ERICA Mid-term Review

Meeting & Sorption Workshop

24th-26th of September 2019

University of Bologna

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Characterization of first sorption cycle by ^{1}H NMR

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H2020-MSCA-ITN-2017 Grant Agreement no. 764691

Presentation outline

- Introduction
- Aims of the project
- Work in progress
- Methods and Materials
- Results and analysis
- What's next
- Outreach. Secondments

Introduction

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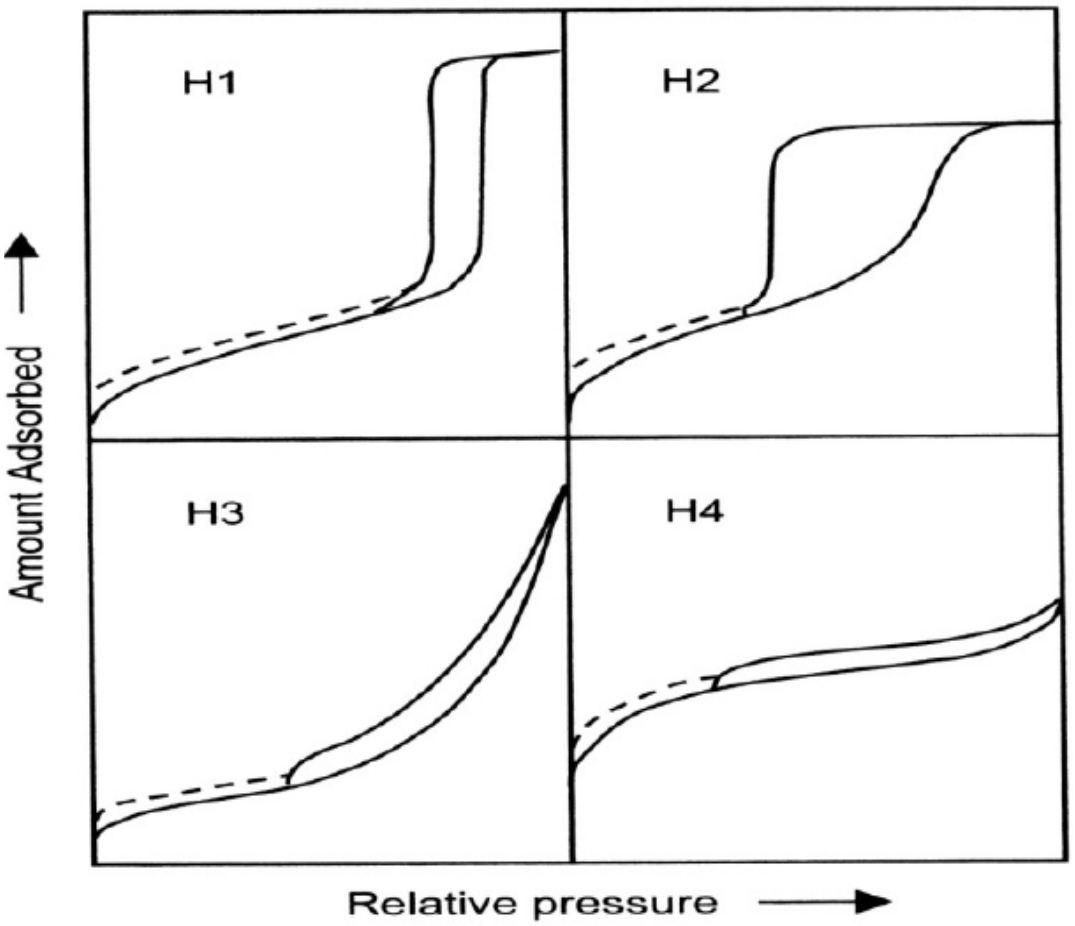

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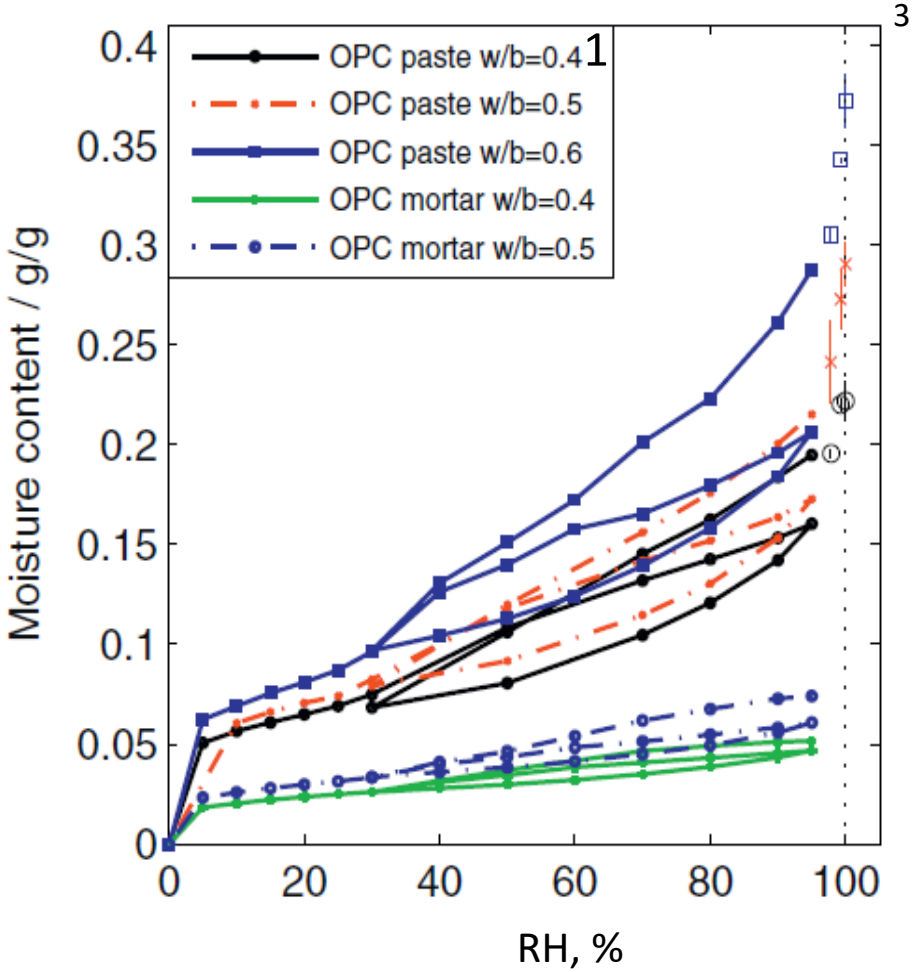


1

Why hysteresis does happen? How different pores are changing? What factors play role through different RH points?

[1] A model for hydrated Portland cement paste as deduced from sorption-length change and mechanical properties / R. F. Feldman and P. J. Sereda
[2] IUPAC classification of adsorption isotherms
[3] Moisture equilibrium of cement based materials containing slag or silica fume and exposed to repeated sorption cycles / M. Saeidpour , L.Wadsö

Aims of the project

Investigate the porosity dependence on the relative humidity in hydrates of different oxide compositions with slow (months) and quick (hours) cycling of full and partial drying/wetting cycles

Quantify the reversible and irreversible changes that occur and the severity of drying required for "structural relaxation"

Understand the effects of absolute RH achieved, time at RH and temperature

Correlate results with NMR porosity and other analyses in ERICA Project 2

Methods and Materials

Samples of cylindrical shape (10 mm height, 8 mm in diameter) were prepared in a specifically created Teflon mold with w/c = 0.5.

For slow drying home-made camera for Relative Humidity control was used (potassium chloride, silica gel, glycerol).

Oven was used for fast drying.

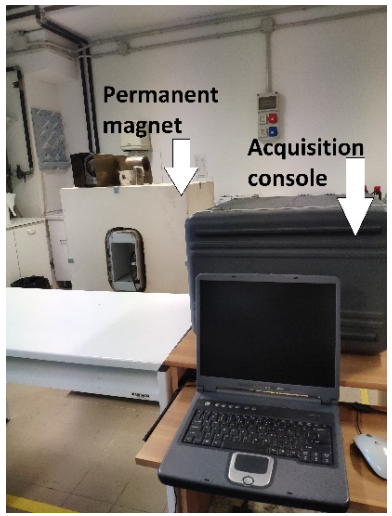
Relaxometer ARTOSCAN ESAOTE Magnet/Stelar Console (0.2 T ; 8 MHz) at 25 °C was used for NMR experiments.

a)

Picture of the Home-made RH chamber with RH data logger

b)

Oven



c)

NMR console

Methods and Materials

Longitudinal relaxation data were acquired by inversion-recovery (IR) pulse sequences ($\pi_x - t_{IR} - (\pi/2)_x$ – FID acquisition) and by a-Periodic Saturation Recovery (LAPSRQE) pulse sequence with parameters listed in the table below.

Transvers relaxation data were measured by Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence $(\pi/2)_x - (\tau - (\pi)_y - \tau -$ echo acquisition $-)_n$ with parameters listed in the table below.

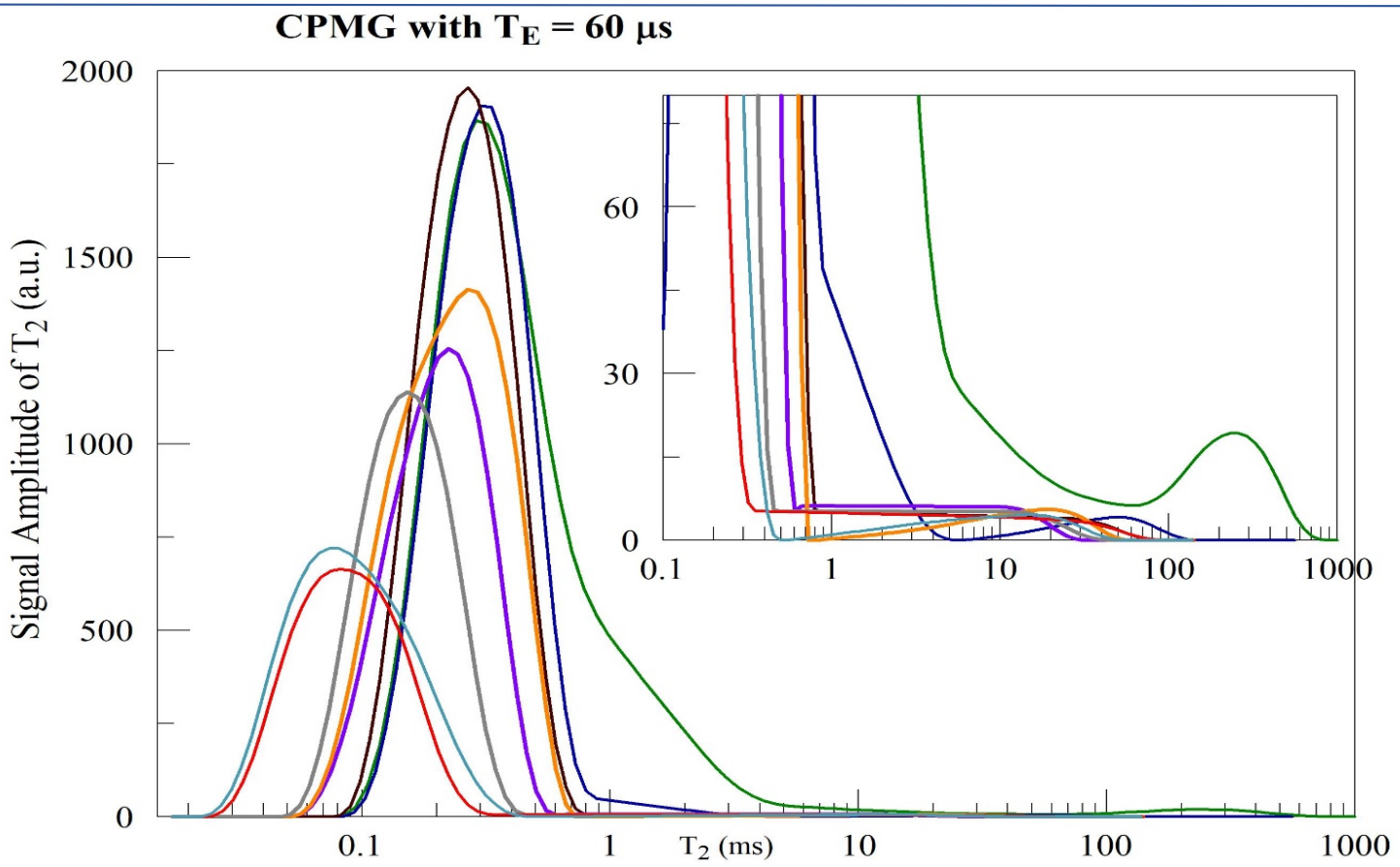
Relaxation time of the solid component was measured by Quadrature Echo (QE) pulse sequence $((\pi/2)_x - \tau - (\pi/2)_y - \tau -$ acquisition) with parameters listed in the table below.

Frequency of the instrument 8.175 MHz; 90° pulse width is 4.5 µs

Parameter name	IR	LAPSRQE	CPMG	QE
RD (s)	0.8-1	1E-05	0.8-1	1
Dead time (µs)	23	-	-	-
Number of scans	36-40	40	60-200	100-200
Number of blocks/ echoes/ Block size	128 (512 BS)	128 (512 BS)	256-2048	1024
Echo time (µs)		25	25; 30; 50; 100	20; 22; 24; 26; 30; 32; 36

Results. Spline interpolation

Results of the data analysis



Multi-exp fitting
T_2 = 0.11; 0.34; 1.2; 185 ms

RH 100%
T_2 = 245.8; 0.3 ms
Xsig = 2853 a.u.

RH 80%
T_2 = 0.3 ms
Xsig = 2230 a.u.

RH 71%
T_2 = 0.27 ms
Xsig = 2169 a.u.

RH 60%
T_2 = 0.27 ms
Xsig = 1978 a.u.

RH 46%
T_2 = 0.2 ms
Xsig = 1471 a.u.

Non-linear fit T_2=0. 08; 0.3; 6.5 ms

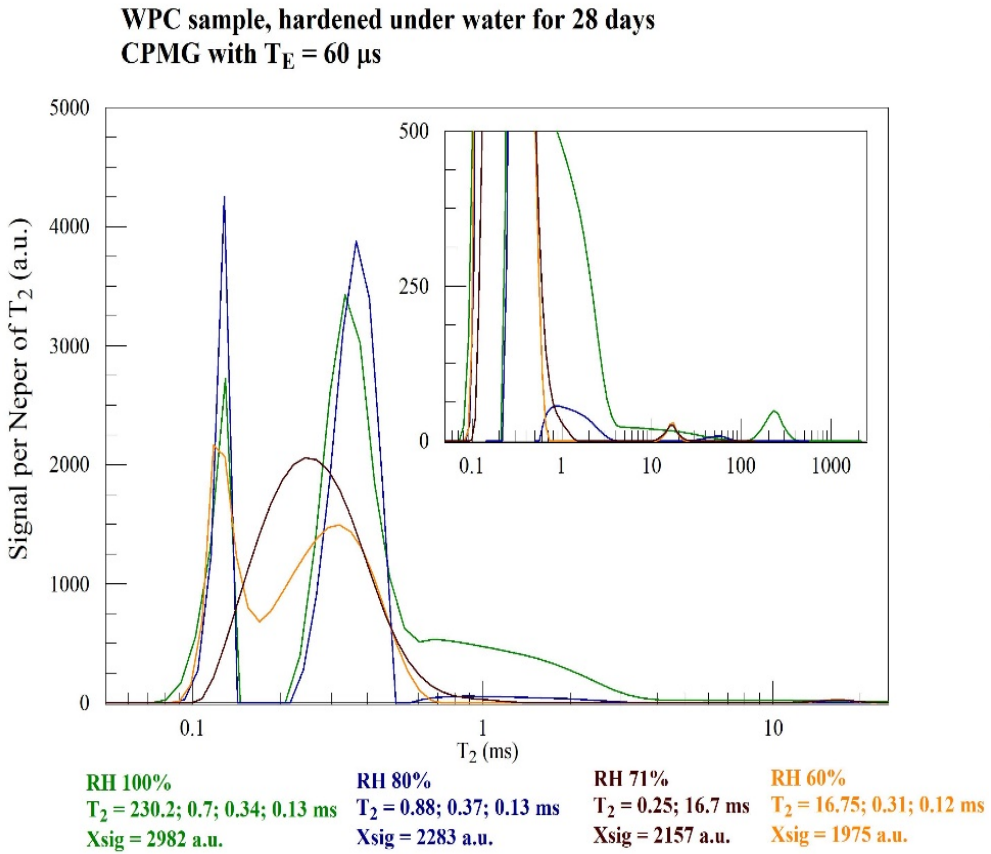
RH 33.8%
T_2 = 0.15 ms
Xsig = 1268 a.u.

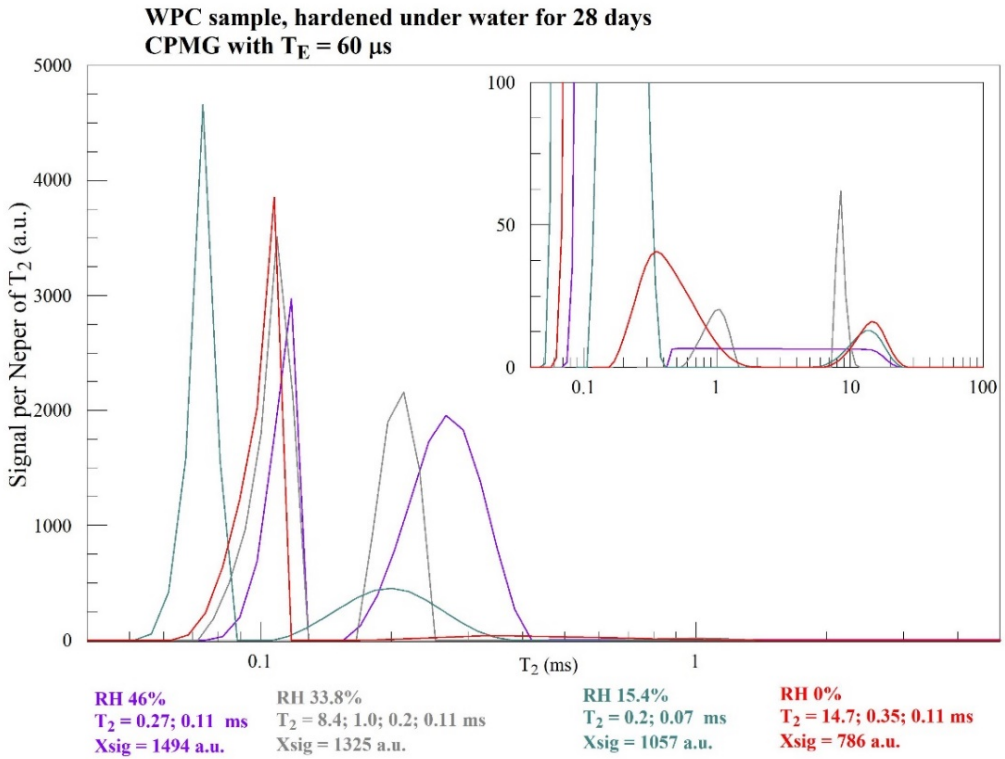
RH 15.4%
T_2 = 0.08 ms
Xsig = 1093 a.u.

RH 0%
T_2 = 0.08 ms
Xsig = 924.5 a.u.

*Drying to 0 RH with the vacuum pump. Here, “0 RH” is reference dry state, assumed “0”.

Results. For questions. Upen with increased smoothing parameter

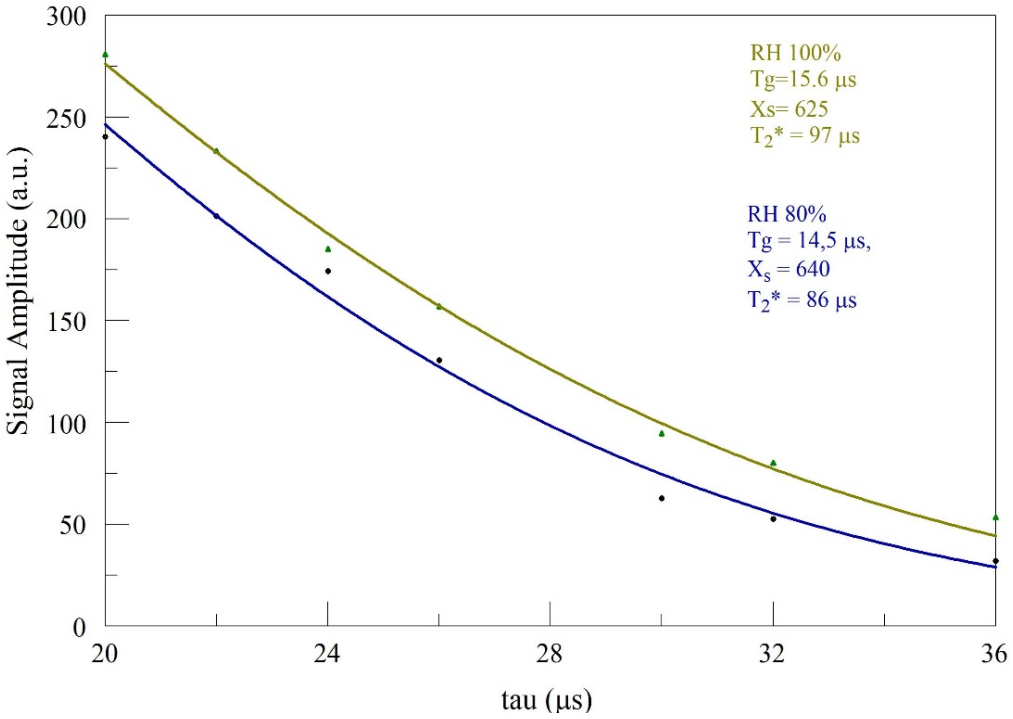


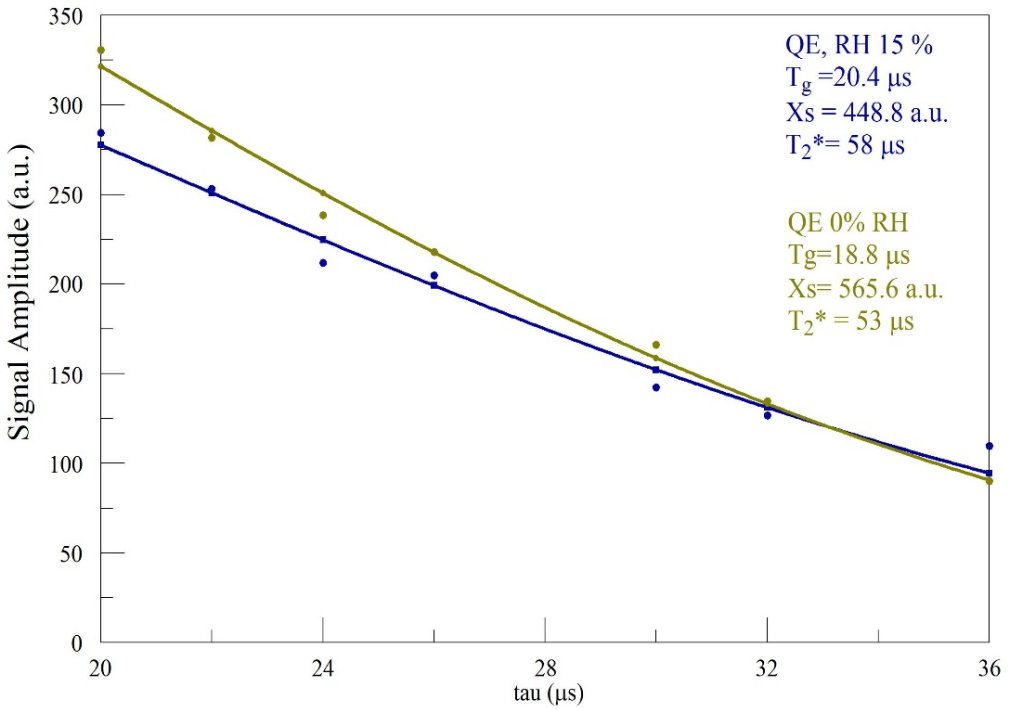


*Drying to 0 RH with the vacuum pump. Here, “0 RH” is reference dry state, assumed “0”.

Results

QE or SE of the WPC sample, dried to different RH levels and re-saturated



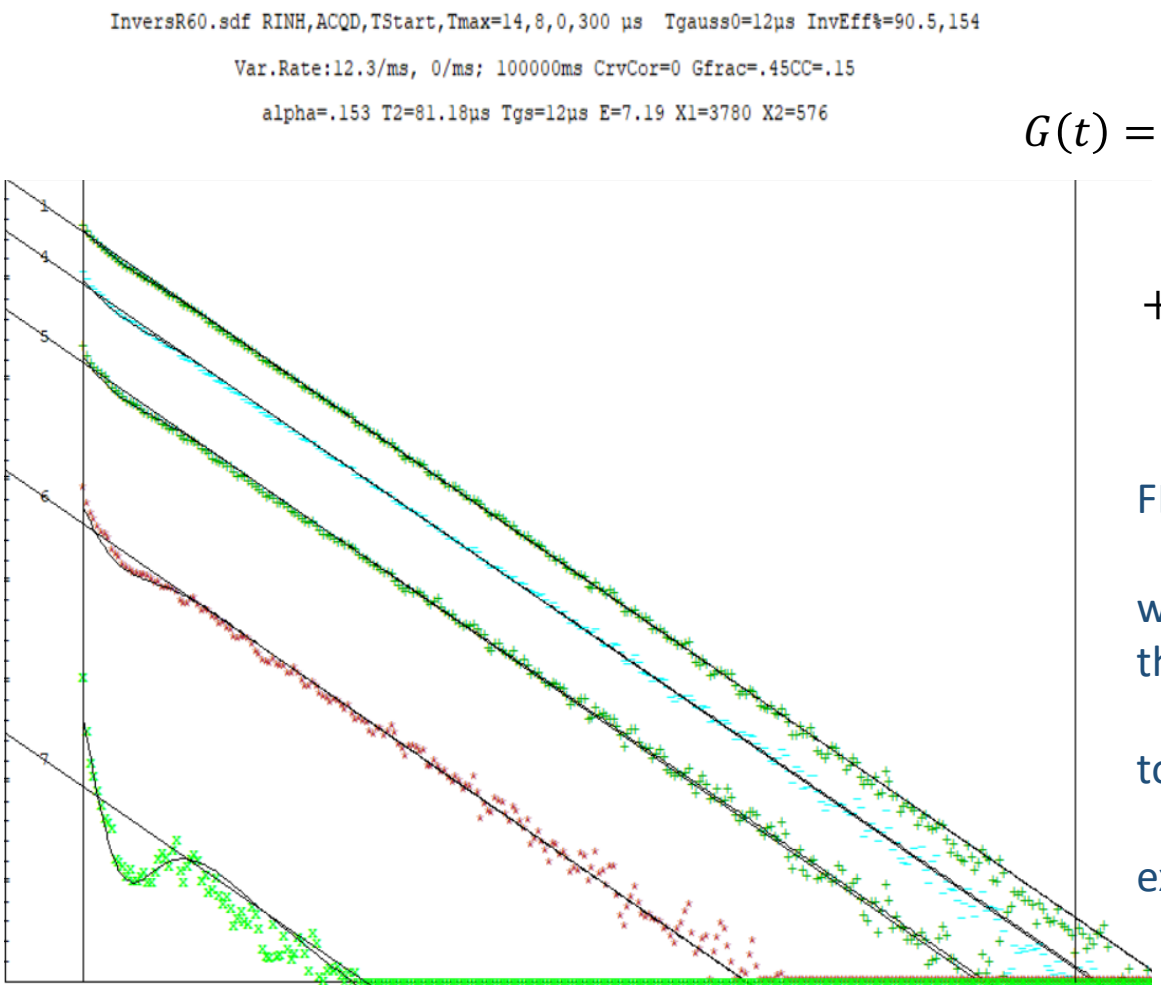


The T_2*, which is liquid component is decreasing as RH levels are decreasing.
Needs further experiments. Comparison with Tg from IR experiments.

Solid signal could be compared to the solid signal from IR. The T_{gauss} and T_2* from IR is in agreement with T_{gauss} and T_2* from QE.

Results

Separation of lower mobility from higher-mobility ^1H nuclei on the basis of their free induction decay (FID) signals



The 128 FID signals are analyzed by fitting to the following equation

$$G(t) = X_1 e^{-1/2 G_{frac}\left(\frac{t}{T_g}\right)^2}\left[1 - \frac{1}{2}\left(1 - G_{frac}\right)\left(\frac{t}{T_g}\right)^2 + \right.$$

$$\left. + \frac{1}{4} C_c \left(1 - G_{frac}\right)^2 \left(\frac{t}{T_g}\right)^4\right] + X_2 e^{-t/T_2}$$

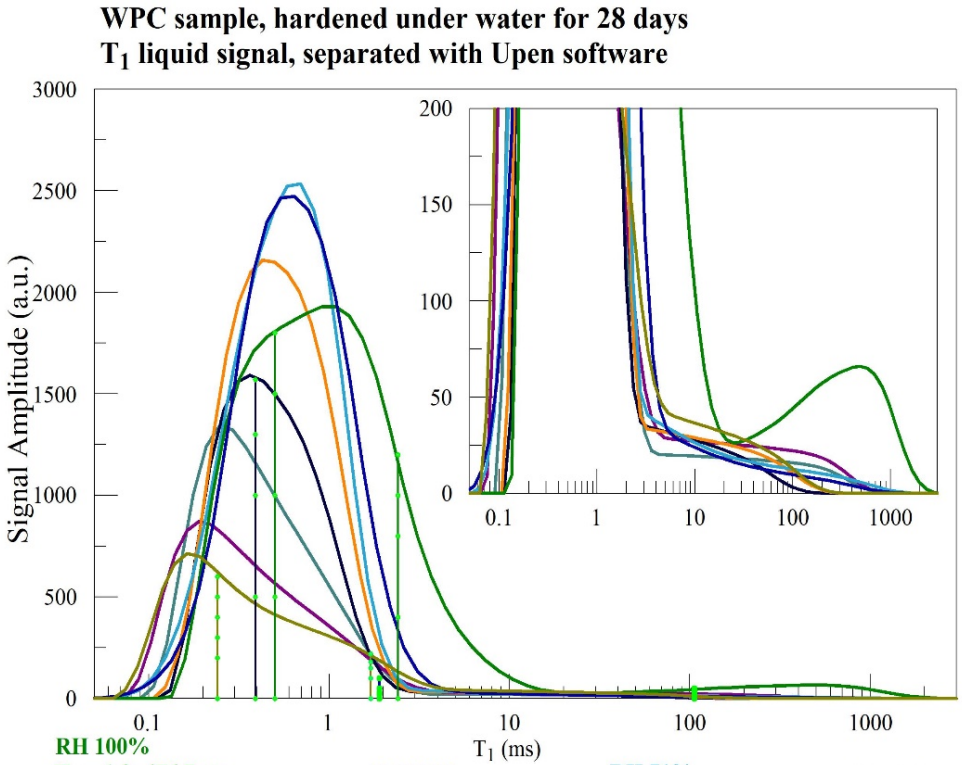
Where X_1 and X_2 are the solid and liquid FID amplitudes

Tg is the time constant of the Gaussian with the same initial curvature in a log plot as that of the solid component of the FID

G_{frac} is the fraction of that curvature due to the Gaussian factor

C_c affects recovery from the negative excursion due to the algebraic factor

Results. T_1, Inversion Recovery



RH 100%
T_1 = 1.0; 476.7 ms
Xsig = 5133 a.u.
non-linear fitt 0.5 ms (54%), 2.4 ms (32%), 106 ms

RH 80%
T_1 = 0.6 ms
Xsig = 4523 a.u.

RH 71%
T_1 = 0.65 ms
Xsig = 4381 a.u.

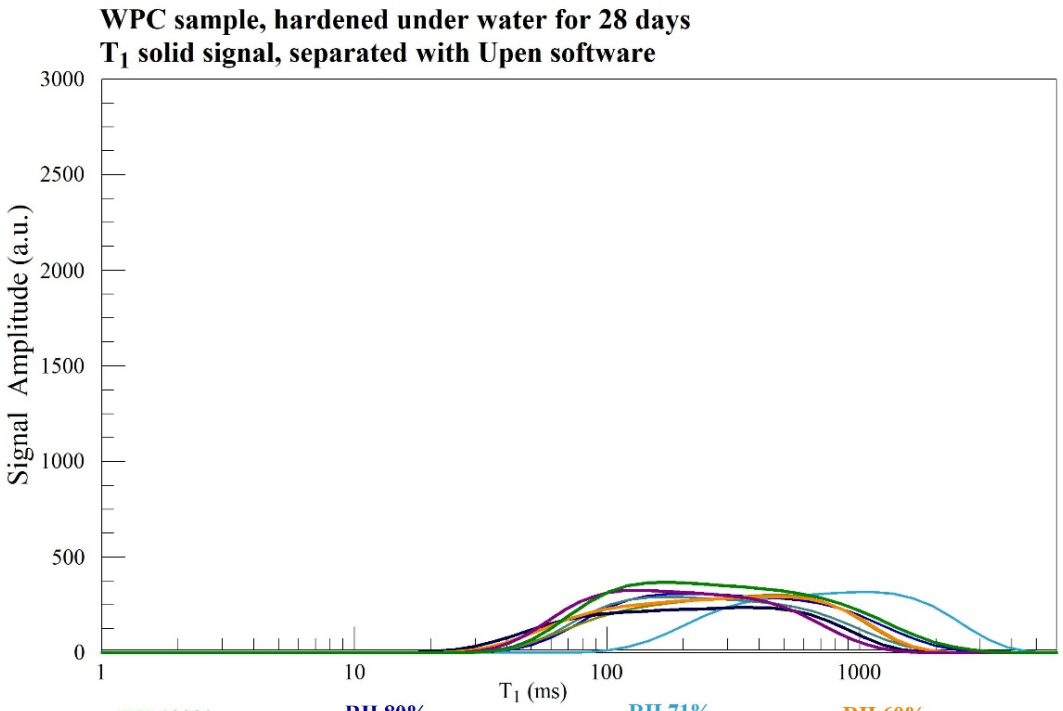
RH 60%
T_1 = 0.45 ms
Xsig = 3829 a

RH 46%
T_1 = 0.37 ms
Xsig = 2778 a.u.
non-linear fitting 0.4 ms (69%) 2 ms (19%)

RH 33.8%
T_1 = 0.26 ms
Xsig = 2392 a.u.

RH 15.4%
T_1 = 0.2 ms
Xsig = 1809 a.u.

RH 0%
T_1 = 0.17 ms
Xsig = 1563 a.u.
non-linear fitting 0.24 ms (53%), 1.6 ms (26%)



RH 100%
T_1 = 186.3 ms
Xsig = 1007 a.u.

RH 80%
T_1 = 256 ms
Xsig = 825.2 a.u.

RH 71%
T_1 = 722 ms
Xsig = 762.4 a.u.

RH 60%
T_1 = 457.2 ms
Xsig = 813.8 a.u.

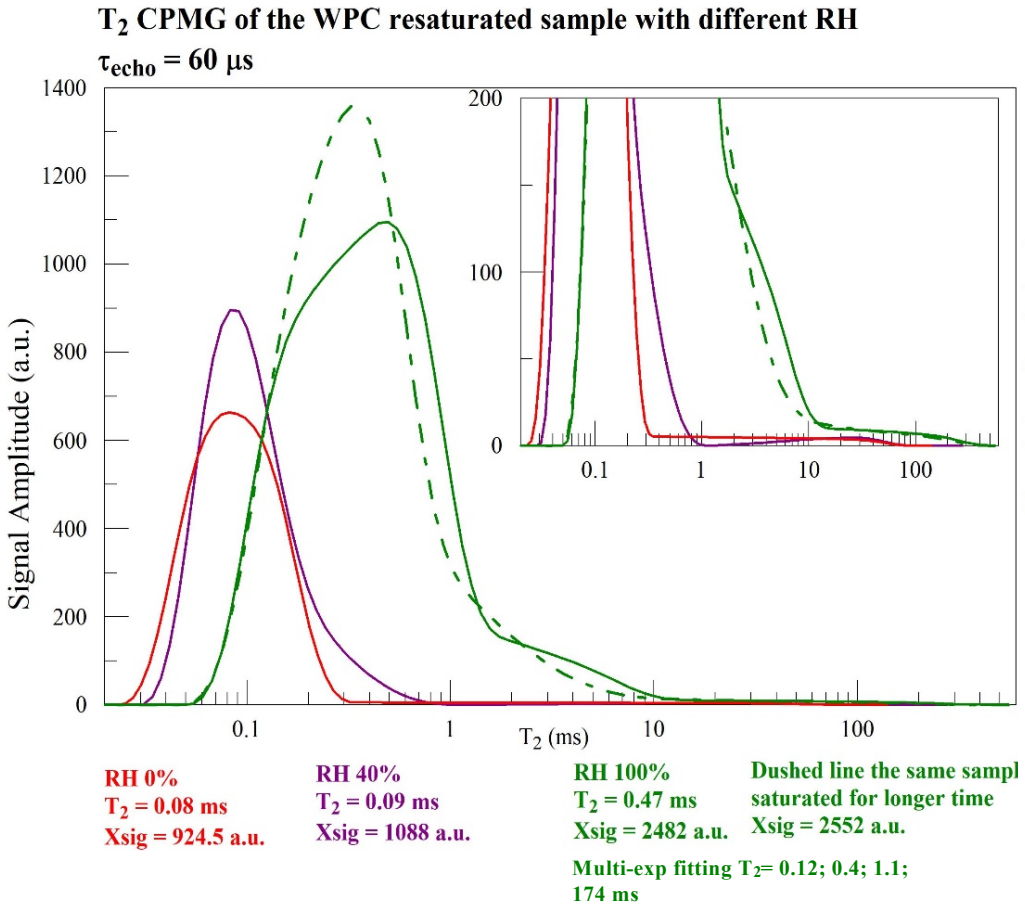
RH 46%
T_1 = 150 ms
Xsig = 664 a.u.

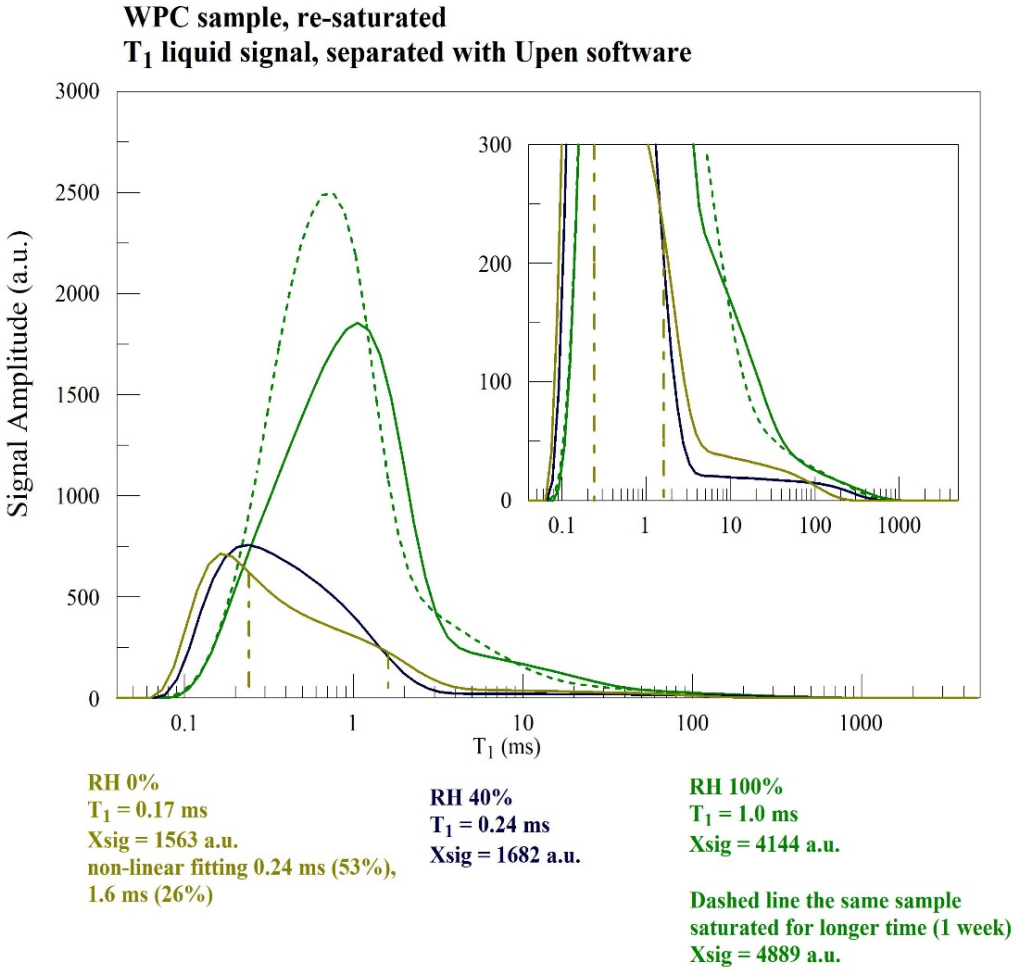
RH 33.8%
T_1 = 170 ms
Xsig = 729.9 a.u.

RH 15.4%
T_1 = 133 ms
Xsig = 780.3 a.u.

RH 0%
T_1 = 250 ms
Xsig = 757.7 a.u.

Results. Re-saturation

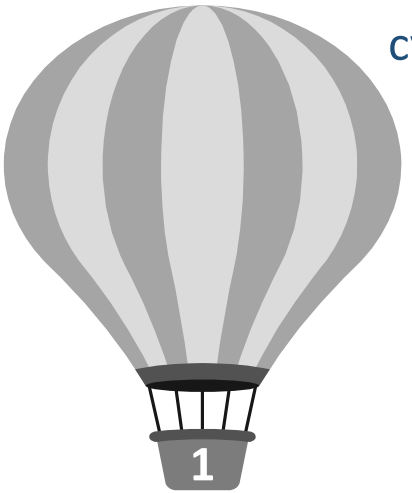




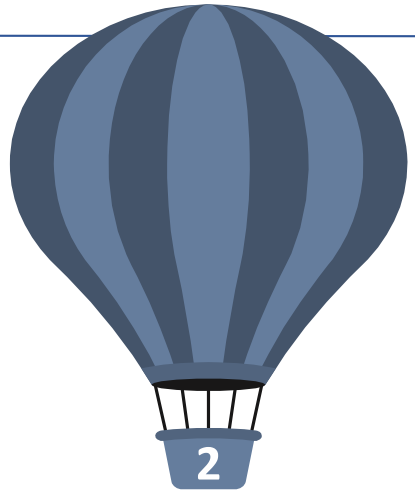
During re-wetting sample needs longer time to accomplish “as-prepared” amount of signal

*Drying to 0 RH with the vacuum pump. Here, “0 RH” is reference dry state, assumed “0”

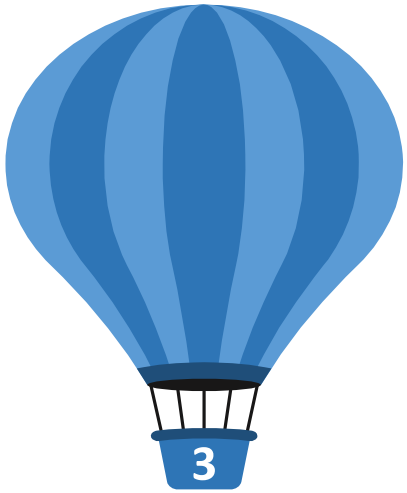
What's next?



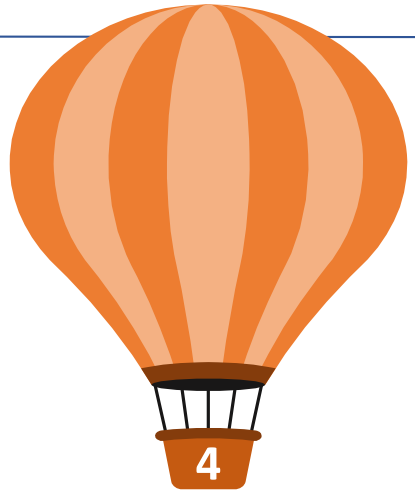
Continuing literature review;



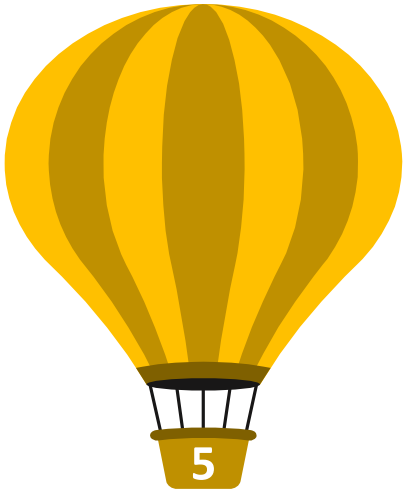
Second sorption cycle of the same sample;



Sorption cycles for samples with different compositions;



Fast sorption cycles with different technique;



Repeatability verification.

Outreach. Secondments

Outreach was done in Kazan National Research Technological University, Kazan, Russia.

With Bachelor and PhD students we discussed theory of Nuclear Magnetic Resonance and its practical application with cement materials as examples.

- USurrey. NMR training: two-day hands-on laboratory practice and data analysis session
- MR Solutions. Around two months in 2019-2020 with ESR5.
- HEIDELBERG CEMENT AG for 4 months

Results. For questions

Continuous distribution of T_2 relaxation time done by Upen. Peak value

De-saturation		
RH %	T_2 relaxation time (ms)	
100	0.3	245.8
80	0.3	
71	0.27	
60	0.27	
46	0.2	
33.8	0.15	
15.4	0.08	
0	0.08	

Re-saturation		
RH 100%	T_2 relaxation time (ms)	
0	0.08	
18	0.07	
23	0.07	
40	0.09	
60	0.11	
70	0.15	
100	0.47	

Continuous distribution of T_2 relaxation time done by Upen with increased smoothing parameter. Peak value

De-saturation					
RH %	T_2 relaxation time (ms)				
100	230.2	16.7	0.7	0.34	0.13
80		16.7	0.88	0.37	0.13
71				0.25	
60		8.4		0.31	0.12
46				0.27	0.11
33.8		14.7	1.0	0.2	0.11
15.4		16.7		0.2	0.07
0				0.35	0.11