradients for the horizontal bore magnet, to arrive in ~12 weeks time.

Moreover, all the results obtained in last half a year are not reliable and experiments have to be repeated.

- How does increase in the curing temperature affect the C-S-H microstructure, pore size distribution and evolution, quantity of hydration products and their density and composition?
- How does addition of silica fume influence on microstructure of cement paste?
- Why is peak correlated with capillary water not present in T_2-T_2 spectrum? → Is sampel at low RH?
- What is the reason for stopping inter-pore exchange after 3-7 days of hydration?
- What drives the movement of water molecules between pore reservoirs and what is the manner of this movement?
- How does the pore network in the microstructure of cement paste develop?
- How does quantity of exchanged water change with hydration time?
- What is the influence of cement composition on loss of water path connectivity?
- How does reduction in relative humidity affect the pore connectivity and amount of exchanged water?
- What is the threshold value of RH at which the water path connectivity is lost?

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