Nuclear magnetic relaxation in cement-based materials

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J.-P. Korb, School of FC NMR relaxometry, Mede, 1-3 June 2009
Annual consumption of concrete per inhabitant on earth (1 m³)
1Kg of CO₂ for 1Kg of cement (clinker) at 1400°C
Importance of microstructure

Concrete from today

Concrete from yesterday

Elorn river, close to Brest (France)
Concrete for tomorrow:
Ultra-high performance concretes (ductal)

- Resistance on compression similar to steel
- Low cost

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Formulation of concrete

- Cement
- Aggregates (gravels, sands, ...)
- Water
- Ultrafines (silica fumes, ...)
- Adjuvant

Result: Concrete
The paradigm of concrete: a heterogeneous material from macroscopic to microscopic scales
Structure of anhydrous cement (clinker)

**Notations:**
- C : CaO
- S : SiO$_2$
- H : H$_2$O
- A : Al$_2$O$_3$
- F : Fe$_2$O$_3$

**Elements:**
- CaO
- Al$_2$O$_3$
- SiO$_2$
- C$_3$S : tricalcic silicate (50-70%)
- C$_2$S : bicalcic silicate (15-30%)
- C$_3$A : tricalcic aluminate (5-10%)
- C$_4$AF : tétracalcic alumino-ferrite (5-15%)

1400°C

SEM
Objectives

1. **Probe directly the specific surface area** of the pores and proton species surface dynamics by new and non invasive NMR techniques
   - Field cycling relaxometry
   - 2D correlation of relaxation times

2. **Use these new techniques associated with NMR spectroscopy** to follow continuously the setting of the materials in various conditions (w/c, T°C, additives)

3. **Application** to new concretes: water leaching and nuclear waste storage
**Cement hydration**

*Le Châtelier (1887)*

### Notations

- **C**: CaO
- **S**: SiO₂
- **H**: H₂O
- **A**: Al₂O₃
- **F**: Fe₂O₃

### 3 mechanisms

- dissolution
- diffusion
- precipitation

### Hydration of C₃S and C₂S

- **C₃S + 5.2 H → 1.3 CH + C₁.₇SH₄**
- **C₂S + 4.3 H → 0.3 CH + C₁.₇SH₄**

**Portlandite formation (CH)**

\[ Ca^{2+} + 2 OH^- \rightarrow Ca(OH)₂ \]

**Pouzzolanic reaction**

- **1.1 CH + S + 2.8 H → C₁.₁SH₃.₉**
- **C₁.₇SH₄ + S → 2 C₀.₉SH₂**

**Calcium silicate hydrates**

**CSH**

C/S = 1.7

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Different scales:

**Scale 1**: Capillary porosity coming from defects of packing of cement grains and filling with hydrates: > 50 nm:

D. Damidot (2006)
Scale 2: Inter-C-S-H porosity corresponding to defects of packing of C-S-H « nodules »: 6 - 50 nm
Scale 3: Intra-C-S-H corresponding to interlamellar layered structures of C-S-H: < 6 nm
Indirect investigation of the cement structure? But probe continuously the proton-species dynamics by non perturbative $^1$H NMR relaxation.
Outline

1. Distribution of average pore sizes

2. Identification of moving proton species
   Structure (Surface fractal, hierarchy of pores)

4. Progressive setting of microstructure
   (pore sizes, surface area) and surface dynamics

5. Water exchange between connected micropores
   (Very new in cement)

Processes

NMR Techniques

Usual 1 D NMR relaxation

$T_1$ – NMR Spectroscopy MAS

Field cycling relaxometry $T_1(\omega_0)$

2D NMR correlations
   $T_1 - T_2$
   $T_2$ - Storage - $T_2$
1. Characterize the « average pore sizes » of various cement based materials by usual 1D relaxation techniques
$T_2$ is the NMR signal lifetime following excitation in an experiment.

$T_2$ distribution

ESR Calibration

Pore size Distribution
under biphasic fast exchange model

$T_2$ is very sensitive to $^1H$ low frequency molecular motion and confinement.
$T_2$ relaxation is a marker for pore-size analysis because it is very sensitive to $^1$H molecular motion and confinement.

**Model of biphasic fast exchange:** Averaging between slowly relaxing “bulk” molecules and rapidly relaxing “surface” molecules: \( \tau_{\text{ex}} \ll T_2 \)

\[
\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \frac{\varepsilon S}{V} \frac{1}{T_{2,\text{surface}}}
\]

\[
T_2 = \frac{\langle d_{\text{pore}} \rangle}{\rho_2}
\]

with \( \rho_2 = \frac{\varepsilon}{T_{2,\text{surface}}} \)
\[ \langle d_{\text{pore}} \rangle = \rho_2 T_2 \]

Relation $T_2$ – average pore size

Calibrated ESR needed

$\sigma_s = 2.5 \times 10^{11} \text{Fe}^{3+}\text{cm}^{-2}$

Magnetic field (Gauss)
Verification of the biphasic fast exchange model

[Jehng, Halperin 1995]

Measure $T_2$ during the progressive drying of a white cement paste

\[
T_2 = \frac{1}{\rho_2} \frac{V / V_0}{S / V_0}
\]

\[
V / V_0 = \text{water content}
\]

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$T_2$ pore size distribution of mortar

(R. Valckenborg (2001))

Fig. 5.6: Pore water distribution in the middle of the sample for 10 hour steps as determined from relaxation measurements. In the inset, the total amount of water, the water in the capillary pores, and the water in the gel pores is given as a function of time. The curves are only guides to the eye.
2. Characterize the microstructure by mixing 1D NMR spectroscopy and $T_1$ relaxation ($T_1$-MAS)

- Identification of the dynamics of the different proton species
- Probing the progressive setting

  Phys. Rev. E72, 0414101 (2005)
Longitudinal $T_1$ relaxation of 1-year aged $\mathrm{C}_3\mathrm{S}$ paste

500 MHz

Raw Data

Successive adjustments

Laplace inversion

Proportion of $^1\mathrm{H}$ $\propto T_1^{-0.6}$

[Plaïsais, Lequeux, Korb, Petit 2005]
$^1$H relaxation of C$_3$S at long times

Hydration and advance of chemical reactions

Induction

Multi-exponential relaxation
Several $T_1$

Cure time (hours)

H. Lequeux, Korb, Petit 2005
$T_1$ distribution of hydrated $C_3S$ (4 months at 20 °C)

Different proton species?

or different porosities?

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High resolution proton NMR MAS Spectroscopy

$C_3S$ paste hydrated 4 months at w/c=0.4 (500 MHZ, MAS 30 kHZ)


Chemical characterization

But also gives Information on dynamics from linewidth

4 different proton species (3 mobile and 1 non mobile protons)
NMR Spectroscopy and proton relaxation: $T_1$-MAS

$=>$ Separate the different proton-species dynamics by measuring their respective $T_1$

**Power law $T_1$ distribution for mobile $^1$H**

H-OH, Ca-OH, and Si-OH-(2) have the same 4 $T_1$

So the $T_1$ distribution is not due to site distributions but to proton dynamics restricted to pores with different sizes

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Interpretation of the pore size distribution

C$_3$S cured during 4 months at 20°C

Solid protons » SiOH, CaOH within nanocrystallites of CSH

Mobile surface protons HOH, SiOH, CaOH outside CSH intercrystallites $T_1 \propto V/S \propto R$

Free water and Portlandite

Proportion of $^1$H $\propto T_1^{-0.6}$
Progressive texturation at long times of C$_3$S after completion of hydration ($\alpha = 1$)

$R^2$-Df, $D_f \sim 2.6$

- Scale invariance (hierarchy, (2 - 500 nm))
- Universal process for the texturation

$T_1 (\text{ms}) \propto R = \text{Pore size}$

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Similar $D_f$ as USAXS and SANS [Allen, 2005]

\[ d_{\text{surf}} = 2.6, \]
\[ \text{from 30Å to 1 µm} \]
3. **Use of the surface fractal dimension to improve the functionality of a high performance concrete (ductal)**

4. Progressive setting of microstructure by proton FFC $T_1(\omega_0)$

- Vary the magnetic field
- Change the time scale
- Change the length scale

- Probe the $^1$H dynamics from fast (~10 ps) and local motions to slow and delocalized motions (~20 µs)
- Separation of the bulk and pore surface dynamics
- Probe the specific surface area and pore size more directly

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Field cycling relaxometry

$\omega_0 = \gamma B_0$

(Spin clock)

$\omega_0 \tau_c = 1$

**Conventional relaxometry**

$T_2, T_1$

$T_1(\omega_0)$

**Spectroscopy**

Physical chemistry

Surface dynamics

Exchange, interaction, wettability

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Dynamics of water in pores with paramagnetic impurities Fe$^{3+}$ at surface


At long time an anisotropy occurs

\[ P(r_i,\tau) \approx P_{//}(\tau)P_{\perp}(\tau) \]

\[ P_{//}(\tau) \rightarrow \frac{1}{d} = \text{Cte} \]

\[ P_{\perp}(\tau) \approx \frac{1}{V(\tau)} \approx \frac{1}{\langle r^2 \rangle^{d/2}} \approx \frac{1}{\tau^{d/2}}, \text{ For } d = 2, G(\tau) \propto P(r_i = 0,\tau) \approx \frac{1}{\tau} \]

Complete calculation in the pore slit model and by taken into account the eigenvalues and eigenvectors of the Laplacian operator in the pore slit model

\[ G^{(0)}(\tau) \approx \frac{3\pi}{8} \frac{\sigma_s}{d^2\delta^2} \left( \frac{\tau_m}{\tau} \right), G^{(1)}(\tau) = \frac{1}{4} \frac{\pi\sigma_s}{\delta^4} \left( \frac{\tau_m}{\tau} \right)^2, G^{(2)}(\tau) = \frac{1}{16} \frac{\pi\sigma_s}{\delta^4} \left( \frac{\tau_m}{\tau} \right)^2 \]

\[ J(\omega) = A\omega^2_{\text{dip}}\tau_m \ln \left[ \frac{1 + \omega_i^2\tau^2_m}{\left( \frac{\tau_m}{\tau_S} \right)^2 + \omega_i^2\tau^2_m} \right] \]
Theory of relaxation in cements

\[
\frac{1}{T_1(\omega_I)} = \frac{1}{T_{1,\text{bulk}}} + \frac{N_{\text{surf}}}{N} \frac{1}{T_{1,\text{surf}}(\omega_I, \omega_S)} + \frac{N_{\text{Fe}}}{N} \frac{1}{T_{1,H-Fe}(\omega_I, \omega_S)}
\]

Solid hydrates

\[
\omega_c = 22 \text{ kHz}
\]

Specific surface area \( S_{\text{P,NMR}} \)

Cross relaxation at the interfaces

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First measurement of proton FFC profile of RPC mortar


\[ R_{1,w} = R_{1,\text{bulk}} + \frac{N_s}{N} R_{1,\text{surface}}(\omega_I, \omega_S) \]

\[ w/c = 0.65 \]

Diagram showing relaxation rate \(1/T_1\) vs frequency (MHz) with data points marked at different times:
- 00:47
- 06:13
- 06:51
- 07:26
- 08:19
Renormalisation of $1/T_1$ dispersion data obtained for different durations of hydration allows to probe surface dynamics of $1H$ species.

$$\frac{1}{T_{1,\text{eau}}(\omega_0, t)} \propto S_{pNMR}(t) f(\omega_O, \omega_S, \tau_m)$$

Solid hydrates

Water 2D diffusion

$\tau_m = 1$ ns

$\omega_c = 22$ kHz

J.-P. Korb, School of FC NMR relaxometry, Mede, 1-3 June 2009
Time evolution of the specific surface area of white cement paste

\[ \frac{1}{T_{1,\text{surface}}(t)} \propto S_p(t) \]

at 10 kHz

[J.-P. Korb et al 2005]
Calibrating the pore sizes of $\text{C}_3\text{S}$:
(1 year-aged, w/c = 0.4, 20°C)


$\langle R \rangle \in \{1.8, 5, 50, 500 \text{ nm}\}$
Probing the surface correlation time in white cement and OPC (W/C=0.4)

Universal $T_1(\omega)$ relaxation features due to 2D Water diffusion close to CSH

<table>
<thead>
<tr>
<th>Sample</th>
<th>White cement w/c=0.4</th>
<th>OPC w/c=0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_m$</td>
<td>1 ns</td>
<td>0.8 ns</td>
</tr>
<tr>
<td>$D_{surf} = \varepsilon^2/4\tau_m$</td>
<td>$3.6 \times 10^{-7}$ cm$^2$/s</td>
<td>$4.5 \times 10^{-7}$ cm$^2$/s</td>
</tr>
<tr>
<td>$D_{surf}/D_{bulk}$</td>
<td>1/60</td>
<td>1/50</td>
</tr>
</tbody>
</table>

Confirm the MD simulations of Kirkpatrick, Kalinichev, Pellenq
Progressive setting (early aged) of specific surface area of hydrated C₃S

Two main steps from calorimetry

Three main steps from $1/T_1$ (10 kHz)

Probing the increase of relaxation of surface protons (specific surface area)
Surface developed by CSH during the growth vs degree of hydration at different temperatures

Weak surface in contact (high density)
Limit the diffusion through this dense layer
Weak modulus and large pores

Large surface in contact (low density)
The diffusion is thus enhanced
Better modulus and small pores

\[ m_{45} \approx m_{25} \approx m_5 \quad \text{same mass of CSH} \]
\[ S_{45} < S_{25} < S_5 \quad \text{different specific surfaces} \]
Compatible with mechanical resistances at long times and at different temperatures

![Graph showing compressive strenght (MPa) vs. time (days) for different temperatures and C_3S types.]

[A. Nonat]
4. Track liquids moving between connected pores

2D NMR $T_2$-(z-storage)-$T_2$ correlation spectrum
2D NMR $T_1$-$T_2$ correlation spectrum

New opportunity arising from developments in petro-chemicals / rock-analysis / inversion algorithms which probes correlations between two relaxation parameters

Correlate at two different times, the distribution of molecules in pores, as probed by their respective relaxation times

$$T_{1,2} = \rho_{1,2,\text{Surface}} \left< d_{\text{pore}} \right>$$
2D $T_1$-$T_2$ correlation spectrum

Correlate at two different times, the distribution of molecules in pores, as probed by their respective relaxation times $T_{1,2} = \rho_{1,2,\text{Surface}} < d_{\text{pore}}>$.

Measure $T_1$ → Measure $T_2$

$T_2/T_1 < 1$ in pores

No Exchange

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2D $T_1$-$T_2$ correlation spectrum

Measure $T_1$ → Measure $T_2$

\[
\begin{bmatrix}
\frac{dM_a}{dt} \\
\frac{dM_b}{dt}
\end{bmatrix} =
\begin{bmatrix}
-R_{a1} - k_{a1} & k_{b1} \\
k_{a1} & -R_{b1} - k_{b1}
\end{bmatrix}
\begin{bmatrix}
M_a - M_a^0 \\
M_b - M_b^0
\end{bmatrix}
\]

J.-P. Korb, School of FC NMR relaxometry, Mede, 1-3 June 2009
2D correlation $T_1$ - $T_2$ spectrum

Measure $T_1$

Measure $T_2$

$\pi$

$\pi/2$

$\pi$

$\pi$

$\pi$

$\tau_1$

$\tau_2$

Inversion recovery $T_1$

CPMG sequence $T_2$

$M(\tau_1, \tau_2) = \int \int \left(1 - 2e^{-\tau_1/T_1}\right)e^{-\tau_2/T_2} F(T_1, T_2) dT_1 dT_2 + E(\tau_1, \tau_2)$

2D Inverse Laplace transform

J.-P. Korb, School of FC NMR relaxometry, Mede, 1-3 June 2009
Calibrating the pore sizes and water in cement paste by 2D $T_2$-$T_1$ correlations


$$T_{1,2} = \rho_{1,2,\text{Surface}} < d_{\text{pore}} >$$

White cement paste
$w/c = 0.4$, 4 days

+ Calibrated ESR

- Discrete pore sizes
- Exchange between connected micropores

J.-P. Korb, School of FC NMR relaxometry, Mede, 1-3 June 2009
Measuring the surface residence time $\tau_{\text{surf}}$

**2D surface diffusion model for conserving the dipolar correlations $^1\text{H} – \text{Fe}^{3+}$**

$$J(\omega_I) = \ln\left(\frac{(1 + \omega_I^2 \tau_m^2)}{(\tau_m / \tau_{\text{surf}})^2 + \omega_I^2 \tau_m^2}\right)$$

$$\frac{T_2}{T_1}(\omega_I) = \frac{2[3J(\omega_I) + 7J(\omega_S)]}{[J(0) + 3J(\omega_I) + 13J(\omega_S)]}$$

\[ T_1(\omega_0) \] Surface correlation time $\tau_m = 1$ ns

\[ D_{\text{surf}} = D/60 \]

\[ \tau_{\text{surf}} \approx 10^3 \]

Surface residence time $\tau_{\text{surf}} = 1$ $\mu$s

**Exp.**

From 2D exp

$$\tau_{\text{surf}} / \tau_m = 10^4$$

Logarithmic graph with 2D exp

$22$ MHz

$\tau_m = 1$ ns

Anisotropy
Confirmation of water exchange: 2D relaxation $T_2$-storage-$T_2$ correlations

$M(\tau_1, \tau_{\text{store}}, \tau_3)$

$T_2^2$

No exchange

2D relaxation $T_2$-store-$T_2$ correlations

$M(\tau_1, \tau_{\text{store}}, \tau_3)$

$T_2^2$

$T_2^1$

Varying the time of storage $\tau_{\text{store}}$ allows to follow the evolution of intensities of the 4 peaks by exchange

\[
\begin{bmatrix}
\frac{dM_a}{dt} \\
\frac{dM_b}{dt}
\end{bmatrix} =
\begin{bmatrix}
-R_{a2} - k_{a2} & k_{b2} \\
-k_{a2} & -R_{b2} - k_{b2}
\end{bmatrix}
\begin{bmatrix}
M_a \\
M_b
\end{bmatrix}.
\]
$T_2$-store-$T_2$ correlations for white cement paste, w/c=0.4, 4 days

**Experiments**

- $\tau_{\text{store}} = 10$ ms
- 4 days

- $\tau_{\text{store}} = 1$ ms
- 4 days

**Theory**

- $k = 0.2$ ms$^{-1}$
- $\tau_{\text{store}}$
  - 5 ms
  - 1 ms
  - 0.2 ms

$\tau_{\text{exchange}} = 5$ ms

Conclusion

Length

Time

1 Å 1 nm 10 nm 0.1 µm 1 µm 10 µm 100 µm 1 mm 1 cm

Tortuosity

Functionalized Imaging of hydration

Exchange between Connected micropores

Identification Pore size distribution Surface dynamics

NMR

Portable MRI

Coment block

P. J. McDonald, J.-P. Korb, CCR 37, 303-309 (2007)

J.-P. Korb, School of FC NMR relaxometry, Mede, 1-3 June 2009